Tricoordinate Coinage Metal Complexes with a Redox-Active Tris-(Ferrocenyl)triazine Backbone Feature Triazine–Metal Interactions

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SUPPORTING INFORMATION

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1. Experimental Procedures

1.1. General Procedures

Syntheses

All reactions and manipulations were carried out under an atmosphere of either nitrogen or argon using standard Schlenk line techniques unless stated otherwise. Thin-layer chromatography (TLC) with silica gel 60 F_{254} on glass or aluminium sheets available from Merck KGaA was used for monitoring the ligand synthesis reactions. Column chromatography was performed using a Biogel Isolera 1 automatic purification system with SNAP (silica, particle diameter: 0.040 to 0.065 mm) and SNAP Ultra (silica, spherical particle, diameter: 0.025 mm) cartridges using solvents purged with nitrogen prior to use. The fractions were detected by an integrated UV/Vis detector.

Molecular sieves (3 and 4 Å) were activated at 300 °C in vacuo for a minimum of 3 h. Dry, oxygen-free solvents (THF, acetonitrile, CH₂Cl₂, Et₂O, hexanes, and toluene) were obtained from an MBraun Solvent Purification System MB SPS-800 and directly stored over 4 Å molecular sieves, except for THF, which was further distilled from potassium/benzophenone and stored over 4 Å molecular sieves.

1.2. Dichloroethane was degassed using the freeze-pump-thaw method and stored over 4 Å molecular sieves. For the use in NMR measurements, THF-d₈ was distilled from potassium/benzophenone, CD₂Cl₂, CDCl₃, and CD₂CN were dried by stirring over P₂O₅ at room temperature for several days, followed by vacuum transfer into a storage flask and degassing by the freeze-pump-thaw method. The solvents were stored over 4 Å (THF-d₈, CD₂Cl₂, CDCl₃) or 3 Å (CD₂CN) molecular sieves.

[P(η⁵Bu₂C(CH)₂CH₄Pd(μ-Cl))][¹] 1,1'-dibromoferrocene,[²] Na[B(3,5-C₆H₄(CF)₂)]₄ (Na[BAr⁶]),[³] (nBu[N][B(3,5-C₆H₄(CF)₂)]₄ ((nBu[N])BAr⁶)),[⁴] and [thianthrenium]tetrfluoroborate[⁵] were synthesised as described in the literature. [Cu(CH₃CN)₄]BF₄ was prepared in a modified version of the procedure for [Cu(CH₃CN)₄]PF₆ using aqueous HBF₄. [Au(η²-nbe)]OTf was prepared in a modified version of the published synthesis for [Au(η²-nbe)]SBF₆ using AgOTf. Ph₃PCI was distilled and stored under nitrogen prior to use. Cyanuric chloride was recrystallised from hot heptanes and stored under nitrogen prior to use. All other chemicals were used as purchased.

NMR spectra were recorded with a BRUKER Avance III HD 400 MHz NMR spectrometer at 25 °C (frequencies of ¹H: 400.13 MHz; ¹³C: 128.38 MHz; ¹⁹F: 376.53 MHz; ³¹P: 161.99 MHz). Pseudo-triplets of ferrocenylium protons are abbreviated as pt and their observable H, H coupling constants are given. TMS was used as the internal standard in the ¹H and ¹³C NMR spectra, and spectra of all other nuclei were referenced to TMS using the δ scale.[⁸]

Electrospray ionisation mass spectrometry was performed with an ESI ESQUIRE 3000 PLUS spectrometer with an IonTrap analyser from Bruker Daltonics, or a MicroTOF spectrometer from Bruker Daltonics with a ToF analyser in positive mode. As solvents for the measurements, THF, CH₂Cl₂, CH₃CN, MeOH, or mixtures of these solvents were used. Dry, oxygen-free solvents were used for air-sensitive species. Elemental analyses were performed with a VARIO EL elemental analyser from Heraeus. Melting points were determined with a Gallenkamp MPD350-BM2.5 melting point device and are reported uncorrected. FTIR spectra were obtained with a PerkinElmer FT-IR spectrometer Spectrum 2000 as KBr pellets and with a Thermo Scientific Nicolet iS5 with an ATR unit in the range from 4000 to 400 cm⁻¹. UV/Vis spectra were recorded on a PerkinElmer UV-VIS-NIR Lambda 900 spectrometer in quartz cuvettes (d = 10 mm). Sample concentration was in the range of 3·10⁻⁵ mol L⁻¹.

Electrochemistry

Cyclic voltammetry (CV) measurements on 1.0 mmol L⁻¹ analyte solutions in dry, oxygen-free dichloromethane containing 0.1 mol L⁻¹ (nBu[N])BF₄ or (nBu[N])[B(3,5-C₆H₄(CF)₂)]₄ as supporting electrolyte have been conducted in a three-electrode setup (GAMRY Instruments, SP-50 potentiosot by BioLogic Science Instruments) under a blanket of nitrogen at room temperature. The glassy-carbon working electrode (ALS; surface area 0.07 cm²) and the counter electrode (neolab; platinum wire, 99.9%) were put in the analytic solution, while the reference electrode (ALS; Ag/AgNO₃ (0.01 mol L⁻¹) in 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate in dry, oxygen-free CH₂CN) was connected to the cell via a bridge tube (filled with the supporting electrolyte) through Vycor tips. The reference electrode was calibrated against decamethylferrocene as an internal standard at the end of the CV experiment,[⁹] and the results were converted to the FcH/[FcH⁺] scale in accordance with the IUPAC requirements.[¹⁰]

Spectroelectrochemistry was performed using an optically transparent thin-layered electrode (OTTLE) cooled using a liquid nitrogen cryostat as described previously.[¹¹]

X-ray crystallography

The data were collected on a Gemini-CCD diffractometer (RIGAKU INC.) using Mo-Kα radiation (λ=0.71073 Å), ω-scan rotation. Data reduction was performed with CrysAlis Pro[¹²] including the program SCALE3 ABSPACK[¹³] for empirical absorption correction. The structure solutions for 1, 1BH₄, 1Cu, 1CuBF₄, 1CuBAr⁶, 1Ag, 1Au, and 5 were performed with SHELXS-97 (direct methods).[¹⁴] The anisotropic full-matrix least-squares refinement on F² of all non-hydrogen atoms was performed with SHELXL-97.[¹⁵] Except for disordered solvent molecules, all non-hydrogen atoms were refined with anisotropic thermal parameters and the HFIX command was used to locate all hydrogen atoms for non-disordered regions of the structure. Structure figures were generated with Mercury (versions 3.8 and 3.10).[¹⁶] CCDC 1960989 (1), 1960985 (1BH₄), 1960986 (1Cu), 1960991 (1CuBF₄), 1960987 (1CuBAr⁶), 1960992 (1Ag), 1960988 (1Au), and 1960990 (5) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
Computational methods
All calculations were carried out with the ORCA program package.\textsuperscript{[16]} All geometry optimisations were performed at the BP86-D3BJ/def2-TZVP\textsuperscript{[17]} level of theory in the gas phase. For calculations involving silver and gold the respective effective core potentials, namely def2-ECPP\textsuperscript{[16]} were used. Frequency calculations were carried out to confirm the nature of stationary points found by geometry optimisations. Density fitting techniques, also called resolution-of-identity approximation (RI),\textsuperscript{[19]} were used for GGA calculations, whereas the RI-JCOSX\textsuperscript{[20]} approximation was used for time-dependent DFT (TDDFT) calculations. Wiberg bond indices (WBI) were calculated using the built-in NBO3.1.\textsuperscript{[21]} module of Gaussian09\textsuperscript{[22]} on the geometries obtained with ORCA (using the BP86 functional in combination with the LANL2DZ\textsuperscript{[23]} basis set). \textsuperscript{1}H NMR shieldings were calculated at the TPSS/def2-TZVP\textsuperscript{[24,17c]} level of theory in the gas phase using the calculated proton shift of tetramethylsilane as reference.

1.2. Synthesis of 2,4,6-tris(1-bromo-1'-ferrocenylene)-1,3,5-triazine (4)

A stirred solution of 3.50 g (10.2 mmol, 3.30 eq.) 1,1'-dibromoferrocene in 30 mL THF was cooled to ~80 °C (ethyl acetate/N\textsubscript{2}0), and 6.30 mL nBuLi in n-hexane (1.54 mol·L\textsuperscript{-1}, 9.72 mmol, 3.15 eq.) were added dropwise over the course of 10 min. A dark-orange precipitate formed, and the solution was kept stirring at this temperature for a further 30 min. A freshly prepared solution of 1.45 g (10.6 mmol, 3.45 eq.) zinc chloride in 10 mL THF and transferred to the reaction mixture. In a separate flask, 570 mg (3.08 mmol, 1.00 eq.) cyanuric chloride and 32 mg (46 μmol, 1.5 mol%) [P(Bu)\textsubscript{3}]\textsubscript{2}C(CH\textsubscript{3})\textsubscript{2}CH\textsubscript{2}Pd(μ-Cl)]\textsubscript{2} were dissolved in 15 mL THF and transferred to the reaction mixture via cannula, immediately followed by a darkening of the red colour. The reaction mixture was left stirring at room temperature overnight. TLC (CH\textsubscript{2}Cl\textsubscript{2}/hexanes, 3:1) then indicated the complete conversion of the cyanuric chloride; all further work-up was carried out under ambient conditions. For quenching, 30 mL of brine were added, and the phases were separated. The aqueous phase was extracted with ethyl acetate (2x 5.32 mL), the combined organic phases were dried over Na\textsubscript{2}SO\textsubscript{4}, followed by filtration over neutral alumina using ethyl acetate as the eluent. Column chromatography (CH\textsubscript{2}Cl\textsubscript{2}/hexanes, gradient 25--100%) allowed for isolation of 4 (1.41 g, 53% yield) as a deep red microcrystalline solid.

\[
R = 0.62 \text{ (CH}_2\text{Cl}_2/\text{hexanes 3:1); m.p. 156--157 °C; } \textsuperscript{1}H \text{ NMR (CD}_2\text{Cl}_2): \delta \text{ [ppm]} = 5.32 \text{ (pt, } \delta_{CH} = 1.9 \text{ Hz, 6H, H3), 4.61 \text{ (pt, } \delta_{CH} = 1.9 \text{ Hz, 6H, H4), 4.39 \text{ (pt, } \delta_{CH} = 1.9 \text{ Hz, 6H, H6), 4.12 \text{ (pt, } \delta_{CH} = 1.9 \text{ Hz, 6H, H7); } \textsuperscript{13}C[\textsuperscript{1}H] \text{ NMR (CD}_2\text{Cl}_2): } \delta \text{ [ppm]} = 175.0 (s, C1), 82.9 (s, C2), 79.1 (s, C5), 74.3 (s, C3), 72.5 (s, C4), 72.2 (s, C6), 69.4 (s, C7); IR (KBr): ν [cm\textsuperscript{-1}] = 2927 (m), 2297 (w), 1418 (m), 1366 (m), 1084 (m), 1037 (w), 844 (vs, br), 743 (m), 560 (s), 484 (m); UV/Vis (CH\textsubscript{2}Cl\textsubscript{2}): λ\textsubscript{max} [nm] (ε [mol·L\textsuperscript{-1}·cm\textsuperscript{-1}]) = 463 (3200), 350 (7200), 288 (34500), 248 (45500); HRMS (ESI): m/z calcd. for C\textsubscript{33}H\textsubscript{2}Br\textsubscript{5}Fe\textsubscript{3}N\textsubscript{5}: 869.7628 [M\textsuperscript{+}]; found: 869.7621; elemental analysis calcd. [%] for C\textsubscript{33}H\textsubscript{2}Br\textsubscript{5}Fe\textsubscript{3}N\textsubscript{5}: C 45.57, H 2.78, N 4.83; found: C 45.36, H 2.54, N 4.84.

Figure S1. \textsuperscript{1}H NMR spectrum of 4 in CD\textsubscript{2}Cl\textsubscript{2}.
Figure S2. $^{13}$C{H} NMR spectrum of 4 in CD$_2$Cl$_2$.

Figure S3. UV/Vis spectrum of 4 in CH$_2$Cl$_2$. 
1.3. Synthesis of 2,4,6-tris(1-(diphenylphosphanylidene)-1'-ferrocenyle)1,3,5-triazine (1)

A stirred solution of 1.41 g (1.62 mmol, 1.00 eq.) 4 in 50 mL THF was cooled to −80 °C (ethyl acetate/N2) and 3.47 mL (1.54 mol L−1, 5.35 mmol, 3.30 eq.) nBuLi in n-hexane were added dropwise over the course of 30 min, resulting in a strong intensification of the red colour. The mixture was kept stirring for 2 hours at −80 °C, followed by the dropwise addition of 1.23 g (5.59 mmol, 3.45 eq.) chlorodiphenylphosphane dissolved in 20 mL THF at the same temperature. After slowly warming to room temperature overnight and stirring at 60 °C for 1 hour, TLC (CH2Cl2/hexanes, 4:1) indicated full conversion of 4. For quenching, a degassed saturated aqueous solution of NH4Cl was added to the fervently stirred mixture via cannula. The phases were separated, and the aqueous phase was extracted with diethyl ether (2x 10 mL). The combined organic phases were dried over degassed MgSO4, filtered, and then the product mixture was adsorbed on Celite® and subjected to column chromatography (CH2Cl2/hexanes, gradient 20–100%). Crystals suitable for single crystal X-ray diffraction analysis were grown from a so-obtained fraction at 7 °C. Following the unification of the fractions and the removal of solvent under reduced pressure, 1 was filtered over degassed silica using CH2Cl2, and the solvent removed in vacuo, yielding 1 (1.00 g, 52% yield).

![Figure S4. 1H NMR spectrum of 1 in CDCl3.](image)
Figure S5. $^{13}$C{[H]} NMR spectrum of 1 in CD$_2$Cl$_2$; the inserts show details of the phenyl (top right) and the ferrocenyl region (bottom right) of the spectrum.

Figure S6. $^{31}$P{[H]} NMR spectrum of 1 in CD$_2$Cl$_2$. 
1.4. Synthesis of 2,4,6-tris(1-(diphenylphosphanyl) borane)-1'-ferrocenylene)-1,3,5-triazine (1BH₃)

A stirred solution of 90 mg (76 μmol, 1.0 eq.) 1 in 10 mL CH₂Cl₂ was cooled to 0 °C (ice/water) and 0.13 mL (2.0 mol·L⁻¹, 270 μmol, 3.5 eq.) BH₃·SMe₂ in THF were carefully added. After the gas evolution had ceased, the reaction mixture was kept stirring at room temperature for 45 min after which TLC (CH₂Cl₂/hexanes 3:1) indicated full conversion of 1. Further work-up was carried out under ambient conditions. The volatiles were removed under reduced pressure and the residue was filtered over a plug of silica, yielding pure 1BH₃ (74 mg, 80% yield) after solvent removal. Crystals suitable for single crystal X-ray diffraction analysis were obtained by slow evaporation of a solution of 1BH₃ in CH₂Cl₂/hexanes.

Figure S7. UV/Vis spectrum of 1 in CH₂Cl₂.

\[ \text{UV/Vis (CH}_2\text{Cl}_2): \lambda_{\text{max}}[^\text{nm}] (\varepsilon[^\text{mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}]) = 463 (3100), 350 (7500), 288 (43500), 248 (46800); \]

HRMS (ESI): m/z calcd. for C₇₉H₆₃B₃Fe₃N₃P₃: 1228.2669 [M+H]+, found: 1228.2683; elemental analysis calcd. [%] for C₇₉H₆₃B₃Fe₃N₃P₃: C 67.53, H 5.17, N 3.42; found: C 67.46, H 5.23, N 3.41.
Figure S8. $^1$H NMR spectrum of 1BH₃ in CD₂Cl₂. The integral of the borane region centred around 1.15 ppm is overestimated due to NMR solvent impurities.

Figure S9. $^{11}$B$^{[1]H}$ NMR spectrum of 1BHs in CD₂Cl₂.
Figure S10. $^{13}$C{[H]} NMR spectrum of 1BH$_3$ in CD$_2$Cl$_2$, the inserts show details of the phenyl (top right) and the ferrocenyl region (bottom right) of the spectrum.

Figure S11. $^{31}$P{[H]} NMR spectrum of 1BH$_3$ in CD$_2$Cl$_2$. 
1.5. Synthesis of \{2,4,6-tris\{1-diphenylphosphanyl-1'-ferrocenylen\}-1,3,5-triazine-\(x\)P\} copper(I) trflate (1Cu)

Under stirring, a solution of 41.5 mg (110 \(\mu\)mol, 1.00 eq.) \{Cu\[MeCN\]4\}OTf in 12 mL CHCl3 was added to 150 mg (127 \(\mu\)mol, 1.15 eq.) 1 and kept stirring at room temperature for 1 hour. The reaction mixture was filtered via cannula, layered with 30 mL toluene and kept at 7 °C for 2 days. The so-obtained crystalline material, suitable for single crystal X-ray diffraction analysis, was isolated by filtration and dried in vacuo overnight at 40 °C, causing the deep red crystals to brittle, yielding a red powder (124 mg, 81% yield) which can be handled in air but which was stored under nitrogen.

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\text{Supporting Information}
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\(^{1}\) For the sake of clarity, the two overlapping spectra for the \(C_7\)-symmetric form 1Cu\(_{\text{op}}\) and for the \(C_7\)-symmetric open form 1Cu\(_{\text{op}}\) are presented one after the other. For Cu\(_{\text{op}}\) (Figure S16) not all of the 24 expected proton signals can be unambiguously identified, since there is considerable overlap with signals attributable to 1Cu\(_{\text{op}}\) (Figure S15).
HRMS (ESI): m/z calcd. for C_{69}H_{54}CuFe_{3}N_{3}P_{3}+: 1248.0878 [M−OTf]^+, found: 1248.0894; elemental analysis calcd. [%] for C_{70}H_{54}CuFe_{3}N_{3}O_{3}P_{3}S: C 60.13, H 3.89, N 3.01; found: C 60.62, H 3.95, N 2.92.

Figure S13. $^1$H NMR spectrum of 1Cu in CD$_2$Cl$_2$ recorded at 25 °C.

Figure S14. $^1$H NMR spectrum of 1Cu in CD$_2$Cl$_2$ recorded at −80 °C, displaying the equilibrium between Cu_i (Figure S15) and Cu_op (Figure S16).

Even after prolonged drying in vacuo, residual toluene and/or grease might account for the deviations.
Figure S15. Detail of the $^1$H NMR spectrum of $^{1}$Cu in CD$_2$Cl$_2$ recorded at $-80$ °C. Only peaks attributable to Cu$^{cl}$ are labelled. Signals marked with an asterisk * denote an overlap with signals arising from $^{1}$Cu$_{op}$, thus their integrals are overestimated.

Figure S16. Detail of the $^1$H NMR spectrum of $^{1}$Cu in CD$_2$Cl$_2$ recorded at $-80$ °C. Only peaks attributable to Cu$^{op}$ are labelled. Signals marked with an asterisk * denote an overlap with signals arising from $^{1}$Cu$_{cl}$, thus their integrals are overestimated.
Figure S17. $^1$H NMR spectrum of 1Cu in CD$_3$CN recorded at 25 °C.

Figure S18. $^{13}$C($^1$H) NMR spectrum of 1Cu in CD$_2$Cl$_2$ recorded at 25 °C using the zgpg pulse sequence for fast-relaxing nuclei (NS = 14400, 18 h).
Figure S19. $^{13}$C($^{1}$$H$) NMR spectrum of $^{1}$Cu in D$_2$CN recorded at 25 °C (NS = 8192, 10 h), the inserts show details of the phenyl (left) and the ferrocenyl region (right) of the spectrum.

Figure S20. $^{19}$F($^{1}$$H$) NMR spectrum of $^{1}$Cu in CD$_2$Cl$_2$ recorded at 25 °C.
Figure S21. $^{31}$P($^1$H) NMR spectrum of 1Cu in CD$_2$Cl$_2$ recorded at 25 °C (exponential $\text{l}_{	ext{b}}$ = 20 Hz).

Figure S22. $^{31}$P($^1$H) NMR spectrum of 1Cu in CD$_2$Cl$_2$ recorded at −80 °C, displaying signals for both the C-symmetric Cu$_{\text{sl}}$ and the C-symmetric Cu$_{\text{op}}$ isomers. The expansion displays the Cu-mediated $^{2}$J$_{P,P}$ coupling of Cu$_{\text{op}}$ resulting in the multiplet of an AA' spin system in detail.
1.6. **Synthesis of [2,4,6-tris{1-diphenylphosphanyl-1'-ferrocenylene}-1,3,5-triazine-κP³] copper(I) tetrafluoroborate (1CuBF₄)**

Under stirring, a solution of 23.1 mg (73.3 μmol, 1.00 eq.) [Cu(MeCN)₄]BF₄ in 8 mL CH₂Cl₂ was added to 100 mg (84.3 μmol, 1.15 eq.) 1 and kept stirring at room temperature for 1 hour. The reaction mixture was filtered via cannula, concentrated to half its original volume, layered with 12 mL toluene and kept at 7 °C for 2 days. The so-obtained crystalline material, suitable for single crystal X-ray diffraction analysis, was isolated by filtration and dried in vacuo overnight at 40 °C, causing the deep red crystals to brittle, yielding a red powder (75 mg, 77% yield) which can be handled in air, but which was stored under nitrogen.

- **IR (KBr):** \( \tilde{\nu} \text{[cm}^{-1}] = 2965 \text{ (w), 2924 \text{ (w), 1512 \text{ (s), 1485 \text{ (m), 1436 \text{ (w), 1320 \text{ (w), 1262 \text{ (w), 1166 \text{ (w), 1123 \text{ (w), 1084 \text{ (m), 1031 \text{ (m), 831 \text{ (w), 747 \text{ (m), 697 \text{ (m), 503 \text{ (m), UV/Vis (CH₂Cl₂):}}} \lambda_{\text{max}} \text{[nm (ε [mol}^{-1}\text{L} \cdot \text{cm}^{-1}]) = 512 \text{ (4400), 349 \text{ (8800), 290 \text{ (36200), 249 \text{ (47300), HRMS (ESI): m/z calcd. for}}} C_{69}H_{54}CuFe_3N_3P_3+: 1248.0878 \text{ [M-BF}_4^{-}]^-, \text{ found: 1248.0842; elemental analysis calcd. [\%] for}} C_{69}H_{54}CuFe_3N_3P_3+: C 62.03, H 4.07, N 3.15; found: C 62.54, H 4.10, N 3.04. \)
Figure S24. $^1$H NMR spectrum of $^{1}$CuBF$_4$ in CD$_2$Cl$_2$.

Figure S25. $^{13}$C($^1$H) NMR spectrum of $^{1}$CuBF$_4$ in CD$_2$Cl$_2$ (exponential $J_B$ = 20 Hz).
Figure S26. $^{19}$F{$^{1}$H} NMR spectrum of $^{1}$CuBF$_4$ in CD$_2$Cl$_2$, the expansion showing the two isotopemic $^{19}$F shifts due to $^{10}$B in detail.

Figure S27. $^{31}$P{$^{1}$H} NMR spectrum of $^{1}$CuBF$_4$ in CD$_2$Cl$_2$ (exponential $\tau$ = 20 Hz).
1.7. Synthesis of \( \{2,4,6\text{-tris}(1\text{-diphenylphosphanyl}-1'\text{-ferrocenyl}e ne)-1,3,5\text{-triazine}\text{-κP}^3\}\) copper(I) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (1CuBarF\(_4\))

In a Schlenk flask, 15 mg (11 \( \mu \)mol, 1.0 eq.) 1CuBF\(_4\) and 48 mg NaBArF\(_4\) (56 \( \mu \)mol, 5.0 eq.) were dissolved in 2 mL CH\(_2\)Cl\(_2\) and stirred for 30 min at room temperature. The deep red solution was cooled to \(-20^\circ\)C (ice/NaCl 3:1) and subsequently filtered from the colourless solid. After removal of the volatiles, the solidified red oil was dried in vacuo and immediately used for VT NMR studies, thus no yield was determined. Crystals suitable for single crystal X-ray diffraction analysis were obtained from layering a CH\(_2\)Cl\(_2\) solution of 1CuBarF\(_4\) with hexanes and storing it at 7 \( ^\circ\)C overnight.

\[ \text{1H NMR (CD}_2\text{Cl}_2): \delta 25^\circ\text{C [ppm]} = 7.75\text{–}7.69 (m, 8H, B\text{-}C(H(o-H))_2(CF}_3)_2), 7.57\text{–}7.54 (m, 4H, B\text{-}C(H(p-H))_2(CF}_3)_2), 7.65\text{–}7.10 (m, 30H, P(C}_6\text{H}_5)_2), 5.80\text{–}5.21 (m, 6H, fCH), 4.65 (pt, \text{J}_{HH} = 2.0 \text{Hz}, 6H, fCH), 4.43 (s (br), 6H, fCH), 3.99 (s (br), 6H, fCH)), 11B\{1H\} NMR (CD\(_2\)Cl\(_2\)): \delta 25^\circ\text{C [ppm]} = -6.7 (s, BAR)); 19F\{1H\} NMR (CD\(_2\)Cl\(_2\)): \delta 25^\circ\text{C [ppm]} = -62.9 (s, CF\(_3\)); 31P\{1H\} NMR (CD\(_2\)Cl\(_2\)): \delta 25^\circ\text{C [ppm]} = -7.2 (s, 2P, P(Ph)_2\text{-Cu}), -20.6 (s, 1P, P(Ph)_2)); HRMS (ESI): m/z calcd. for C\(_{69}\)H\(_{54}\)CuFe\(_3\)N\(_3\)P\(_3\): 1248.0878 [M–BAR\(_4\)]\(^+\), found: 1248.0886.

Figure S28. \textsuperscript{1}H NMR spectrum of 1CuBarF\(_4\) in CD\(_2\)Cl\(_2\).
Figure S29. $^{11}$B ($^1$H) NMR spectrum of $^{1}$CuBAr$_4^*$ in CD$_2$Cl$_2$.

Figure S30. $^{19}$F ($^1$H) NMR spectrum of $^{1}$CuBAr$_4^*$ in CD$_2$Cl$_2$. 
1.8. Synthesis of [2,4,6-tris(1-diphenylphosphanyl-1'-ferrocenylene)-1,3,5-triazine-kP] silver(I) triflate (1Ag)

Under stirring and protected from direct light, a solution of 150 mg (127 μmol, 1.15 eq.) AgOTf and kept stirring at room temperature for 1 hour, after which the protection from light was discontinued. The reaction mixture was filtered via cannula, layered with 36 mL toluene and kept at 7 °C overnight. The so-obtained crystalline material was isolated by filtration and dried in vacuo overnight at 40 °C, causing the deep red crystals to brittle, yielding a light-insensitive red powder (131 mg, 82% yield) which can be handled in air, but which was stored under nitrogen. Crystals suitable for single crystal X-ray diffraction analysis were obtained from layering a 1,2-dichloroethane solution of 1Ag with toluene, stored at 7 °C for several days.

Figure S31. 31P{1H} NMR spectrum of 1CuBARF₄ in CD₂Cl₂ (exponential lb = 20 Hz).
Figure S32. $^1$H NMR spectrum of 1Ag in CD$_2$Cl$_2$ recorded at 25 °C.

Figure S33. $^1$H NMR spectrum of 1Ag in CD$_2$Cl$_2$ recorded at −60 °C.
Figure S34. $^{13}$C($^1$H) NMR spectrum of $^{1}$Ag in CD$_2$Cl$_2$ recorded at 25 °C using the z,φ pulse sequence for fast-relaxing nuclei (NS = 5760, 7 h). The inserts show details of the phenyl (top right) and of the ferrocenyl region (bottom right), showing the two pseudo-quadruplets arising from both $^{1}$J$_{C,P}$ and $^{2}$J$_{C,Ag}$ coupling as supported by the corresponding $^{13}$C($^{31}$P,$^1$H) NMR experiment (cf. Figure S35) in detail.

Figure S35. Overlay of the $^{13}$C($^1$H) (bold maroon) and $^{13}$C($^{31}$P,$^1$H) (thin teal) NMR spectra of $^{1}$Ag in CD$_2$Cl$_2$ recorded at 25 °C, highlighting the collapse of the pseudo quadruplets in both the ferrocene (top) and the phenyl ring (bottom) region of the spectrum when $^{31}$P decoupling is employed. Residual coupling to $^{107/109}$Ag can be registered for the signal at 73.5 ppm (top), while such coupling is not resolved in case of the signal at 131.5 ppm (bottom).
Figure S36. $^{19}$F{$_1^1$H} NMR spectrum of 1Ag in CD$_2$Cl$_2$ recorded at 25 °C.

Figure S37. $^{31}$P{$_1^1$H} NMR spectrum of 1Ag in CD$_2$Cl$_2$ recorded at 25 °C, the insert showing the set of two doublets representing the two isotopomers due to distinguishable $J_{P,Ag}$ coupling to both $^{107}$Ag and $^{109}$Ag in detail.
1.9. Synthesis of \(\{2,4,6\text{-tris(1-diphenylphosphanyl-1'-ferroceny1)-1,3,5-triazine-κP}^3\}\) gold(I) triflate (1Au)

Under stirring and protected from direct light, a solution of 235 mg (198 μmol, 1.13 eq.) \(\text{1 in 20 mL CH}_2\text{Cl}_2\) was added to 110 mg (175 μmol, 1.00 eq.) \([\text{Au(nbe)}_2]\text{OTf}\) and kept stirring at room temperature for 1 hour, after which the protection from light was discontinued. The reaction mixture was filtered via cannula, layered with 50 mL toluene and kept at 7 °C for 2 days. The so-obtained crystalline material was isolated by filtration and dried at 40 °C \textit{in vacuo} overnight, causing the deep red crystals to brittle, yielding a light-insensitive red powder (190 mg, 71% yield) which can be handled in air, but which was stored under nitrogen. Crystals suitable for single crystal X-ray diffraction analysis were obtained from layering a 1,2-dichloroethane solution of 1Au with toluene, stored at 7 °C for several days.

Figure S38. \(^1\text{H NMR spectrum of 1Au in CD}_2\text{Cl}_2\) recorded at 25 °C.

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3 The quaternary ipso carbon atoms of the P-bound phenyl and cyclopentadienyl rings are not detectable, owing to both the \(J_{P,C}\) coupling and the intramolecular dynamics regarding the inversion of helicity.
Figure S39. $^1$H NMR spectrum of 1Au in CD$_2$Cl$_2$ recorded at $-60$ °C.

Figure S40. $^{13}$C($^1$H) NMR spectrum of 1Au in CD$_2$Cl$_2$ (exponential $f_b = 5$ Hz) recorded at 25 °C, the insert shows details of the ferrocene region.
**Figure S41.** $^{19}$F{${}^1$H} NMR spectrum of 1Au in CD$_2$Cl$_2$.

**Figure S42.** $^{31}$P{${}^1$H} NMR spectrum of 1Au in CD$_2$Cl$_2$ (exponential $T_1 = 100$ Hz) recorded at 25 °C.
1.10. Oxidation of 1Au to yield [2,4-bis(1-diphosphorylphosphinyl-1'-ferrocene)-6-(1-diphosphorylphosphinyl)-1,3,5-triazin-1-um-xP]²⁺ gold(I) bis[tetrakis(3,5-bis(trifluoromethyl)phenyl)borate] (5)

Under argon and maintaining gentle stirring, 23 mg (27 μmol, 6.0 eq.) NaBAR₄ and 12 mg (14 μmol, 3.0 eq.) NaBAR₄ were separately suspended in 5 mL CH₂Cl₂ and 3 mL CH₂Cl₂ over molecular sieves (4 Å) respectively and kept stirring overnight. Both suspensions were decanted from the molecular sieves via cannula onto 2.8 mg [thianthrenium]tetrafluoroborate (9.2 μmol, 2.0 eq.) and 7.0 mg 1Au (4.6 μmol, 1.0 eq.), respectively, and were stirred for 30 min at room temperature. The intensely purple suspension of [thianthrenium]BAR₄ was cooled to 0 °C (ice/water), allowed to settle, and filtered into the suspension of the gold complex. This suspension was stirred for another 30 min at room temperature. Filtration from the colourless precipitate afforded a vibrant violet solution from which an HR-ESI mass spectrum, a ¹⁹F[¹H] and a ³¹P[¹H] spectrum were recorded, identical to the analytical data obtained from the crystalline material (vide infra).

The volatiles were removed in vacuo, the solid violet residue was washed with hexanes (2 x 5 mL) and dried in vacuo. Crystals suitable for single crystal X-ray diffraction analysis were obtained from layering a 1,2-dichloroethane solution of 5 with hexanes, stored at 7 °C for several days and subsequent tempering at 35 °C for 4 days. No yield was determined, and the product obtained by crystallisation was found to be impure by means of NMR spectroscopy, yet an attributable set of spectra could be recorded and analysed at 25 °C (¹¹B, ¹⁹F, ³¹P) and ~40 °C (¹H).⁴

**SUPPORTING INFORMATION**

We found that using [thianthrenium]BF₄⁻ rather than the anion-exchanged oxidant led to decomposition of the BF₄⁻ anion, as monitored by ¹⁹F[¹H] NMR spectroscopy. Drying the suspension of NaBAR₄ in CH₂Cl₂ over 4 Å molecular sieves has also been found crucial for obtaining 5, however, residual water in NaBAR₄, might still account as the source for oxygen and the proton at the C₅N₅ core.

The ¹H NMR spectrum recorded at 25 °C is just dominated by the ¹H resonances of the BAR₄⁻ anion, while all other signals of interest are considerably broadened. As for the heteronuclear spectra, no difference between 25 °C and ~40 °C can be detected, thus the signal sharpening is attributed to slowed intramolecular dynamics of the ferrocenylene moieties which do not affect the heteronuclei.

Due to the impurities and other species, the ¹H NMR signal for the proton at the C₅N₅ core cannot unambiguously be allocated. It is further expected to be significantly broadened due to its binding to quadrupolar ¹⁴N and, possibly, due to coupling to the ³¹P nucleus of the phosphoryl moiety.

Since 5 was found impure even after crystallisation, no extinction coefficients can be provided as no exact concentration of the species in solution could be determined. It should furthermore be noted that the UV/Vis spectrum (Figure S47), due to the impurities, is a sum spectrum of all species in solution and not all transitions might thus originate from 5 itself.
Figure S43. $^1$H NMR spectrum of 5 in CD$_2$Cl$_2$ recorded at −40 °C; the insert magnifies the region of the ferrocene protons which, through a $^1$H,$^1$H COSY NMR experiment conducted at −40 °C, have been assigned to six individual C$_5$H$_4$ rings A to F. The plus sign (+) denotes signals attributable to a second species in solution, the asterisk (*) denotes the solvent signals (CH$_2$Cl$_2$, CHDCl$_2$). The integrals for the $^1$H resonances of the BAr$_4^-$ anion are too large, most likely due to the presence of dissolved NaBAr$_4^-$.

Figure S44. $^{11}$B($^1$H) NMR spectrum of 5 in CD$_2$Cl$_2$ recorded at 25 °C.
Figure S45. $^{19}$F-$^1$H NMR spectrum of 5 in CD$_2$Cl$_2$ recorded at 25 °C.

Figure S46. $^{31}$P-$^1$H NMR spectrum of 5 in CD$_2$Cl$_2$ recorded at 25 °C. The asterisks (*) denote signals attributable to a second component in solution.
Figure S47. UV/Vis spectrum of 5 in CH₂Cl₂.
2. Results and Discussion

2.1. Single Crystal X-Ray Diffraction Analyses

|                  | 1           | 1BH₃        | 1Cu         | 1CuBF₄      | 1CuBAR₄     |
|------------------|-------------|-------------|-------------|-------------|-------------|
| **Empirical formula** | C₆₉H₅₄Fe₃N₃P₃·CH₂Cl₂ | C₆₉H₆₃B₃Fe₃N₃P₃ | C₆₉H₅₄CuFe₃N₃P₃·Cu₃BF₄·1.35(CH₂Cl₂) | C₆₉H₅₄CuFe₃N₃P₃·BF₄·C₇H₈·CH₂Cl₂ | C₆₉H₅₄CuFe₃N₃P₃·C₃₂H₁₂BF₂₄ |
| **Formula weight [g mol⁻¹]** | 1270.53 | 1227.11 | 1638.40 | 1513.02 | 2112.37 |
| **T [K]** | 130(2) | 130(2) | 130(2) | 130(2) | 130(2) |
| **Crystal system / Space group** | Triclinic / P ̅ | Trigonal / R̅₃ | Triclinic / P ̅ | Triclinic / P ̅ | Monoclinic / P2₁/c |
| **a, b, c [Å]** | 13.401(1), 15.021(1), 17.009(1) | 28.3139(4), 28.3139(4), 12.6860(3) | 13.2878(3), 16.5913(5), 18.2263(6) | 13.0612(2), 17.2516(3), 17.8635(4) | 13.9342(2), 34.1657(4), 20.1810(3) |
| **α, β, γ [°]** | 99.247(6), 104.500(6), 93.598(6) | 90, 90, 120 | 113.779(3), 93.192(2), 102.445(2) | 112.720(2), 94.454(2), 104.621(2) | 90, 96.808(1), 90 |
| **V [Å³]** | 3252.5(4) | 8807.5(3) | 3544.7(2) | 3522.7(1) | 9539.9(2) |
| **Z** | 1          | 6          | 2          | 2          | 4          |
| **ρcalc [g cm⁻³]** | 1.297 | 1.388 | 1.535 | 1.426 | 1.471 |
| **Θmax [°]** | 28.282 | 26.367 | 30.585 | 29.065 | 27.968 |
| **F(000)** | 1308 | 3816 | 1677 | 1548 | 4264 |
| **Refins collected** | 29172 | 30216 | 57576 | 51940 | 54648 |
| **Independent refin** | 16105 | 4009 | 19559 | 18609 | 20727 |
| **R₁ /wR₁ (l > 2σ(l))** | 0.1103/0.2369 | 0.0350/0.0705 | 0.0480/0.0947 | 0.0455/0.1076 | 0.0552/0.1094 |
| **R₁ /wR₁ (all data)** | 0.2641/0.3013 | 0.0489/0.0757 | 0.0797/0.1069 | 0.0651/0.1152 | 0.0906/0.1242 |
| **Largest diff. peak/hole [e Å⁻³]** | 1.970~/1.011 | 0.306~/0.238 | 0.755~/0.687 | 1.291~/0.574 | 0.823~/0.595 |

[a] Given as Compound·Solvent or Cation-Anion·Solvent for reasons of clarity.
### Supporting Information

**Table S2. Crystallographic data for complexes 1Ag, 1Au, and 5.**

|          | 1Ag                                      | 1Au                                      | 5                                |
|----------|------------------------------------------|------------------------------------------|----------------------------------|
| **Empirical formula**[^a^] | C_{69}H_{54}AgFe_3N_3P_3·CF_3O_3S·C_2H_5Cl_5 | C_{69}H_{54}AuFe_3N_3P_3·CF_3O_3S·C_2H_5Cl_5 | C_{69}H_{54}AuFe_3N_3P_3·(C_{32}H_{12}BF_2)_2·C_2H_5Cl_2·C_2H_5Cl_14 |
| **Formula weight [g mol^{-1}]** | 1541.50                                  | 3310.67                                  | 3268.87                          |
| **T [K]** | 130(2)                                   | 130(2)                                   | 130(2)                           |
| **Crystal system / Space group** | Triclinic / P ̅                         | Triclinic / P ̅                          | Triclinic / P ̅                   |
| **a, b, c [Å]** | 13.3745(3), 16.8049(4), 17.9030(4)      | 13.3154(4), 16.8045(5), 17.9304(6)      | 16.3845(3), 17.6125(3), 25.0125(4) |
| **α, β, γ [°]** | 111.620(2), 94.970(2), 103.191(2)       | 112.378(3), 94.692(2), 103.020(2)       | 103.380(2), 90.449(1), 110.656(2) |
| **V [Å^3]** | 3576.7(2)                                | 3551.5(2)                                | 6538.8(2)                         |
| **Z**     | 2                                        | 2                                        | 2                                |
| **ρ_{calc} [g cm^{-3}]** | 1.431                                    | 1.548                                    | 1.660                            |
| **Θ_{max} [°]** | 30.508                                    | 30.570                                   | 30.508                           |
| **F(000)** | 1564                                     | 1653                                     | 3250                            |
| **Refns collected** | 72078                                     | 40691                                    | 154729                           |
| **Independent refns** | 21809                                     | 19248                                    | 39928                            |
| **R_{I/w|F_b} (I > 2σ(I))** | 0.0404/0.0848                             | 0.0586/0.1336                            | 0.0425/0.0951                    |
| **R_{I/w|F} (all data)** | 0.0599/0.0910                             | 0.0972/0.1496                            | 0.0604/0.1048                    |
| **Largest diff. peak/hole [e Å^{-3}]** | 0.641/~0.648                             | 3.005/~1.218                             | 1.399/~1.318                     |

[^a^]: Given as Cation-Anion-Solvent(s) for reasons of clarity.
Ligand 1 crystallises with no crystallographic symmetry, but key structural parameters for the three ferrocenylene moieties are in good accordance with each other and within the typical values reported for related compounds. The all-syn arrangement of the three 1-diphenylphosphanyl groups with respect to the central triazine core does not seem to arise from either intra- or intermolecular contacts.

For the closely related compounds 1,3,5-tris(ferrocenyl)benzene[25] and 2,4,6-tris(ferrocenyl)pyridine[26] syn,anti,anti conformations are found in the solid state with two ferrocenyl groups on one side of the arene core and the third on the other, while 2,4,6-tris(ferrocenyl)-1,3,5,2,4,6-triselenatriborinane[27] (also containing an aromatic six-membered core) crystallises in the all-syn conformation, as does the 1,3,5-tris(ferrocenyl)benzene moiety with the benzene core η6-bound to a RuCp fragment (V in Figure 1 in the main article).[28] The tris(borane) adduct 1BH3 crystallises with crystallographic C3 symmetry, obviously also resulting in an all-syn conformation. Its structural parameters are in line with expectations towards such phosphanyl boranes.

Table S3. Selected bond lengths [Å], distances [Å], and angles [°] of ligand 1 and borane-protected 1BH3. Numbering scheme according to the respective depiction of the solid-state structures.

|   | 1 | 1BH3 | 1 | 1BH3 |
|---|---|------|---|------|
| C(9)–P(1) / C(31)–P(2) / C(53)–P(3) | 1.815(8) / 1.809(9) / 1.813(1) | 1.784(2) | 177.82 / 178.72 / 178.89 | 176.59 |
| C(1)–C(4) / C(2)–C(26) / C(3)–C(48) | 1.47(1) / 1.46(1) / 1.45(1) | 1.460(3) | 3.32 / 2.15 / 0.33 | 4.72 |
| C(1)–Fe(1) / C(2)–Fe(2) / C(3)–Fe(3) | 1.653 / 1.634 / 1.653 | 1.648 | 32.42 / 125.05 / 131.27 | 27.21 |
| C(1)–Fe(1) / C(2)–Fe(2) / C(3)–Fe(3) | 1.654 / 1.630 / 1.637 | 1.642 | P(1)–B(1) / P(2)–B(2) / P(3)–B(3) | 1.919(3) |

[a] Due to crystallographic C3 symmetry, only one value is shown. [b] CtC denotes the calculated centre of gravity of the carbon-substituted cyclopentadienyl ring. [c] CtP denotes the calculated centre of gravity of the phosphorus-substituted cyclopentadienyl ring. [d] Angle between the mean planes through the substituted cyclopentadienyl (CpP) rings. [e] Torsion about the CpP(centroid)⋯Fe⋯CpP(centroid) axes.
**Figure S49.** Schematic representation of key structural parameters for the compounds under investigation.

**Table S4.** Selected bond lengths [Å], distances [Å], and angles [°] of complexes 1Cu, 1Ag, and 1Au. Numbering scheme according to the respective depiction of the solid-state structures (cf Figure 2 in the main article).

|          | 1Cu                | 1Ag                | 1Au                |
|----------|--------------------|--------------------|--------------------|
| C(9)−P(1) / | 1.803(2)          | 1.796(2)          | 1.798(6) / 1.798(6) / |
| C(31)−P(2) / | 1.792(3)          | 1.801(2)          | 1.802(7) / 1.802(7) / |
| C(53)−P(3) / | 1.807(3)          | 1.794(2)          | 1.796(7) / 1.796(7) / |
| P(1)−M(1)−P(2) / | 117.14(3)        | 119.46(2)        | 119.63(6) / 119.63(6) / |
| P(2)−M(1)−P(3) / | 117.64(3)        | 117.59(2)        | 118.48(6) / 118.48(6) / |
| P(3)−M(1)−P(1) / | 120.35(3)        | 116.02(2)        | 117.28(6) / 117.28(6) / |
| C(1)−C(4) / | 1.471(4)          | 1.475(4)          | 1.472(9) / 1.472(9) / |
| C(2)−C(26) / | 1.459(3)          | 1.460(3)          | 1.451(8) / 1.451(8) / |
| C(3)−C(48) / | 1.459(3)          | 1.463(3)          | 1.459(8) / 1.459(8) / |
| P(1)—M(1) / | 2.3266(7)         | 2.480(7)          | 2.393(2) / 2.393(2) / |
| P(2)—M(1) / | 2.3178(7)         | 2.496(5)          | 2.402(1) / 2.402(1) / |
| P(3)—M(1) / | 2.3338(6)         | 2.4881(6)         | 2.393(2) / 2.393(2) / |
| Θ(fc(1)) / | 7.49 / 8.15       | 6.79              | 7.28 / 6.48 / 6.98 |
| Θ(fc(2)) / | 7.60 / 6.31       | 7.34              | 7.60 / 6.31 / 7.34 |
| Θ(fc(3)) / | 173.20 / 171.94   | 172.91            | 173.32 / 173.49 / 173.55 / 173.22 / |
| τ(fc(1)) / | 173.55 / 173.22   | 172.85            | 172.57 |
| τ(fc(2)) / | 22.33 / 24.03     | 20.22             | 23.13 / 22.43 / 24.58 |
| τ(fc(3)) / | 24.73 / 22.52     | 25.96             | 24.58 |

[a] C中心 denotes the calculated centre of gravity of the carbon-substituted cyclopentadienyl ring. [b] Ct中心 denotes the calculated centre of gravity of the phosphorus-substituted cyclopentadienyl ring. [c] Angle between the mean planes through the substituted cyclopentadienyl (CpR) rings. [d] Torsion about the Cp(centroid)−Fe−Cp(centroid) axes.

**Figure S50.** Exemplary depiction of the unit cell for complexes 1M in the case of 1Au with special emphasis on the P (turned away from viewer, gold beneath C3N3 plane) and M (facing the viewer, gold above C3N3 plane) enantiomers both being present in the unit cell due to the inversion centre. Thermal displacement ellipsoids shown at the 50% probability level. For clarity, P-bound phenyl rings are depicted in wireframe style, and solvent molecules, anions, and H atoms are not shown.
The three copper(I) complexes 1Cu, 1CuBF₄, and 1CuBArF₄ (Figure S51) share the same key structural parameters (cf. Table S5), thus not revealing any anion influence in their solid-state structures. 1CuBArF₄ crystallises in the monoclinic space group P2₁/c, in contrast to both 1Cu and 1CuBF₄ which both crystallise in the monoclinic space group P1̅, most likely due to the significantly changed spatial requirements of the BArF₄⁻ anion.

Table S5. Selected bond lengths [Å], distances [Å], and angles [°] of complexes 1Cu, 1CuBF₄, and 1CuBArF₄. Numbering scheme according to the respective depiction of the solid-state structures (cf. Figure S51).

|          | 1Cu       | 1CuBF₄    | 1CuBArF₄ |
|----------|-----------|-----------|-----------|
| C(9)–Cu(1) / C(1)–Cu(2) / C(3)–Cu(3) | 1.803(2) / 1.792(3) / 1.807(3) | 1.803(2) / 1.801(3) / 1.798(3) | 1.801(3) / 1.807(3) / 1.795(3) |
| C(1)–O(1) / C(2)–O(2) / C(3)–O(3) | 1.471(4) / 1.454(3) / 1.474(4) | 1.466(4) / 1.468(4) / 1.456(4) | 1.466(4) / 1.468(4) / 1.456(4) |
| P(1)–Cu(1) / P(2)–Cu(2) / P(3)–Cu(3) | 2.3266(7) / 2.3178(7) / 2.3338(6) | 2.3324(7) / 2.3418(6) / 2.3245(7) | 2.340(1) / 2.3444(9) / 2.3316(8) |
| C≡(1)–Fe(1) / C≡(2)–Fe(2) / C≡(3)–Fe(3) | 1.662 / 1.660 / 1.655 | 1.664 / 1.660 / 1.667 | 1.658 / 1.665 / 1.666 |
| [a] Ct denotes the calculated centre of gravity of the carbon-substituted cyclopentadienyl ring. [b] CtP denotes the calculated centre of gravity of the phosphorus-substituted cyclopentadienyl ring. [c] Angle between the mean planes through the substituted cyclopentadienyl (Cp) rings. [d] Torsion about the Cp(centroid)⋯Fe⋯Cp(centroid) axes.

The three copper(I) complexes 1Cu, 1CuBF₄, and 1CuBArF₄ (Figure S51) share the same key structural parameters (cf. Table S5), thus not revealing any anion influence in their solid-state structures. 1CuBArF₄ crystallises in the monoclinic space group P2₁/c, in contrast to both 1Cu and 1CuBF₄ which both crystallise in the monoclinic space group P1̅, most likely due to the significantly changed spatial requirements of the BArF₄⁻ anion.

Table S5. Selected bond lengths [Å], distances [Å], and angles [°] of complexes 1Cu, 1CuBF₄, and 1CuBArF₄. Numbering scheme according to the respective depiction of the solid-state structures (cf. Figure S51).

|          | 1Cu       | 1CuBF₄    | 1CuBArF₄ |
|----------|-----------|-----------|-----------|
| C(9)–Cu(1) / C(1)–Cu(2) / C(3)–Cu(3) | 1.803(2) / 1.792(3) / 1.807(3) | 1.803(2) / 1.801(3) / 1.798(3) | 1.801(3) / 1.807(3) / 1.795(3) |
| C(1)–O(1) / C(2)–O(2) / C(3)–O(3) | 1.471(4) / 1.454(3) / 1.474(4) | 1.466(4) / 1.468(4) / 1.456(4) | 1.466(4) / 1.468(4) / 1.456(4) |
| P(1)–Cu(1) / P(2)–Cu(2) / P(3)–Cu(3) | 2.3266(7) / 2.3178(7) / 2.3338(6) | 2.3324(7) / 2.3418(6) / 2.3245(7) | 2.340(1) / 2.3444(9) / 2.3316(8) |
| C≡(1)–Fe(1) / C≡(2)–Fe(2) / C≡(3)–Fe(3) | 1.662 / 1.660 / 1.655 | 1.664 / 1.660 / 1.667 | 1.658 / 1.665 / 1.666 |

[a] Ct denotes the calculated centre of gravity of the carbon-substituted cyclopentadienyl ring. [b] CtP denotes the calculated centre of gravity of the phosphorus-substituted cyclopentadienyl ring. [c] Angle between the mean planes through the substituted cyclopentadienyl (Cp) rings. [d] Torsion about the Cp(centroid)⋯Fe⋯Cp(centroid) axes.
Figure S52. Molecular structure and corresponding labelling of 5 without (left) and including (right) the two BArF$_4^-$ anions present in the asymmetric unit. Thermal displacement ellipsoids are shown at the 50% probability level. For clarity, P-bound phenyl rings are depicted in wireframe style, and solvent molecules as well as H atoms with the exception of H(1) are not shown.
The other relevant structural parameters, confirming the phosphoryl moiety in the 1Au–Au(1) distance (closer to 180°) suggest. Relating to the hydrogen bond in 5, among themselves as would be the case if any of the iron centres in 5 would be in oxidation state +III. The deviation of the ideal linear binding mode (180°) is most likely due to a weak interactions between N(2) and Au(1) (d = 4.412(2) Å). This bidentate mode seems to put slightly less strain on the general geometry of ligand 1 than the tricordinate mode found in 1M, as the more relaxed values of Θ (closer to 0°) and α (closer to 180°) suggest. The P–O distance of 1.500(2) Å fits well with a previously reported value (1.4866(9) Å) for 1-diphenylophosphoryl-1'−cyanoferrocene, as do the other relevant structural parameters, confirming the phosphoryl moiety in 5.32 Relating to the hydrogen bond in 5 between the phosphoryl group and the protonated triazine, all its parameters fall within the expected range33 allowing it to be classified as a heteronuclear resonance-assisted hydrogen bond (RAHB), given the ferrocenyleno group is treated as a resonant spacer in the sense of Gilli.31 It is worth noting that the protonation of N(1) and its involvement in hydrogen bonding lead to a distortion of the otherwise regular C3N2 geometry that can be observed in 1Au. The C(1/2)−N(1) bonds become elongated, while the other non-involved C−N bonds shorten; in the same way, the torsion angles in the C3N2 ring increase (7.3° to ~5.6° in 5 vs. 3.0° to ~3.9° in 1Au). This puckering is also observable in N(1) moving away from a calculated C3N2 plane by 0.07 Å and from H(1) being away from a calculated C3N2 plane by 0.253 Å.

Table S6. Selected bond lengths [Å], distances [Å], and angles [°] of complexes 1Au and its oxidation product 5. Numbering scheme according to the respective depiction of the solid-state structures (cf. Figure 2 in the main article and Figure S52).

|       | 1Au       | 5          | 1Au      | 5          |
|-------|-----------|------------|----------|------------|
| C(9)–P(1) | 1.798(6) | 1.782(3)  | P(1)–O(1) | 1.500(2)  |
| C(31)–P(2) | 1.802(7) | 1.781(3)  | O(1)–H(1) | 1.72(4)  |
| C(33)–P(3) | 1.789(7) | 1.778(3)  | O(1)–N(1) | 2.678(3)  |
| Ct       | 2.393(2) | 2.302(1)  | O(1)–H(1)′–O(1) | 9.96(4)  |
| Ct       | 1.649(8) | 1.452(4)  | N(1)–H(1)–O(1) | 172(3)  |

[a] Ct denotes the calculated centre of gravity of the carbon-substituted cyclopentadienyl ring. [b] Ct denotes the calculated centre of gravity of the phosphorus-substituted cyclopentadienyl ring. [c] Angle between the mean planes through the substituted cyclopentadienyl (Cp") rings. [d] Torsion about the Cp"(centroid)–Fe"–Cp"(centroid) axes, given as its modulus.

Comparing oxidation product 5 to its starting material 1Au is very instructive. The two BArF2− anions compensate the positive charges located at the gold(I) ion and the protonated triazine core (N1) and not, as could have been expected from the oxidation of 1Au, positive charges located at any of the iron centres. This is backed by the Ct−Fe distances (Table S6) which do not differ strongly between 1Au and 5 and among themselves as would be the case if any of the iron centres in 5 would be in oxidation state +III.
2.2. CSD Searches and Results for Comparison

In the following tables (Table S7 – Table S9), molecular structures of trigonal-planar coinage metal complexes with three phosphane ligands are assembled and their individual and average P–M–P bond angles \( \beta \) and \( \beta_0 \) as well as their individual and average P–M bond lengths are listed. For the CSD search, the number of ligands on the metal M was not restricted. No restraints on the P–M bond lengths were set. The three bond angles \( \beta \) were set to a range of 115 to 125° each, to retrieve only trigonal-planar structures. Metal clusters and ligands other than phosphanes (i.e., phosphanides and (aromatic) phosphacycles) were manually sorted out. Additional donor atoms or groups in close contact to the metal M are indicated, and the column “1:1 Complex” is checked when a tris-phosphane ligand was found to bind the metal.

The number of such complexes is obviously rather small given the vast number of (phosphane) complexes of the coinage metals. As becomes apparent, trigonal-planar 1:1 complexes are even rarer and seem to require the presence of a supporting apical ligand or group (e.g., an arene).

Table S7. Comparison of solid-state molecular structures of trigonal-planar tris-phosphate Cu complexes regarding (and sorted according to) their Cu–P bond lengths and P–Cu–P bond angles \( \beta_0 \) (set to 115–125°). Only trivalent phosphane donors were considered, i.e. phosphacycles and phosphanides are not part of this overview. CSD entries with more than one CuP3 unit in the same solid-state structure are labelled with (1) and (2).

| CSD Identifier Code | \( \beta_1 \) [°] | \( \beta_2 \) [°] | \( \beta_3 \) [°] | \( \beta_0 \) [°] | \( P(1)–Cu \) [Å] | \( P(2)–Cu \) [Å] | \( P(3)–Cu \) [Å] | \( P–Cu \) [Å] | Apical atom(s) | 1:1 Complex |
|---------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-------------|--------------|-------------|
| PUDYUG              | 120.179        | 115.007        | 120.179        | 118.46         | 2.220          | 2.226          | 2.226          | 2.224       | I'           | -           |
| FAYYEK (1)          | 118.745        | 119.525        | 121.186        | 119.82         | 2.233          | 2.238          | 2.239          | 2.237       | -            | -           |
| WEWKIU              | 115.597        | 115.597        | 115.60         | 2.239          | 2.239          | 2.239          | 2.239          | 2.239       | I'           | -           |
| RAZHEI              | 120.23         | 119.498        | 119.904        | 119.88         | 2.239          | 2.245          | 2.237          | 2.240       | -            | -           |
| MEZKAS              | 118.557        | 121.937        | 117.034        | 119.18         | 2.238          | 2.241          | 2.255          | 2.245       | B'           | X           |
| TONSAQ (1)          | 121.617        | 121.238        | 116.57         | 119.81         | 2.249          | 2.232          | 2.253          | 2.245       | -            | -           |
| AHUKAP (1)          | 118.408        | 120.093        | 121.221        | 119.91         | 2.239          | 2.250          | 2.246          | 2.245       | -            | -           |
| FAYYEK (2)          | 120.124        | 118.113        | 121.667        | 119.97         | 2.248          | 2.246          | 2.252          | 2.249       | -            | -           |
| SEFRIH              | 117.979        | 115.232        | 115.232        | 116.15         | 2.250          | 2.250          | 2.246          | 2.249       | I'           | -           |
| WEMNAD              | 119.507        | 122.353        | 116.654        | 119.50         | 2.266          | 2.258          | 2.249          | 2.258       | N            | X           |
| AHUKAP (2)          | 121.166        | 117.646        | 121.174        | 120.00         | 2.257          | 2.257          | 2.261          | 2.258       | -            | -           |
| MEZWOF              | 117.892        | 121.201        | 119.935        | 119.68         | 2.271          | 2.265          | 2.275          | 2.270       | B            | X           |
| TONSAQ (2)          | 119.218        | 117.356        | 121.236        | 119.27         | 2.266          | 2.264          | 2.274          | 2.272       | -            | -           |
| FEPVUU              | 122.58         | 118.45         | 117.751        | 119.59         | 2.272          | 2.268          | 2.284          | 2.275       | -            | -           |
| UKOKOV              | 116.996        | 120.091        | 122.755        | 119.95         | 2.257          | 2.291          | 2.280          | 2.276       | -            | -           |
| UJITIR              | 116.512        | 117.587        | 116.963        | 117.02         | 2.281          | 2.274          | 2.276          | 2.277       | O'           | -           |
| EDICOL              | 123.983        | 119.124        | 116.765        | 119.96         | 2.279          | 2.265          | 2.288          | 2.277       | -            | -           |
| QOZHOC (1)          | 118.261        | 124.151        | 117.485        | 119.97         | 2.282          | 2.262          | 2.294          | 2.279       | -            | -           |
| OKAXOP              | 115.836        | 118.725        | 123.524        | 119.36         | 2.288          | 2.280          | 2.273          | 2.280       | -            | -           |
| QOZHOC (2)          | 120.263        | 122.307        | 116.792        | 119.79         | 2.281          | 2.263          | 2.299          | 2.281       | -            | -           |
| SUXIX               | 119.991        | 119.991        | 119.991        | 119.99         | 2.286          | 2.286          | 2.286          | 2.286       | -            | -           |
| WIMLEK              | 121.025        | 119.086        | 119.783        | 119.96         | 2.278          | 2.292          | 2.29    | 2.287       | -            | -           |
| XOCNIO (1)          | 120.252        | 120.132        | 118.879        | 119.75         | 2.278          | 2.290          | 2.297          | 2.288       | Al           | X\[1\]      |
| LAXKIE              | 117.933        | 123.156        | 117.005        | 119.36         | 2.303          | 2.287          | 2.293          | 2.294       | -            | -           |
| TPCUFB (1)          | 115.213        | 115.215        | 115.208        | 115.21         | 2.295          | 2.295          | 2.295          | 2.295       | -            | -           |
| DEZYUC              | 119.965        | 122.569        | 117.464        | 120.00         | 2.293          | 2.296          | 2.297          | 2.295       | -            | -           |
SUPPORTING INFORMATION

Table S8. Comparison of solid-state molecular structures of trigonal-planar tris-phosphate Ag complexes regarding (and sorted according to) their Ag–P bond lengths and P–Ag–P bond angles $\beta_{\text{apical}}$ (set to 115–125°). Only trivalent phosphate donors were considered, i.e. phosphacycles and phosphanides are not part of this overview. CSD entries with more than one AgP unit in the same solid-state structure are labelled with (1) and (2).

| CSD Identifier Code | $\beta_{\text{apical}}$ [°] | $\beta_{\text{point}}$ [°] | $\beta_{\text{VO}}$ [°] | P(1)–Ag [Å] | P(2)–Ag [Å] | P(3)–Ag [Å] | <P–Ag> [Å] | Apical atom(s) | 1:1 Complex |
|---------------------|----------------|----------------|----------------|-------------|-------------|-------------|-------------|---------------|-------------|
| FAYYIO              | 119.693        | 122.156        | 117.879        | 119.91      | 2.44        | 2.425       | 2.438       | 2.434         | Ag$^+$       | X[34]       |
| POPVIZ              | 120.209        | 121.811        | 117.353        | 119.79      | 2.443       | 2.443       | 2.467       | 2.451         | -            | -           |
| QAHKAL (1)          | 120.328        | 120.171        | 119.428        | 119.98      | 2.45        | 2.442       | 2.461       | 2.451         | -            | -           |
| PIFYUY              | 115.392        | 115.392        | 115.392        | 115.39      | 2.463       | 2.463       | 2.463       | 2.463         | N[34]       | X           |
| REDHUE              | 118.712        | 118.832        | 119.675        | 119.07      | 2.461       | 2.457       | 2.473       | 2.464         | -            | -           |
| HAJTOC              | 116.962        | 117.203        | 118.325        | 117.50      | 2.458       | 2.463       | 2.470       | 2.464         | O$^-$        | -           |
| QAHKAL (2)          | 117.674        | 118.349        | 121.698        | 119.24      | 2.456       | 2.467       | 2.472       | 2.465         | -            | -           |
| HEJXEZ              | 122.894        | 115.655        | 119.639        | 119.40      | 2.455       | 2.462       | 2.484       | 2.467         | -            | -           |
| TUGTUK              | 116.494        | 121.02         | 122.466        | 119.99      | 2.483       | 2.476       | 2.457       | 2.472         | Ag$^+$       | X[34]       |
| FUJQIM (1)          | 120.745        | 117.733        | 121.472        | 119.98      | 2.484       | 2.488       | 2.479       | 2.484         | Ag$^+$       | X[34]       |
| IBOQIZ              | 115.611        | 116.575        | 117.447        | 116.54      | 2.503       | 2.478       | 2.495       | 2.492         | -            | -           |
| QOSWAX              | 116.665        | 116.719        | 116.66         | 116.68      | 2.500       | 2.498       | 2.499       | 2.499         | B, Cl$^-$    | X           |
| MUCVOV              | 120.963        | 123.525        | 115.472        | 119.99      | 2.522       | 2.509       | 2.498       | 2.510         | Ag$^+$       | X[34]       |
| RIRZAT              | 116.218        | 117.06         | 116.579        | 116.62      | 2.519       | 2.510       | 2.517       | 2.515         | O$^-$        | X           |
| FUJQIM (2)          | 116.839        | 121.871        | 121.234        | 119.98      | 2.523       | 2.518       | 2.533       | 2.525         | Ag$^+$       | X[34]       |
| HIBCUO              | 117.515        | 123.24         | 116.943        | 119.23      | 2.533       | 2.522       | 2.531       | 2.529         | -            | -           |
| KIGZAB              | 117.395        | 117.391        | 117.396        | 117.39      | 2.544       | 2.544       | 2.544       | 2.544         | BCl$^-$      | -           |

[a] Even though the CSD does not recognise the Al–Cu$^+$ distances as signifier of a bond, the group of Bourissou presents convincing arguments for treating the Al–Cu$^+$ distance of 3.004(2) Å as a weak Z-type interaction.[32]

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| CSD Identifier Code | β1 [°] | β2 [°] | P(1)−Au [Å] | P(2)−Au [Å] | P(3)−Au [Å] | <P−Au> [Å] | Apical atom(s) | 1:1 Complex |
|---------------------|--------|--------|-------------|-------------|-------------|------------|---------------|------------|
| IZOGAF             | 119.736 | 118.499 | 119.214    | 119.15      | 2.337       | 2.345      | 2.316         | 2.333 | Ti− X[α] |
| TIPZEX             | 119.965 | 117.965 | 117.965    | 117.97      | 2.334       | 2.334      | 2.334         | 2.334 | I− -     |
| IKASYI             | 119.595 | 119.551 | 119.638    | 119.59      | 2.338       | 2.340      | 2.339         | 2.339 | - -      |
| IKASOE             | 117.300 | 120.450 | 119.797    | 119.18      | 2.348       | 2.351      | 2.334         | 2.344 | - -      |
| DUVYUO (1)         | 121.543 | 120.659 | 117.795    | 120.00      | 2.345       | 2.342      | 2.356         | 2.348 | Au+ X[α] |
| VUSJEY (1)         | 122.087 | 122.102 | 115.789    | 119.99      | 2.366       | 2.338      | 2.355         | 2.353 | - -      |
| DUVYUO (2)         | 120.079 | 122.298 | 119.99     | 2.349       | 2.354       | 2.358      | 2.354         | 2.354 | Au+ X[α] |
| PIFYEI             | 116.412 | 117.305 | 117.281    | 117.00      | 2.367       | 2.351      | 2.354         | 2.357 | N X[β]  |
| YAZTEY             | 119.072 | 119.072 | 117.431    | 118.53      | 2.362       | 2.352      | 2.362         | 2.359 | Au+ -    |
| SEKVOT             | 118.703 | 118.69  | 118.649    | 118.68      | 2.361       | 2.360      | 2.362         | 2.361 | X[α]    |
| PIFYIM             | 116.931 | 118.148 | 115.372    | 116.82      | 2.369       | 2.361      | 2.362         | 2.364 | N X[β]  |
| POPVEV             | 120.796 | 115.827 | 121.23     | 119.28      | 2.357       | 2.368      | 2.37            | 2.365 | - -      |
| HOVBAY (1)         | 116.062 | 123.168 | 117.786    | 119.01      | 2.372       | 2.361      | 2.363         | 2.365 | Na+ -    |
| SEKSOO             | 120.501 | 120.583 | 115.790    | 118.96      | 2.367       | 2.364      | 2.367         | 2.366 | - X[α]  |
| VUSJEY (2)         | 118.055 | 118.578 | 121.967    | 119.53      | 2.357       | 2.384      | 2.362         | 2.368 | - -      |
| HOVBAY (2)         | 119.377 | 120.273 | 117.564    | 119.07      | 2.366       | 2.370      | 2.369         | 2.369 | Na+ -    |
| LODNUN (1)         | 116.963 | 120.297 | 120.787    | 119.35      | 2.371       | 2.368      | 2.37            | 2.370 | - -      |
| NAVTAG             | 124.611 | 115.426 | 117.492    | 119.18      | 2.366       | 2.351      | 2.392         | 2.370 | Cl+ -    |
| MIPBAO             | 120.102 | 120.436 | 119.334    | 119.96      | 2.369       | 2.369      | 2.374         | 2.371 | - -      |
| YIQIQU             | 115.044 | 115.044 | 115.044    | 115.04      | 2.372       | 2.372      | 2.372         | 2.372 | Sn -     |
| AVAVCUE            | 119.978 | 119.978 | 119.978    | 119.98      | 2.374       | 2.374      | 2.374         | 2.374 | Ag+ X[α] |
| NOZDUD             | 119.975 | 120.004 | 120.018    | 120.00      | 2.374       | 2.375      | 2.374         | 2.374 | - -      |
| ZETBJU (1)         | 123.897 | 119.747 | 116.353    | 120.00      | 2.376       | 2.365      | 2.383         | 2.375 | - -      |
| HOTZUL (1)         | 116.68  | 123.773 | 118.068    | 119.51      | 2.381       | 2.368      | 2.377         | 2.375 | Ti+ X[α] |
| PABDOO             | 116.548 | 118.734 | 124.409    | 119.90      | 2.369       | 2.390      | 2.367         | 2.375 | - -      |
| RABDEE             | 119.395 | 119.466 | 119.443    | 119.43      | 2.376       | 2.376      | 2.375         | 2.376 | - -      |
| WUHSID             | 119.482 | 119.482 | 119.482    | 119.48      | 2.378       | 2.378      | 2.378         | 2.378 | Si X[δ]  |
| XOCNEK (1)         | 120.619 | 119.018 | 119.291    | 119.64      | 2.376       | 2.370      | 2.388         | 2.378 | Al X[δ]  |
| LODNUN (2)         | 122.232 | 116.725 | 118.573    | 119.18      | 2.377       | 2.371      | 2.387         | 2.378 | - -      |
| LOFRON             | 115.077 | 124.420 | 120.347    | 119.95      | 2.383       | 2.372      | 2.38            | 2.378 | Cl+ -    |
| ZETBJU (2)         | 121.518 | 118.238 | 120.244    | 120.00      | 2.375       | 2.382      | 2.378         | 2.378 | - -      |
| NIWKOV             | 119.998 | 115.181 | 121.956    | 119.05      | 2.359       | 2.403      | 2.382         | 2.381 | Ti+ X[α] |
| HOTZUL (2)         | 118.848 | 120.150 | 120.181    | 119.73      | 2.38          | 2.388      | 2.381         | 2.383 | Ti+ X[α] |
| ROZREE (1)         | 120.818 | 119.219 | 118.653    | 119.56      | 2.376       | 2.384      | 2.39          | 2.383 | Ga X[δ]  |
| XOCNEK (2)         | 118.648 | 121.469 | 118.968    | 119.70      | 2.392       | 2.373      | 2.39          | 2.385 | Al X[δ]  |
The following two tables, Table S10 (coinage metals) and Table S11 (all other metals), give an overview of published solid-state structures of metal complexes featuring C₃N₂–M contacts, including the respective C₃N₂–M distances and deviation angles γ. For the search in the CSD, the maximum distance between the C₃N₂-centroid and the metal was set to 4 Å and the maximum angle γ between the C₃N₂ plane normal and the C₃N₂–M vector was set to 20° in accordance with the definition of delocalised C₃N₂–M interactions by Tiekink and co-workers.⁴⁹

Table S10. Overview of published solid-state molecular structures of coinage-metal complexes featuring C₃N₂–M contacts alongside (and sorted according to) their respective C₃N₂–M distances (≤ 4 Å) and the angles between their C₃N₂–M axis and the normal of the C₃N₂ plane (γ ≤ 20°). The coordination number of the metal C.N. is given without considering the C₃N₂ ring as additional donor. All contacts are observed between discrete molecules or within polymeric structures.

| CSD Identifier Code | C₃N₂–M [Å] | γ [°] | M   | C. N. |
|---------------------|-------------|-------|------|-------|
| WIPDOQ              | 3.763       | 5.80  | Ag   | 5     |
| IKUHUT              | 3.746       | 18.44 | Cu   | 4     |
| VOBTAJ              | 3.746       | 18.35 | Cu   | 4     |
| VOBTAJ02            | 3.745       | 18.38 | Cu   | 4     |
| ZOTFEV              | 3.722       | 13.80 | Cu   | 4     |
| HEBDAV01            | 3.678       | 16.65 | Ag   | 3     |
| RIGCOUR             | 3.570       | 15.05 | Ag   | 2     |
| RIGCER              | 3.511       | 10.70 | Au   | 2     |

[a] These two related structures mark the only cases in which a C₃N₂–M contact closer than in our system has been described.⁴⁹ For both copper(I) and silver(I), no shorter contact has been published to the best of our knowledge. In no case has a intramolecular C₃N₂–M contact been disclosed so far.
Table S11. Overview of published solid-state molecular structures of non-coinage metal complexes featuring C\(3\)N\(3\)\(\cdots\)metal contacts alongside (and sorted according to) their respective C\(3\)N\(3\)\(\cdots\)M distances \(d\) (\(d_{\text{max}} = 4\ \text{Å}\)) and the angles between their C\(3\)N\(3\)\(\cdots\)axis and the normal of the C\(3\)N\(3\) plane \(\gamma\) (\(\gamma \leq 20^\circ\)). The coordination number of the metal (C.N.) is given without considering the C\(3\)N\(3\) ring as additional donor. Intramolecular contacts (i.e. those that are not observed between discrete molecules or within polymeric structures) are highlighted in light grey. CSD entries with more than one C\(3\)N\(3\)\(\cdots\)metal contact in the same solid-state structure are labelled with (1) and (2).

| CSD Identifier Code | \(d\) [Å] | \(\gamma\) [°] | M  | C. N. |
|---------------------|----------|-------------|----|------|
| RECJOB              | 3.996    | 7.64        | Zn | 4    |
| YEHBUL (1)          | 3.994    | 14.88       | W  | 6    |
| VUKYUX              | 3.993    | 7.60        | Zn | 4    |
| YEHBUL (2)          | 3.991    | 15.27       | W  | 6    |
| YEBBOF              | 3.977    | 5.05        | W  | 6    |
| CENCAC              | 3.972    | 5.85        | Zn | 4    |
| RECHUF              | 3.970    | 6.13        | Zn | 4    |
| CENCIC              | 3.967    | 8.53        | Zn | 4    |
| RECJAN              | 3.962    | 8.83        | Zn | 4    |
| IYOHOU              | 3.955    | 7.25        | Zn | 4    |
| RECJER (1)          | 3.931    | 5.47        | Zn | 4    |
| RECJER (2)          | 3.930    | 7.94        | Zn | 4    |
| RECKAO              | 3.901    | 5.89        | Zn | 4    |
| CENBIJ              | 3.877    | 4.52        | Zn | 4    |
| WASQAJ (1)\[^{[a]}\] | 3.560    | 16.15       | Pt | 4    |
| PADVUO              | 3.535    | 15.87       | Pd | 4    |
| KEGQAQ (1)\[^{[b]}\] | 3.533    | 12.84       | Pt | 4    |
| WASQAJ (2)\[^{[c]}\] | 3.530    | 14.04       | Pt | 4    |
| KEGQAQ (2)\[^{[c]}\] | 3.497    | 6.63        | Pt | 4    |
| POZJOE (1)\[^{[d]}\] | 3.458    | 18.51       | Ni | 4    |
| POZJOE (2)\[^{[d]}\] | 3.427    | 15.79       | Ni | 4    |
| PIZRAS (1)\[^{[d]}\] | 3.414    | 5.41        | Pt | 4    |
| PIZRAS (2)\[^{[d]}\] | 3.397    | 2.87        | Pt | 4    |

\[^{[a]}\] Platinum is, as two stacked \((d(\text{Pt} \cdots \text{Pt}) = 3.32\ \text{Å})\) bis(acetylacetonato)platinum(II) ions, encapsulated in a \(C_3\)-symmetric coordination cage; the authors do not comment on the close C\(3\)N\(3\)\(\cdots\)Pt distances.\[^{[31]}\] \[^{[b]}\] Platinum is, as one discrete molecule of bis(acetylacetonato)platinum(II), encapsulated in a \(C_3\)-symmetric coordination cage; the authors note the close C\(3\)N\(3\)\(\cdots\)Pt distance but attribute the encapsulation mainly to donor–acceptor \(\pi \cdots \pi\) stacking interactions.\[^{[32]}\] \[^{[c]}\] Nickel is, as two stacked molecules of \((\text{N},\text{N}-\text{ethylenbis(acetylacetoneiminate)})\text{nickel}(\text{II})\), encapsulated in a \(C_3\)-symmetric coordination cage; the authors do not comment on the close C\(3\)N\(3\)\(\cdots\)Ni distances.\[^{[27]}\] \[^{[d]}\] Platinum is, as one discrete molecule of bis(acetylacetonato)platinum(II), encapsulated in a \(C_3\)-symmetric coordination cage; the authors note the small C\(3\)N\(3\)\(\cdots\)Pt separation but do not link it to the successful encapsulation.\[^{[34]}\]
2.3. VT NMR Studies

Variable-temperature $^1$H and $^{31}$P{$^1$H} NMR studies for all complexes have been conducted in the temperature ranges according to solvent and/or solubility limitations. For $^{1}$Ag and $^{1}$Au, the breakdown from $C_3$ to $C_3$ symmetry due to the inversion of helicity becoming slow at the NMR timescale can be followed nicely. For $^{1}$Cu, the high-temperature limit spectra in CD$_2$Cl$_2$ and CD$_2$CN suggest $C_3v$ symmetry, while cooling down reveals a slow equilibrium between the $C_2$-symmetric Cu$_{cl}$ and a bidentate, open form Cu$_{op}$. No significant anion influence can be discerned going from $^{1}$Cu over $^{1}$CuBF$_4$ to $^{1}$CuBAr$_4$F$_4$ in CD$_2$Cl$_2$.

Figure S53. Stacked VT $^1$H NMR spectra of $^{1}$Ag in CD$_2$Cl$_2$ over a temperature range from 40 °C to −70 °C. The asterisks denote toluene (*) and the residual CHDCl$_2$ (**) solvent signals. The coalescence-temperature spectrum is highlighted in light blue.
Figure S54. Stacked VT $^{31}$P($^1$H) NMR spectra (exponential $\text{lb} = 10$ Hz) of 1Ag in CD$_2$Cl$_2$ over a temperature range from 40 °C to −70 °C. No changes in coordination mode are observed.
Stacked VT $^1$H NMR spectra of $^1$Au in CD$_2$Cl$_2$ over a temperature range from −80 °C to 40 °C. The asterisks denote the CHDCl$_2$ signal.

For $^1$Au, a $^1$H,$^1$H COSY experiment at −50 °C was carried out (Figure S57) to determine the connectivities in the phenyl rings, in order to understand the reason for the significant shielding and deshielding of certain resonances (Figure S55). The cross peaks observed in this experiment also unambiguously establish the connectivities in the substituted cyclopentadienyl rings (v, orange, and w, purple) of this complex and, given the similarities between the low-temperature $^1$H NMR spectra, also of $^1$Ag (and, to the Cu fraction of $^1$Cu, $^1$CuBF$_4$, and $^1$CuBAr$_4$F$_4$). After the two phenyl rings had been separated regarding their resonances (x, green, and o, red), DFT calculations were carried out to assign the resonances to the DFT-optimised structure (depicted as simplified model in Figure S56).

Shielding tensors were calculated for all 54 protons of $^1$Au (cf. section 1.1, Computational methods), combined into isotropic chemical shielding (in ppm), averaged for the three protons that, due to the $C_3$ symmetry of the $^1$H NMR spectra at low temperatures, are expected to be equivalent for the solution-state structure of $^1$Au (standard deviations are given in brackets), and referenced to the chemical shift for TMS obtained by the same method. Results are summarised in Table S12. Since the error of the method is quite high and the chemical shifts so obtained are far from realistic values, only the general trend can be discussed. For an easier discussion of these trends, the calculated shifts have been scaled to match the experimental spectra separately for the ferrocenyl and the phenyl region.

From the calculations, it is obvious that proton x yields the most deshielded resonance, while proton o appears as most shielded. Following the cross peaks showing only $^3$J$_{H,H}$ couplings for the phenyl rings, the other resonances can then be tentatively assigned to the respective protons. For the ferrocenyl moieties, both $^3$J$_{H,H}$ and $^4$J$_{H,H}$ coupling result in cross peaks, thus no unambiguous assignment is possible.

The unusual proton shifts for $x'$ (proton 1 in Figure S56) and $o^5$ (proton 10 in Figure S56) are in line with their distinguished positions in close vicinity to the respective metal ions. Protons $x'$ have a mean Fe···H distance of 3.60 Å, the sum of the van der Waals radii being 3.61 Å,[38] however, this distance is far from that of a covalent bond for which distances between 1.34 Å and 1.62 Å have been experimentally determined.[55] It is interesting to note that for an Fe-bound hydride in [Cp$_2$Fe(H)]PF$_6$, a $^1$H NMR chemical shift of −1.3 ppm was recorded (in HF/PF$_5$), showing intense shielding in contrast to the deshielding observed for $x'$.[55] Alternatively, the strong deshielding could thus also relate to the vicinity to the C$_3$N$_3$ nitrogen atoms (mean N···H distance 2.36 Å, sum of van der Waals radii 2.86 Å). For protons $o^5$, the mean Au···H distance amounts to 3.31 Å with the sum of the van der Waals radii equaling 3.66 Å.[38]
Figure S56. Optimised structure of 1Au used for the calculation of its $^1$H NMR shifts.

**Table S12.** Results of a DFT calculation of the isotropic shielding parameters for 1Au, the corresponding chemical shifts vs. TMS, and a tentative assignment to the signals experimentally found through VT NMR experiments. Phenyl protons 1–10 are highlighted in light grey.

| Proton[a] | Averaged shielding $\delta$ (± MD)[b] [ppm] | Chemical shift vs. TMS [ppm] | Scaled shift[c] [ppm] | Tentative Assignment[d] (experimental shift [ppm]) |
|-----------|---------------------------------------------|-----------------------------|----------------------|-----------------------------------------------|
| 1         | 3.76 (±5.12)                                | 27.96                       | 9.62                 | $\delta^1$ (9.62)                            |
| 2         | 13.31 (± 3.12)                              | 18.41                       | 9.00                 | $\delta^2$ (8.07)                            |
| 3         | 20.24 (± 3.29)                              | 11.48                       | 8.55                 | $\delta^3$ (7.68)                            |
| 4         | 28.02 (±2.94)                               | 3.70                        | 8.05                 | $\delta^4$ (7.27)                            |
| 5         | 39.86 (± 4.88)                              | -8.14                       | 7.28                 | $\delta^5$ (6.39)                            |
| 6         | 35.38 (± 5.22)                              | -3.66                       | 7.57                 | $\delta^6$ (6.24)                            |
| 7         | 34.12 (±3.03)                               | -2.40                       | 7.65                 | $\sigma^7$ (7.20)                            |
| 8         | 38.53 (± 0.97)                              | -6.81                       | 7.37                 | $\sigma^8$ (7.27)                            |
| 9         | 44.49 (± 3.15)                              | -12.77                      | 6.98                 | $\sigma^9$ (6.30)                            |
| 10        | 64.09 (± 6.29)                              | -32.37                      | 5.72                 | $\omega^1$ (5.72)                            |
| 11        | 15.35 (± 1.38)                              | 16.37                       | 5.53                 | $\psi^{1\alpha}$ (5.53/5.27)                |
| 12        | 20.70 (± 2.71)                              | 11.02                       | 4.37                 | $\psi^{1\beta}$ (4.75/4.62)                 |
| 13        | 21.10 (± 3.31)                              | 10.62                       | 4.29                 | $\psi^{2\alpha}$ (4.75/4.62)                |
| 14        | 15.72 (± 4.06)                              | 16.00                       | 5.45                 | $\psi^{2\beta}$ (5.53/5.27)                 |
| 15        | 22.61 (± 6.87)                              | 9.11                        | 3.96                 | $\omega^{2\alpha}$ (4.27/4.20)              |
| 16        | 25.94 (± 1.94)                              | 5.78                        | 3.23                 | $\omega^{2\beta}$ (3.33/3.23)               |
| 17        | 25.55 (± 3.86)                              | 6.17                        | 3.32                 | $\omega^{3\alpha}$ (3.33/3.23)              |
| 18        | 23.89 (± 4.87)                              | 7.83                        | 3.68                 | $\omega^{3\beta}$ (4.27/4.20)               |

[a] Referring to the numbering scheme shown in Figure S56. [b] Mean deviations (MD) were calculated as the deviations of the three individual shielding parameters obtained for the non-identical protons at the chemically equivalent positions. [c] Scaling was carried out separately for the phenyl (1–10) and for the ferrocenylene (11–18) resonances by setting the experimental chemical shifts as respective boundaries and solely serves for easier assignment. [d] Referring to the signals depicted in the corresponding $^1$H,$^1$H COSY NMR spectrum (Figure S57) and based on the DFT results and the connectivity inferred from the COSY NMR experiment.
**Figure S57.** $^1$H-$^1$H COSY NMR spectrum of 1Au in CD$_2$Cl$_2$ recorded at −50 °C. Externally measured $^1$H NMR spectra of 1Au are used instead of the original traces due to their higher resolution. Cross peaks between J-coupled resonances are connected using colour-coded lines (green: phenyl ring x, red: phenyl ring o, orange: cyclopentadienyl ring v, purple: cyclopentadienyl ring w). The tentative assignments for the phenyl resonances in upper-case number are based on the results of a DFT calculation (s. text and Table S12).
Figure S58. Stacked VT 31P{1H} NMR spectra of 1Au in CD$_2$Cl$_2$ over a temperature range from 40 °C to −80 °C. No changes in coordination mode are observed. The insert aims to give a better view of the broad resonance at higher temperatures.
Figure S59. Stacked VT $^1$H NMR spectra of 1Cu in CD$_2$Cl$_2$ over a temperature range from 40 °C to −80 °C. The asterisks denote toluene (*) and the residual CHDC$_2$ (** ) solvent signals. The decoalescence into overlapping spectra of both Cu$_{cl}$ and Cu$_{op}$ takes place gradually between 25 °C and −10 °C.
Supporting Information

Figure S60. Stacked VT $^{31}$P{H} NMR spectra of 1Cu in CD$_2$Cl$_2$ over a temperature range from 40 °C to -80 °C. The low-temperature signals for the C$_3$-symmetric Cu$_{cl}$ (+) and the bidentate Cu$_{op}$ (#) are correspondingly labelled.

Although at 40 °C 1Cu appears C$_3$-symmetric in CD$_2$Cl$_2$, its corresponding $^{31}$P{H} NMR spectrum at the same temperature still hints at the swiftly equilibrating bidentate form Cu$_{op}$. This is most likely due to the greater difference in resonance frequencies for the two nuclei which leads to a higher temperature to attain coalescence in the $^{31}$P{H} NMR spectrum.

In CD$_3$CN, 1Cu appears C$_3$-symmetric, as judged from both its $^1$H and $^{31}$P{H} NMR spectra, already at room temperature, the signals sharpening considerably at higher temperature. Lowering the temperature, decoalescence in both the $^1$H and the $^{31}$P{H} NMR spectrum is observable, indicating that CD$_3$CN acts as an auxiliary ligand promoting the fast equilibration between the three theoretical coordination modes for 1Cu$_{op}$ (for this, see also the titration experiment with CN$^-$ (followed by UV/Vis) in section 2.5). In the $^1$H NMR spectra at -20 °C, 1Cu$_{cl}$ cannot be detected from its well-distinguishable resonances x at 9.7 ppm (cf. Figure S57 and Figure S59), suggesting that CD$_3$CN acts as ligand rather than the third phosphanyl group.
Figure S61. Stacked VT $^1$H NMR spectra of 1Cu in CD$_3$CN over a temperature range from 70 °C to −30 °C.

Figure S62. Stacked VT $^{31}$P($^1$H) NMR spectra (exponential $\tau$ = 50 Hz) of 1Cu in CD$_3$CN over a temperature range from 70 °C to −30 °C.
Figure S63. Stacked $^1$H NMR spectra of $\text{1Cu}$ (purple, bottom), $\text{1CuBF}_4$ (teal, middle), and $\text{1CuBArF}_4$ (maroon, top) in CD$_2$Cl$_2$ recorded at −70 °C. The signals for the ortho and para protons of the BA$^{2-}$ anion are labelled with asterisks (*). Residual solvents (toluene: $\mathsection$, CHDCl$_2$: $\sim$, THF: $\&$, Et$_2$O: $\$) are labelled as well. The boxes denote the signals used for the determination of the ratio of Cu$_{\text{cl}}$: Cu$_{\text{op}}$.

A comparison of the $^1$H NMR spectra of three Cu(I) complexes with triflate ($\text{1Cu}$), tetrafluoroborate ($\text{1CuBF}_4$), and BA$^{2-}$($\text{1CuBArF}_4$) as their respective anion at −70 °C (Figure S63) does not reveal significant differences in both position and multiplicity for the signals attributed to Cu$_{\text{cl}}$ and Cu$_{\text{op}}$. With respect to their relative intensities, the two signal sets centred at 3.90 ppm (blue box, Cu$_{\text{cl}}$) and 3.17 ppm (red box, Cu$_{\text{op}}$) have been used. The results are assembled in Table S13 and illustrate that, for $\text{1CuBArF}_4$, a slight increase in the relative amount of Cu$_{\text{cl}}$ in this equilibrium can be detected, potentially hinting at a weak involvement of the smaller anions in stabilising the bidentate, open form $\text{Cu}_{\text{op}}$. In the corresponding $^{19}$F($^1$H) NMR spectra in CD$_2$Cl$_2$, no change in the respective signals can be found. In their $^{31}$P($^1$H) NMR spectra at −70 °C (Figure S64), the signal sets appear very similar. Slight differences in signal width and exact position of the free phosphanyl group of Cu$_{\text{op}}$ in the case of $\text{1CuBArF}_4$ are noticeable. The relative integrals are similar, but their exact comparison is hampered by the pulse sequence (zgpg for fast-relaxing nuclei, $^1$H-decoupled) and the uneven baseline.

Table S13. Relative integral intensities and corresponding ratio of Cu$_{\text{cl}}$: Cu$_{\text{op}}$ for $\text{1Cu}$, $\text{1CuBF}_4$, and $\text{1CuBArF}_4$ in CD$_2$Cl$_2$ at −70 °C.

|        | Relative integral 3.90 ppm (2H) | Relative integral 3.17 ppm (6H) | Ratio Cu$_{\text{cl}}$: Cu$_{\text{op}}$ |
|--------|---------------------------------|---------------------------------|------------------------------------------|
| $\text{1Cu}$ | 1.00                           | 2.25                           | 9 : 12                                   |
| $\text{1CuBF}_4$ | 1.00                           | 2.25                           | 9 : 12                                   |
| $\text{1CuBArF}_4$ | 1.00                           | 2.67                           | 9 : 10                                   |
The ratio between 1Cu_{cl} and 1Cu_{op} is, however, solvent-dependent. In MeCN-d₈, the room-temperature ¹H and ³¹P{¹H} spectra suggest C₃ᵥ symmetry (Section 1.5, Figure S61, Figure S62); cooling down again decoalesces the ³¹P resonance (Figure S62). Donor solvents like MeCN and THF might stabilise 1Cu_{op} through weak coordination of the Cu(I) ion to different degrees, even though such complexes cannot be detected by HR-ESI MS from solutions of 1Cu in pure MeCN or THF. In this way, 1Cu(OTf) and 1CuBF₄ exhibit different solvent behaviour in THF-d₈ (Figure S65). While 1CuBF₄ behaves similarly in THF-d₈ and in CD₂Cl₂ when lowering the temperature as monitored by ¹H (Figure S66) and ³¹P{¹H} (Figure S67) NMR spectroscopy — signals for both Cu_{cl} (+) and Cu_{op} (#) are detectable, the ratio being strongly shifted towards Cu_{op}, which seems to be stabilised by THF-d₈ or 1Cu(OTf) gives markedly different results. Most prominently, other complex species seem to emerge at lower temperature as seen from the ³¹P{¹H} NMR spectrum at −60 °C (Figure S68, top left). The ¹⁹F resonance, sharp at 25 °C (Δν = 7.1 Hz), broadens considerably (and much more so than the ¹⁹F resonance of 1CuBF₄, increasing from 4.8 to 16 Hz, determined for the more intense peak attributed to ¹¹BF₄⁻) and splits up into at least three signals, one of which is very broad (Δν = 400 Hz), speaking for an interaction with the quadrupolar ⁶³Cu (I = 3/2) nuclei of 1Cu.

Even more so, the stark colour difference between solutions of 1Cu in DCM, THF and MeCN (Figure S75) is in line with this finding. Notably, 1Cu and 1CuBF₄ yield different UV/Vis spectra in THF (but not in CH₂Cl₂ and MeCN), further supporting an involvement of the anion in this case, triflate being a better donor for Cu(I) than BF₄⁻, thus breaking the C₃N₃=Cu(I) bond in combination with THF, hypsochromically shifting the absorption maximum to that found for both Cu(I) complexes in MeCN.

Figure S64. Stacked ³¹P{¹H} NMR spectra of 1Cu (purple, bottom), 1CuBF₄ (teal, middle), and 1CuBArF₄ (maroon, top) in CD₂Cl₂ recorded at −70 °C. The signal sets for the C₃₅-symmetric Cu_{cl} (+) and the bidentate Cu_{op} (#) are correspondingly labelled.
Figure S65. Stacked $^1$H NMR spectra of $1\text{Cu(OTf)}$ (purple, bottom) and $1\text{CuBF}_4$ (teal, top) in THF-$d_8$ recorded at 25 °C. The asterisk (*) denotes residual toluene.

Figure S66. Stacked VT $^1$H NMR spectra of $1\text{CuBF}_4$ in THF-$d_8$ over a temperature range from 70 °C to −70 °C. The asterisk (*) denotes residual toluene signals, and the ampersand (&) denotes a solvent impurity that comes into focus at very low temperatures. Well-distinguishable signals arising from C$_2$-symmetric CuI are labelled with the hashtag (#) symbol.
Figure S67. Stacked VT $^1$H NMR spectra of 1CuBF$_4$ in THF-d$_8$ over a temperature range from 70 °C to −70 °C. The low-temperature signals for the (almost indiscernible) $C_7$-symmetric Cu$_{cl}$ (+) and the bidentate Cu$_{op}$ (#) are correspondingly labelled.
Figure S68. Comparison between 1Cu(OTf) (purple, top) and 1CuBF4 (teal, bottom) regarding their $^{31}$P (left) and $^{19}$F (right) NMR resonances in THF-$d_8$ at $-60\, ^\circ$C, supporting the notion of a close contact/binding between Cu$^+$ and the triflate anion for 1Cu in THF-$d_8$. Line halfwidths were determined using the fitting module of MestreNova; for 1Cu at $-60\, ^\circ$C, the fitted peaks of the $^{19}$F($^1$H) NMR spectrum (top right) are shown with pink lines. The second $^{19}$F resonance (25 $^\circ$C) / shoulder ($-60\, ^\circ$C) at slightly lower field is due to the isotopic shift between $^{10}$B and $^{11}$B (cf. Figure S26).
2.4. Computational studies

2.4.1. Investigations on the metal-triazine interactions

The calculated Wiberg bond indices (WBI) between the respective metal and the carbon and nitrogen atoms of the triazine ring in 1Cu, 1Ag, and 1Au, as found in their solid-state geometries, are listed in Table S14. From the comparison of the data it can be concluded that the interaction between the triazine core and the coinage metals follows the order Cu < Au < Ag, thus reflecting the covalent radii of the coinage metals.

Table S14. WBI between the triazine ring atoms and the respective coinage metal ion in 1Cu, 1Ag, and 1Au. Numbering scheme according to Figure S51.

|         | 1Cu   | 1Ag   | 1Au   |
|---------|-------|-------|-------|
| N(1)    | 0.0223| 0.0252| 0.0234|
| N(2)    | 0.0223| 0.0252| 0.0235|
| N(3)    | 0.0222| 0.0253| 0.0234|
| C(1)    | 0.0059| 0.0063| 0.0061|
| C(2)    | 0.0059| 0.0064| 0.0061|
| C(3)    | 0.0059| 0.0063| 0.0061|

Next, we investigated the interaction of the parent triazine (C₃H₃N₃) with the coinage metal ions. Therefore, the geometry of the triazine core and the position of the coinage metal were restrained to the structural parameters obtained for the gas-phase structures of 1Cu, 1Ag, and 1Au, respectively. Then, the interaction energy between metal ion and triazine was calculated as E_{int} = E_{Triazine-M} - E_{M} - E_{Triazine}. The results are summarised in Table S15. The same trend as derived from analysis of the WBI of the complexes 1Cu, 1Ag, and 1Au are found with silver showing the largest interaction energy.

Table S15. Interaction energies E_{int} (in kcal·mol⁻¹) between triazine and the coinage metal ions obtained at the BP86-D3BJ/def2-TZVP level of theory.

|         | 1Cu   | 1Ag   | 1Au   |
|---------|-------|-------|-------|
| E_{int} | -8.1  | -10.6 | -9.7  |

To get insights into the nature of the interaction between the triazine core and the coinage metals, energy decomposition analyses (EDA) based on natural orbitals of chemical valence (EDA-NOCV) were carried out at the BP86-D3BJ/def2-TZVP level of theory. In this approach, the interaction between two fragments is decomposed into pairs of corresponding donor and acceptor orbitals. For our model systems, C₃H₃N₃-M⁺, three such pairs account for 71% of the total interaction energy for M = Cu (Ag: 73%, Au: 75%). Looking at the shape of these pairs (Table S16), they clearly correspond to cation–π interactions, namely the donation of electron density from the occupied π orbitals of the triazine core to empty s and p orbitals of the coinage metal ions. Other significant contributions to the interaction energy (Cu: 23 %, Ag: 22 %, Au: 20%) are rearrangements of electron density (polarisation) within the triazine moiety, probably induced by the coordination of the positively charged coinage metals (one pair is exemplarily shown for each metal in Table S16). The remaining part of the interaction energy can be assigned to back-bonding from occupied d orbitals of the metals to the triazine core (M–π* back-bonding, one pair is exemplarily shown for each metal in Table S16). Based on the analyses of the NOCV, the triazine molecule can be classified as a donor ligand toward coinage metal cations, whilst back-bonding interactions play an insignificant role.
Table S16. Corresponding pairs of natural orbitals of chemical valence (NOCV) for C₃H₃N−Cu⁺, C₃H₃N–Ag⁺, and C₃H₃N–Au⁺. The donor orbital is rendered in blue while the acceptor orbital is rendered yellow (isosurface values set to 0.06–0.08).
### 2.4.2. Frontier molecular orbitals of complexes 1M

Table S17. Plots of frontier molecular orbitals (HOMO−1, HOMO, and LUMO) of coinage metal complexes 1Cu, 1Ag, and 1Au (isosurface values set to 0.05), their respective energies rounded to the closest decimal and given below the individual plots.

|        | HOMO−1 | HOMO   | LUMO   |
|--------|--------|--------|--------|
| 1Cu    | ![HOMO−1](image) | ![HOMO](image) | ![LUMO](image) |
|        | ~6.9 eV | ~6.9 eV | ~4.9 eV |
| 1Ag    | ![HOMO−1](image) | ![HOMO](image) | ![LUMO](image) |
|        | ~6.9 eV | ~6.9 eV | ~4.9 eV |
| 1Au    | ![HOMO−1](image) | ![HOMO](image) | ![LUMO](image) |
|        | ~6.9 eV | ~6.9 eV | ~4.8 eV |
The frontier molecular orbitals of the complexes (calculated without considering their respective anions; for \(1\text{Cu}\), the closed, \(C_3\)-symmetric form \(\text{Cu}_{\text{cl}}\) has been considered solely) are degenerate, owing to the threefold symmetry of these molecules. Table S17 thus only representatively shows HOMO−1, HOMO and LUMO, alongside their respective energies in eV, to illustrate that the HOMO is located at and distributed over the three iron atoms of the ferrocenylene moieties, while the LUMO features contributions of both the triazine core and the ferrocenylene moieties.

### 2.4.3. Calculation of UV/Vis spectra

TDDFT calculations on \(1\text{Cu}\), \(1\text{Ag}\), and \(1\text{Au}\) were conducted at the TPSSh/def2-TZVP [17c, 57] level of theory in the gas phase. For the sake of computational cost, only 100 transitions were calculated for \(1\text{Cu}\), whilst 240 transitions were calculated for both \(1\text{Ag}\) and \(1\text{Au}\). The calculated spectra are in good agreement with the experimental spectra (cf. section 2.5.1) measured in dichloromethane (Figure S73 – Figure S75). In the visible part, the spectra are dominated by 3d-\(\pi^*\) transitions from the iron centres to the triazine core (see Table S18 for selected difference densities of \(1\text{Ag}\)). At higher wavelengths, \(\pi-\pi^*\) as well as M-\(\pi^*\) transitions are observed as well.

As can be seen from Figure S72, the hypothetical structure for \(1\text{Cu}_{\text{op}}\) with its presumed Cu–C₃N₃ contact (Figure S72) does lead to a broadening of the 3d-\(\pi^*\) and 3d-3d transitions for the absorption band at about 500 nm, in line with the experimental UV/Vis spectrum which might be understood as the sum of both forms, \(1\text{Cu}_{\text{cl}}\) and \(1\text{Cu}_{\text{op}}\).

Table S18. Selected difference densities for \(1\text{Ag}\) together with the corresponding calculated wavelength. Transitions proceed from blue to yellow (isosurface values set to 0.001).

| Wavelength (nm) | Transition Type                        |
|----------------|----------------------------------------|
| 502            | 3d-\(\pi^*\) and 3d-3d transition      |
| 394            | 3d-\(\pi^*\) and 3d-3d transition      |
| 284            | \(\pi-\pi^*\) transition               |
| 280            | M(Fe,Ag)-\(\pi^*\) transition         |
Figure S69. Measured (bold, in CH$_2$Cl$_2$) and calculated (1Cu$_{cl}$ – dashed black; 1Cu$_{op}$ – dashed grey) UV/Vis spectra of 1Cu.

Figure S70. Measured (bold, in CH$_2$Cl$_2$) and calculated (dotted line) UV/Vis spectra of 1Ag.
**Figure S71.** Measured (bold, in CH\textsubscript{2}Cl\textsubscript{2}) and calculated (dotted line) UV/Vis spectra of 1Au.

**Figure S72.** Possible structure for 1Cu\textsubscript{op} as obtained from a geometry optimisation at the DFT level of theory. For the sake of computational cost, the triflate anion was not included in the geometry optimisation. For clarity, the phenyl rings are drawn in wireframe style and hydrogen atoms have been omitted.
Table S19. Selected bond lengths [Å] and angles [°] for the hypothetical structure of $1\text{Cu}_{\text{IP}}$ as shown in Figure S72.

|                  | d [Å] | Angle [°] |
|------------------|-------|-----------|
| P(1)–Cu(1)      | 2.247 | P(1)–Cu(1)–P(2) | 110.40 |
| P(2)–Cu(1)      | 2.269 | P(1)–Cu(1)–N(1) | 127.62 |
| N(1)–Cu(1)       | 2.026 | P(1)–Cu(1)–N(1) | 121.24 |
| P(1)–C(9)        | 1.800 | C(1)–N(1)–C(2) | 113.08 |
| P(2)–C(31)       | 1.806 | N(1)–C(2)–N(2) | 123.54 |
| P(3)–C(53)       | 1.821 | C(2)–N(2)–C(3) | 115.29 |
|                  |       | N(2)–C(2)–N(3) | 122.22 |
|                  |       | C(3)–N(3)–C(1) | 115.97 |
|                  |       | N(3)–C(1)–N(1) | 122.97 |
2.5. UV/Vis spectroscopy

2.5.1. UV/Vis spectra of metal complexes in CH$_2$Cl$_2$, THF, and CH$_3$CN

Figure S73. UV/Vis spectra of 1Ag in CH$_2$Cl$_2$ (slate blue), THF (navy), and CH$_3$CN (green), the insert magnifying the d(Fe)-π*(C$_3$N$_3$) transitions at about 500 nm to show the almost negligible solvent influence in detail.

Figure S74. UV/Vis spectra of 1Au in CH$_2$Cl$_2$ (pink), THF (purple), and CH$_3$CN (orange), the insert magnifying the d(Fe)-π*(C$_3$N$_3$) at about 500 nm to show the almost negligible solvent influence in detail.
Figure S75. UV/Vis spectra of 1Cu in CH₂Cl₂ (maroon), THF (yellow), and CH₃CN (black), the insert magnifying the d(Fe)-π*(C₃N₃) transitions at about 500 nm to show the prominent solvent influence in detail.

While for 1Ag (Figure S73) and 1Au (Figure S74) the solvent does not result in significant shifts of both the position and the extinction coefficient of the electronic transitions in the UV/Vis region (the strongest influence can be seen for the ligand-centred π–π* and the M(Fe,Au)–π* transitions which decrease in the order CH₂Cl₂ > THF > CH₃CN, correlating with the donor strength of the solvent), 1Cu (Figure S75) shows a more pronounced solvent effect, especially regarding the d(Fe)-π*(C₃N₃)/d(Fe)-d(Fe) transitions which, in CH₂Cl₂ (maroon curve), are batho- and hyperchromically shifted as well as broadened with respect to the peaks in THF (yellow) and CH₃CN (black). This effect also becomes apparent when comparing the three complexes with each other; the visibly more intense and darker colour of 1Cu in CH₂Cl₂ when compared to its heavier homologues is reflected in the UV/Vis spectra (Figure S76). As also noted in the VT NMR experiments, the anion plays a role for 1Cu in THF (Figure S77). In contrast to the BF₄⁻ anion, the triflate anion in 1Cu seems to bind to Cu⁺, disturbing the C₃N₃–Cu⁺ contact responsible for the bathochromic shift.

Figure S76. Comparison of the d(Fe)-π*(C₃N₃) transitions in the UV/Vis spectra of 1Au (top), 1Ag (middle), and 1Cu (bottom) in the three solvents under investigation (CH₂Cl₂ marked in bold), highlighting the stark solvent influence that 1Cu experiences.
Comparison of the d-d transitions in the UV/Vis spectra of $1\text{Cu(OTf)}$ (top) and $1\text{CuBF}_4$ (bottom) in the three solvents under investigation (THF marked in bold), highlighting the anion effect resulting in a hypsochromic shift for $1\text{Cu}$ with respect to $1\text{CuBF}_4$ in THF.

### 2.5.2. UV/Vis titration of 1Cu with (nBu₄N)CN

Figure S78. UV/Vis-monitored titration of 1Cu with (nBu₄N)CN in CH₂Cl₂ in steps of 0.1 eq. (start and endpoint of titration marked in bold), the insert magnifying the ferrocene-based d-d transition and its hypsochromic shift upon continued addition of CN⁻ anions.
The C₃N₃–Cu' contact in 1Cu, persistent in CH₂Cl₂, can be disrupted by adding a strong donor such as CN⁻. Upon addition of up to 1.0 eq. CN⁻ (Figure S78), the d(Fe)–π*(C₃N₃)/d(Fe)–d(Fe) transition of 1Cu is shifted hypsochromically, suggesting the breaking of the C₃N₃–Cu' contact which, by removing electron density from the triazine core and thus also affecting the electronic transitions of the ferrocenylene moieties, is responsible for the original bathochromic shift of 1Cu compared to 1Ag and 1Au. Addition of a second equivalent of CN⁻ (Figure S79) leads to little change concerning the peak position but induces a slight hyperchromic shift of the d–d transition associated with the ferrocenylene groups. This might, comparing the resulting spectrum to that of the free ligand 1 (black, bold), potentially hint at a ligand exchange, yielding free 1 and [Cu(CN)_3]⁻ or [Cu(CN)_4]^{2−}. An HR-ESI mass spectrometric analysis of 1Cu and two equivalents of (nBu₄N)CN did not yield signals for either 1, [1Cu–OTf]⁺ or related anionic species (e.g., [1Cu–OTf+2CN]⁻. Trace amounts of [Cu(CN)_3]⁺ have been detected.

**Figure S79.** Detail of the d(Fe)–π*(C₃N₃) transitions in the titration of 1Cu with (nBu₄N)CN in CH₂Cl₂ (1:1, then in steps of 0.2 eq.; monitored by UV/Vis spectroscopy, start and end point of titration marked in bold) in comparison to the d(Fe)–π*(C₃N₃) transitions of free ligand 1 (black) and complex 1Cu.
2.6. Electrochemistry

Figure S80. Cyclic voltammograms of 2,4,6-tris(1-bromo-1'-ferrocenylene)-1,3,5-triazine (4) (left) and borane-protected ligand 1BH$_3$ (right) in tetrafluoroborate- (top) and BAr$_4$F$^-$-based (bottom) supporting electrolytes (SE) in CH$_2$Cl$_2$. In all cases, the second of three consecutively measured cycles is shown. Arrows represent the starting potential and initial scan direction (100 mV·s$^{-1}$).

Figure S81. Cyclic voltammograms of ligand 1 in (nBu$_4$N)$\text{BF}_4$/CH$_2$Cl$_2$ with different turning potentials. In both cases, the second of three consecutively measured cycles is shown. Arrows represent the starting potential and initial scan direction (100 mV·s$^{-1}$).
While both the ligand precursor 4 and the borane-protected ligand 1BH₃ are reversibly oxidisable in both the BF₄⁻ and the BArF₄⁻-based SE (Figure S80) and even display three individual redox events when measured in the very weakly coordinating BArF₄⁻-based SE, free ligand 1 yields non-reversible oxidation events and, tied to the first of several oxidation events, a delayed reduction hinting at an electron transfer-chemical reaction (EC) oxidation mechanism (Figure S81).

**Figure S82.** Cyclic voltammograms of ligand 1 in (nBu₄N)BF₄/CH₂Cl₂ with different turning potentials (top, 2nd cycles shown), indicating the presence of three oxidation events, and the dependency of the broad reductive events at about −1.5 V on prior oxidation (bottom). Arrows represent the starting potential and initial scan direction (100 mV·s⁻¹). The most anodic scan (pink, bottom) is cropped due to reasons of clarity, as the sharp increase in current only relates to the electrolyte.

The electrochemical behaviour of ligand 1 in the BArF₄⁻-based SE is shown in Figure S82. While the first oxidation at about 340 mV (top, dashed lilac) is reversible to some degree (vide infra), the later oxidations at 500 mV (top, dash-dotted lavender) and 860 mV (top, solid blue) are irreversible and cancel out the partial reversibility of the first oxidation. Similar to the properties of 1 in the BF₄⁻-based SE, the second and third oxidation induce broad yet weak reductive events at cathodic potentials around −1.5 V which are absent if the scan direction is reversed immediately after the first oxidation. The bottom part of Figure S82 confirms this behaviour. If the cycle starts with a cathodic scan, no reductive events can be identified, while the broad reductive features appear after the first oxidations have been carried out in the second cycle.

Recording the first oxidation with three different scanning speeds (20, 100, and 500 mV·s⁻¹) and normalising the currents according to the Randles-Sevčik equation for the square root of the scanning speed (Figure S83), the increase of reversibility indicates an EC(EE) mechanism operating in that case. The first oxidation, likely iron-centred, thus generates a species undergoing a chemical transformation yielding an electroactive product which participates in further redox events.
Figure S83. First oxidation of ligand 1 in (nBu4N)BAR4+CH2Cl2 at and normalised for different scanning speeds (Randles-Sevčik plot), showing the increasing degree of reversibility of this oxidation at faster scanning. In all cases, the second of three consecutively measured cycles is shown.
Figure S84. Cyclic voltammograms of complex 1Au in (nBu4N)BF4/CH2Cl2 with different turning potentials (top, 2nd cycles shown), indicating the presence of three oxidation events, and the dependency of the broad reductive events at about −1.2 V on prior oxidation (bottom). Arrows represent the starting potential and initial scan direction (100 mV s⁻¹).

The electrochemical characterisation of 1Au in the BF₄⁻-based SE (Figure S84) reveals similar behaviour of this complex in comparison to free ligand 1. Two oxidation events at 350 mV (pink dotted, top) and 490 mV (red dash-dotted, top) can be isolated by CV, the first of which has some degree of reversibility, while the second is linked to a cathodically shifted reduction at −1.3 V. This dependence on prior oxidation is also found when the scan direction is reversed (orange dashed, bottom). A third oxidation event at 690 mV appears to be (quasi)reversible, yet leads to a further broadening at the reductive event at around −1.3 V. Analysing a 1:1 mixture of 1 (red dotted) and 1Au (blue dotted) under the same conditions (Figure S85) however demonstrates that the electrochemical characteristics of 1Au are most likely not a result of 1Au degrading into 1 during the experiment, since the recorded cyclic voltammogram (black bold) appears as the sum of both individual traces.
Figure S85. Cyclic voltammograms of a 1:1 mixture of ligand 1 and complex 1Au in (nBu₄N)BF₄/CH₂Cl₂. The arrow represents the starting potential and initial scan direction (100 mV s⁻¹).

In the BArF₄⁻-based SE (Figure S86), the electrochemistry of 1Au displays marked differences. The first (dotted pink) and, to some degree, reversible, and the second (dashed red), less reversible, oxidations appear more separated than in the BF₄⁻-based SE, in line with the lower ability of BArF₄⁻ anions to compensate positive charges by coming in close vicinity to the positive charges. The third oxidation at about 1.2 V is much less reversible. Most notably, the cathodically shifted reduction observed for 1Au in the BF₄⁻-based electrolyte seems almost absent. Only at higher scanning speeds does a reductive event at about −1.2 V become apparent (Figure S87), in line with describing the electrochemistry of 1Au as following an ECE mechanism. This Randles-Sevčík plot also indicates changes in the reductions at more anodic potentials.
Figure S86. Cyclic voltammogram of complex 1Au in (nBu4N)BAR4/CH2Cl2 with different turning potentials (top, 2nd cycles shown), indicating the presence of three oxidation events. Arrows represent the starting potential and initial scan direction (100 mV·s⁻¹).

Figure S87. Cyclic voltammograms of complex 1Au in (nBu4N)BAR4/CH2Cl2 at and normalised for different scanning speeds (Randles-Sevčík plot), showcasing the scan speed dependency. The insert shows the increasing visibility of a cathodically shifted reduction at about -1.2 V with increasing scan speed in detail. In all cases, the second of three consecutively measured cycles is shown.
Figure S88. Cyclic voltammograms of complex 1Ag in (nBu4N)BF4/CH2Cl2 with different turning potentials (top, 2nd cycles shown), indicating the presence of at least three oxidation events, and the dependency of the reductive events at ~500 mV and about ~1.3 V on the prior oxidation (bottom). Arrows represent the starting potential and initial scan direction (100 mV s⁻¹).

Regarding its electrochemical behaviour in the BF₄⁻-based SE (Figure S88), 1Ag behaves similar to 1Au. There are two oxidation events at 255 mV (dotted light green) and 500 mV (dash-dotted forest green) which are not reversible and entail cathodically shifted reduction events at ~500 mV (linked to the first oxidation, itself again inducing another oxidation event at ~450 mV) and ~1.3 V (linked to the second oxidation). Further oxidation events at more anodic potentials intensify the reductive current at both potentials (solid navy), but none of the reductive events is present when the measurement is begun with a cathodic scan (bottom) but only appear after the first oxidative cycle.

Comparing the cyclic voltammograms at different scan rates (Figure S89) confirms these reductions to be linked to one or more chemical transformations that 1Ag undergoes after initial and following oxidations, as both reductions disappear at slow scanning speeds. As for 1Au, one or more EC(E) mechanisms seem to operate here.

In much the same way, following the electrochemistry of 1Ag in the BArF₄⁻-based SE (Figure S90) leads to a disappearance of the reduction events at about ~500 mV, while the even more cathodic and oxidation-dependent reductions are still present. As for the BF₄⁻-based SE, slower scan speeds result in the disappearance of the reductive currents (not shown).
Figure S89. Cyclic voltammograms of complex 1Ag in (nBu4N)BF4/CH2Cl2 at and normalised for different scanning speeds (Randles-Sevčík plot), showcasing the scan speed dependency particularly for the reduction events. In all cases, the second of three consecutively measured cycles is shown.

Figure S90. Cyclic voltammograms of complex 1Ag in (nBu4N)BARF4/CH2Cl2 with different turning potentials (top, 2nd cycles shown), indicating the presence of three oxidation events. Arrows represent the starting potential and initial scan direction (100 mV s⁻¹).
Figure S91. Cyclic voltammograms of complex 1CuBF₄ in (nBu₄N)BF₄/CH₂Cl₂ with different turning potentials (top, 2nd cycles shown), indicating the presence of at least two oxidation events, and the dependency of the reductive events at about −1.5 V on the prior oxidation (bottom). Arrows represent the starting potential and initial scan direction (100 mV s⁻¹).

The electrochemical characterisation of the copper(I) complexes in the BF₄⁻-based SE (Figure S91) was carried out using 1CuBF₄. In contrast to 1Au and 1Ag under the same conditions, only one isolable first oxidation at 270 mV (top, dotted light blue) can be identified, tied to a cathodically shifted reduction event at about −1.4 V which is not present when the complex is initially scanned in cathodic direction (bottom, dashed berry). The first oxidation is followed by a broad oxidation event (bottom, solid dark purple) at about 700 mV (and potentially by further oxidations), which are linked to a comparatively sharp reduction peak at 380 mV and at least one more cathodically shifted reduction at about −1.3 V. While lowering the scanning speeds entails the disappearance of the reduction peaks (Figure S92), it also results in a second prominent yet also irreversible oxidation at higher potential (1.1 V), an unprecedented behaviour in comparison to both 1Au and 1Ag and potentially linked to the generation of an (unstable) Cu⁰ species (vide infra).
Figure S92. Cyclic voltammograms of complex 1CuBF₄ in (nBu₄N)BF₄/CH₂Cl₂ at and normalised for different scanning speeds (Randles-Sevčík plot), showing the scan speed dependency particularly for the reduction events and the most anodic oxidation at about 1.1 V only visible at 20 mV·s⁻¹. In all cases, the second of three consecutively measured cycles is shown.

When following the electrochemistry of 1Cu in the BArF₄⁻-based SE (Figure S93), two oxidations at 640 mV (top, dotted light blue) and 890 mV (top, dash-dotted royal blue) can be identified again. In contrast to both 1Au and 1Ag, an initial cathodic scan (bottom, dashed berry) reveals a reduction at about −2 V original to 1Cu, invariant to scanning speed (Figure S94) unlike the other reduction events at about −1.5 V (bottom, solid dark purple) related to the most anodic oxidation. The nature of this original reduction is only speculative but might correspond to the Cu⁺/Cu⁰ redox couple. The absence of a corresponding oxidation – no corresponding peak is found during the anodic scan even at higher scanning speeds and the oxidation events are independent of prior reduction – would be in line with the reported instability of mononuclear copper(0) complexes which only lately have become synthetically available and for one of which, stabilised by cyclic alkylaminocarbene ligands, \( E_{1/2} \) was determined to be −1.79 V vs. FcH/[FcH]⁺ in THF.⁶⁰d
Figure S93. Cyclic voltammogram of complex 1Cu in (nBu4N)BAF4/CH2Cl2 with different turning potentials (top, 2nd cycles shown), indicating the presence of three oxidation events. Arrows represent the starting potential and initial scan direction (100 mV s⁻¹).
Figure S94. Cyclic voltammograms of complex 1Cu in (rBuN)BARf$_4$/CH$_2$Cl$_2$ at and normalised for different scanning speeds (Randles-Sevčík plot), showing the scan speed dependency particularly for the reduction events at about $-1.55 \text{ V}$ and the contrasting invariance of the reduction at $-2 \text{ V}$ original to un-oxidised 1Cu. In all cases, the second of three consecutively measured cycles is shown.
2.7. Spectroelectrochemistry

2.7.1. Spectroelectrochemical measurements of 1Au

Figure S95. Time-dependent UV/Vis spectra recorded during the oxidation of 1Au at 25 °C in (nBu4N)BARF4/CH2Cl2. The green line represents the starting point, the red line represents the product after oxidation. Arrows indicate the direction of intensity changes.

Figure S96. Time-dependent UV/Vis spectra recorded during the reduction after prior oxidation of 1Au at 25 °C in (nBu4N)BARF4/CH2Cl2. The red line represents the starting point – the spectrum obtained after prior oxidation – and the orange line represents the spectrum after oxidation. Arrows indicate the direction of intensity changes.
Figure S97. Time-dependent UV/Vis spectra recorded during the oxidation of 1Au at −50 °C in (nBu4N)BArF4/CH2Cl2. The green line represents the starting point, the red line represents the product after oxidation. Arrows indicate the direction of intensity changes.

Figure S98. Time-dependent UV/Vis spectra recorded during the reduction after prior oxidation of 1Au at −50 °C in (nBu4N)BArF4/CH2Cl2. The orange line represents the starting point – the spectrum obtained after prior oxidation – while the blue line represents the product after reduction.
Figure S99. Time-dependent UV/Vis spectra recorded during the second oxidation of 1Au at -50 °C in \((\text{nBu}_4\text{N})\text{BARF}_4/\text{CH}_2\text{Cl}_2\). The red line represents the starting point – the spectrum obtained after prior oxidation – the orange line represents the product after second oxidation. Arrows indicate the direction of intensity changes.

Figure S100. Time-dependent UV/Vis spectra recorded during the second reduction of 1Au at -50 °C in \((\text{nBu}_4\text{N})\text{BARF}_4/\text{CH}_2\text{Cl}_2\) after two previous oxidations. The orange line represents the starting point – the spectrum obtained after two prior oxidations – the pink line represents the product after the following reduction. Arrows indicate the direction of intensity changes.
Figure S101. Time-dependent UV/Vis spectra recorded during the first oxidation of 1Au at −80 °C in \((\text{nBu}_4\text{N})\text{BArF}_4/\text{CH}_2\text{Cl}_2\). The green line represents the starting point and the red line represents the spectrum after oxidation. Arrows indicate the direction of intensity changes.

Figure S102. Time-dependent UV/Vis spectra recorded during the second oxidation of 1Au at −80 °C in \((\text{nBu}_4\text{N})\text{BArF}_4/\text{CH}_2\text{Cl}_2\). The red line represents the starting point – the spectrum obtained after the first oxidation – and the orange line represents the spectrum after the second oxidation. Arrows indicate the direction of intensity changes.
Figure S103. Time-dependent UV/Vis spectra recorded during the second oxidation of $^{1}$Au at $-80 \, ^\circ C$ in (nBuN)BAr$^+$-CH$_2$Cl$_2$. The red line represents the spectrum obtained after the first oxidation, the orange line represents the spectrum after the second oxidation, and the blue line represents the spectrum after reduction after the second oxidation.

As becomes apparent from the oxidation and reduction experiments, $^{1}$Au cannot be reversibly oxidised at room temperature or at $-50 \, ^\circ C$; the UV/Vis spectra obtained after one oxidation-reduction cycle are not identical; hence, they most likely correspond to different compounds. The UV/Vis spectral change on the first oxidation at $-80 \, ^\circ C$ is markedly different from the changes recorded at the other temperatures, and only the second oxidation brings about the same spectral features that have been found on oxidation at $-50 \, ^\circ C$ and at $25 \, ^\circ C$.

Comparing the spectra obtained from double oxidation at $-80 \, ^\circ C$ (Figure S103, orange) and from the isolated oxidation product 5 (104, solid red) reveals them to be quite similar, particularly with respect to the intense absorption at about 330 nm and the shifted d(Fe)$-\pi^*(C_3N_3)$ transition at about 575 nm. Though it is only speculative and a reaction with adventitious traces of water in the spectroelectrochemical setup seems unlikely, the similarity of the two spectra could point to the formation of 5 or a very similar species under these conditions, supporting the proposed ECE-type oxidation from $^{1}$Au to 5 concurrent with oxidation at a phosphorus atom.

Figure S104. Comparison of the UV/Vis spectra of $^{1}$Au (black, dotted) and isolated oxidation product 5 (red, solid), both in CH$_2$Cl$_2$. The spectra have been arbitrarily scaled for better comparability.
Figure S105. Time-dependent UV/Vis spectra recorded during the oxidation of 1Ag at ~80 °C in (nBu4N)BArF4·CH2Cl2: The green line represents the starting material, the red line represents the spectrum obtained after the oxidation and the blue line represents the spectrum after the subsequent reduction. Arrows indicate the direction of intensity changes during oxidation.
2.7.3. Spectroelectrochemical measurements of 1Cu

**Figure S106.** Time-dependent UV/Vis spectra recorded during the oxidation of 1Cu at ~80 °C in (nBu4N)BArF4/CH2Cl2. The green line represents the starting material, the red line represents the spectrum obtained after the oxidation. Arrows indicate the direction of intensity changes. The insert shows the region relevant to MMCT/IVCT transitions in detail.

**Figure S107.** Time-dependent UV/Vis spectra recorded during the reduction of 1Cu at ~80 °C in (nBu4N)BArF4/CH2Cl2 after previous oxidation. The green line represents the starting material before oxidation, the red line represents the spectrum obtained after the oxidation and the blue line represents the spectrum obtained after subsequent reduction. Arrows indicate the direction of intensity changes during the reduction (red to blue). The insert shows the region relevant to MMCT/IVCT transitions in detail.
Author Contributions

AS has carried out the syntheses and characterisation of the compounds, including the NMR experiments, and has written the original draft. PC has acquired and solved the solid-state structures of all compounds and carried out as well as analysed the computational investigations. MRR has carried out the variable-temperature spectroelectrochemical experiments and prepared the corresponding graphs as well as aided in their interpretation. EHH has supervised and administered the project, helped in acquiring funding for AS and PC and supported AS in the writing of the draft.

Appendix - Cartesian coordinates of optimised molecular structures

1Cu (as closed form 1Cu_\infty)

| C | 2.57650868769938 | 11.41722040597026 | -2.83191164499309 |
| H | 2.6274119562630 | 12.27717465720373 | -3.49935903041110 |
| C | -1.53835658616125 | 10.54113456567248 | 2.37608161393408 |
| C | 2.49118602577796 | 9.09997588637141 | 1.89448191813260 |
| C | 3.4716447531743 | 14.6924400258391 | 0.86882586510248 |
| C | 5.34351192593789 | 13.74242533495080 | -0.6514071506892 |
| H | 4.74391700307134 | 13.4934914961629 | -1.5190468412542 |
| C | 1.97371331736363 | 15.75286772704642 | 2.22443972095483 |
| C | -1.38174379264918 | 12.2245145894155 | 0.12146711315019 |
| C | -2.64140280750835 | 12.71917597089316 | -0.37416739873530 |
| C | -3.38356098271665 | 13.25008253042284 | 0.21289562407041 |
| C | 5.93282878889900 | 10.96526453050693 | 1.33880638404215 |
| C | -0.68846600226279 | 11.61110471007198 | -0.9832178913220 |
| H | 0.28749004083969 | 11.14445573489834 | -0.9391529206358 |
| C | 6.65396351778318 | 11.18819662203119 | 2.24062238829846 |
| H | 7.46453018547677 | 11.43099713984745 | 2.92140924784963 |
| C | 1.07343495279051 | 13.8748375920299 | 5.5272068320558 |
| H | 0.60690424181382 | 17.8867114970578 | 4.95404961773268 |
| H | -0.16267253989206 | 18.46045876159984 | 5.46418261624701 |
| C | 1.690595041767577 | 16.51982813665997 | 3.4311292177194 |
| C | 2.3953388643006 | 9.21465612104817 | -1.12702578407491 |
| C | 2.33616803709399 | 8.34833012775736 | -0.4699244446169 |
| C | 4.84425802233974 | 14.29507192731300 | 0.58442438560123 |
| C | 5.96491182507145 | 14.46882755844150 | 1.46988992823530 |
| C | 9.50663162674758 | 14.85820113077993 | 2.47839162676721 |
| C | 1.60767462621350 | 14.5541721803469 | 6.68056078373789 |
| C | 2.62142943200845 | 14.4559091975532 | 5.7044719803219 |
| C | 1.33046133760464 | 15.03125498235086 | 0.158110960379 |
| C | 2.31064656967335 | 9.0382592678178 | -2.50999985163917 |
| C | 2.17836608725267 | 8.03526670339000 | -2.91729004458267 |
| C | -0.58953530382647 | 15.23674894559991 | 6.40151021295510 |
| C | -1.53010665567330 | 15.76525601612779 | 6.52574254189695 |
| C | 2.62381400458454 | 16.84890326734276 | 4.48145055310206 |
| C | 3.6532588810577 | 16.51610101236660 | 4.53795564558507 |
| C | 1.3351588018621 | 11.06925773470143 | 5.51410973508160 |
| C | -0.29182568926616 | 14.3054766596200 | 5.36037671343735 |
| C | -0.96931670469915 | 13.97819814594622 | 4.58182478834259 |
## SUPPORTING INFORMATION

### Table 1Cu (as open form 1Cu

| C  | 7.33587767894384 | 5.79829549389304 | 14.868939214536 | 0.52612413928203 | 5.92615326901278 |
|---|---|---|---|---|---|
| H | 7.80766115059287 | 4.87322195919313 | 15.203942912581 | 0.2612413928203 | 5.92615326901278 |
| C | 10.32427187955572 | 4.25637339545691 | 13.659983165405 | 0.52612413928203 | 5.92615326901278 |
| H | 10.70427554198726 | 5.22899951943033 | 13.29508115791329 | 0.52612413928203 | 5.92615326901278 |
| N | 11.19938381642233 | 3.422745338715 | 14.4086194526920 | 0.52612413928203 | 5.92615326901278 |
| C | 12.11642314926189 | 3.75530542759147 | 14.705146969285 | 0.52612413928203 | 5.92615326901278 |
| H | 4.73874568682621 | -0.06574092891423 | 13.688150596839 | 0.52612413928203 | 5.92615326901278 |
| C | 4.28757565685522 | 0.27190853956746 | 14.6185671515013 | 0.52612413928203 | 5.92615326901278 |
| H | 1.8355924243088 | 4.68205645441024 | 13.56923350873452 | 0.52612413928203 | 5.92615326901278 |
| C | 0.60230129202382 | -0.92152894558573 | 10.4030334391823 | 0.52612413928203 | 5.92615326901278 |
| H | 0.16508853787852 | -1.78169338463146 | 10.88300568755077 | 0.52612413928203 | 5.92615326901278 |
| C | 2.17140808407535 | -0.46331437593210 | 16.67346365202703 | 0.52612413928203 | 5.92615326901278 |
| H | 0.19749597736785 | -3.92441839598289 | 14.21878693074238 | 0.52612413928203 | 5.92615326901278 |
| C | -0.275135359122835 | -4.8523941216791 | 14.54226802455749 | 0.52612413928203 | 5.92615326901278 |
| H | 1.10982625633834 | 3.56756833645026 | 13.20273457801787 | 0.52612413928203 | 5.92615326901278 |
| C | 3.90072570005785 | -2.08908832151048 | 17.176262791202687 | 0.52612413928203 | 5.92615326901278 |
| H | 4.95391054340603 | -2.3243699785189 | 17.33282037741792 | 0.52612413928203 | 5.92615326901278 |
| C | 5.89036664743993 | -0.96621092914018 | 11.3141457998241 | 0.52612413928203 | 5.92615326901278 |
| H | 6.339372262328774 | -1.3203557716767 | 10.38547122265168 | 0.52612413928203 | 5.92615326901278 |
| C | 0.33728295461362 | 1.3023796172447 | 18.67759010140621 | 0.52612413928203 | 5.92615326901278 |
| H | 1.24939714756181 | 0.88297191659519 | 19.10433893510366 | 0.52612413928203 | 5.92615326901278 |
| C | 4.04778900057511 | 2.6981779816941 | 15.77305271411116 | 0.52612413928203 | 5.92615326901278 |
| H | 4.10761567132497 | 2.4264022644898 | 14.72365192032333 | 0.52612413928203 | 5.92615326901278 |
| C | -1.94648528156283 | 2.06112653093306 | 18.9455347064473 | 0.52612413928203 | 5.92615326901278 |
| H | -2.80303824676944 | 2.26235373443055 | 19.5892099387842 | 0.52612413928203 | 5.92615326901278 |
### SUPPORTING INFORMATION

| Element | X Coordination | Y Coordination | Z Coordination |
|---------|----------------|----------------|----------------|
| C       | 4.57489121889026 | 10.87966949704277 | 1.30721994579323 |
| H       | 4.69812698521877  | 13.39563984287703 |                |
| C       | 5.30952842281904  | 13.66918598927435 |                |
| C       | 3.45603093383669  | 14.63837795296070 | 0.87          |
| C       | 2.45889964395541  | 9.04888067997534  | 1.75747102778171 |
| H       | 2.57493109965741  | 12.28120398532406 |                |
| Cu      |                |                | 1.48344196279886 |
| Fe      |                |                | 3.45021857979191 |
| P       |                |                | 5.73874675108948 |
| C       |                |                | 1.58192055766208 |
| H       |                |                | 1.48266018299344 |
| C       |                |                | 6.1610684210467 |
| C       |                |                | 5.71038441279190 |
| C       |                |                | 6.17637629593692 |
| C       |                |                | 1.82112429581754 |
| H       |                |                | 1.48266018299344 |
| C       |                |                | 1.02800096777323 |
| C       |                |                | 6.52625541986293 |
| C       |                |                | 7.28495820396221 |
| C       |                |                | 7.33823500267408 |
| C       |                |                | -0.9409768217650 |
| C       |                |                | -1.00754126557409 |
| C       |                |                | 2.93249557663381 |
| C       |                |                | 3.22722503043248 |
| C       |                |                | -0.758848635650658 |
| C       |                |                | -0.691520360568635 |
| C       |                |                | 9.03487267556755 |
| C       |                |                | 4.57201359326715 |
| C       |                |                | 3.57272158454879 |
| C       |                |                | 5.40253236317318 |
| C       |                |                | 6.37329053373954 |
| C       |                |                | 9.373274256213529 |
| C       |                |                | 9.00433533351549 |
| P       |                |                | 1.6625110724887 |
| P       |                |                | 8.080642087322491 |
| P       |                |                | 2.13730705284393 |
| Fe      |                |                | -0.1137643490483 |
| Fe      |                |                | 2.98091563870855 |
| Fe      |                |                | 5.00040364594577 |
| Cu      |                |                | 1.48132350154697 |

**1Ag**

| C       | 2.57915034583885 | 11.40773497427514 | -2.9450101859080 |
| H       | 2.57493109965741 | 12.28120398532409 | -3.5991140953680 |
| C       | -1.64438238784105 | 10.6200824909405 | 2.45660597672398 |
| C       | 2.45889964395541 | 9.04888067997534 | 1.75747102778171 |
| C       | 3.45030939386669 | 14.63837795296070 | 0.8759265804424 |
| C       | 5.30952842281904 | 13.66918598927435 | -0.6584126567533 |
| C       | 6.49812695821877 | 13.39563984278770 | -1.50851770710938 |
| C       | 1.974119820373637 | 15.69958171503610 | 2.25001958123533 |
| C       | -1.4786053912874 | 12.1984126919247 | 1.0387627896621 |
| C       | -2.71050802866155 | 12.6551168434177 | -0.48070342264062 |
| C       | -3.50508029813600 | 13.1737828682136 | 0.04644858065861 |
| C       | 4.57489121890206 | 10.8796949704277 | 1.30721994579323 |
| C       | -0.68750368569946 | 11.59809167274379 | -0.9366880248152 |

**93**
| 1Au |  |  |
|-----|---|---|
| C   | 2.571527 | 11.421766 | -2.887881 |
| H   | 2.602232 | 12.293919 | -3.542975 |
| C   | -1.617497 | 10.566229 | 2.407519 |
| C   | 2.486166  | 9.050454  | 1.817798 |
| C   | 3.463858  | 14.670304 | 0.872043 |
| C   | 5.325231  | 13.703815 | -0.653217 |
| H   | 4.719427  | 13.441797 | -0.963207 |
| H   | 0.290671  | 11.160774 | 0.873166 |
| C   | 6.465480  | 11.207743 | 2.296821 |
| C   | 7.423931  | 11.482839 | 3.002355 |
| C   | 1.078954  | 13.879704 | 5.592117 |
| C   | 1.702050  | 16.501564 | 3.445545 |
| C   | 2.499464  | 9.185910  | -1.216443 |
| C   | 4.77867   | 8.309541  | -0.569738 |
| C   | 5.962068  | 14.453568 | 1.454335 |
| C   | 5.910765  | 14.853274 | 2.459212 |
| C   | 1.558451  | 14.590160 | 6.750289 |
| C   | 2.557477  | 14.512245 | 7.167250 |
| C   | 1.320927  | 15.016581 | 0.172924 |
| C   | 2.410433  | 9.027512  | -2.601127 |
| C   | 2.315004  | 8.026704  | -3.023837 |
| C   | -0.634001 | 15.238769 | 6.364107 |
| C   | -1.584493 | 15.750304 | 6.436990 |
| C   | 2.636090  | 16.820238 | 4.496919 |
| C   | 3.660379  | 16.472117 | 4.558585 |
| C   | 1.410463  | 11.065563 | 5.590581 |
| C   | -0.282345 | 14.290021 | 5.356760 |
| C   | -0.918395 | 13.941694 | 4.552010 |
| C   | 5.567062  | 10.523017 | 0.361863 |
| C   | 5.732314  | 10.174464 | -0.647359 |
| C   | -0.624242 | 14.740233 | -2.992865 |
| C   | -0.781851 | 14.454039 | -4.028594 |
| C   | -2.851129 | 15.663886 | 2.936093 |
| C   | -2.656257 | 16.732716 | 2.834376 |
| C   | -1.468576 | 11.710907 | -2.156897 |
| C   | -1.158000 | 11.377959 | -3.142854 |
| C   | 0.514725  | 11.110195 | 6.667961 |
| C   | 0.119679  | 12.066262 | 7.010413 |
| C   | 3.524217  | 8.257925  | 2.327420 |
| C   | 4.548567  | 8.629425  | 2.320960 |
| C   | 2.640879  | 11.590761 | -1.504867 |
| C   | 2.684186  | 12.594928 | -1.075096 |
| C   | 2.615868  | 10.469702 | -0.661462 |
| C   | -1.927368 | 14.741009 | 2.445250 |
| C   | -0.991561 | 15.085019 | 1.997159 |
| C   | -1.898507 | 8.981269  | 4.222355 |
| C   | -1.747048 | 8.717722  | 5.268526 |
| C   | 3.659172  | 12.804748 | 5.280352 |
| C   | -2.695384 | 12.379129 | -1.838389 |
| C   | -3.477770 | 12.645716 | -2.543267 |
| C   | 0.459292  | 17.158295 | 3.750974 |
SUPPORTING INFORMATION

|  |  |  |
|---|---|---|
| H  | -0.438399 | 17.102139 | 3.148522 |
| C  | 1.915768  | 9.828352  | 5.161576 |
| H  | 2.609019  | 9.781562  | 4.322181 |
| C  | 1.538917  | 8.652857  | 5.807276 |
| H  | 1.942057  | 7.700944  | 5.463513 |
| C  | 6.846678  | 10.708755 | 0.968935 |
| H  | 7.806946  | 10.543069 | 0.488840 |
| C  | 1.430382  | 10.205889 | 3.751031 |
| H  | 0.919102  | 10.884145 | 4.433584 |
| C  | 2.182798  | 13.366347 | 2.562709 |
| H  | 2.576215  | 15.710827 | -2.439995 |
| C  | 2.453011  | 10.143460 | -3.440342 |
| H  | 2.391635  | 10.017111 | -4.521895 |
| C  | 1.171615  | 8.558991  | 1.828046 |
| H  | 0.356401  | 9.168907  | 1.439785 |
| C  | 0.329397  | 14.990637 | -0.895447 |
| H  | 1.449023  | 13.984695 | -2.558144 |
| C  | 0.998257  | 15.553541 | -0.855148 |
| H  | -1.461272 | 16.016992 | 0.008051 |
| C  | 1.975163  | 17.827989 | 5.420894 |
| H  | 2.404356  | 18.083616 | 6.334455 |
| C  | 5.241053  | 11.338970 | 2.517711 |
| H  | 4.764169  | 11.699415 | 3.421253 |
| C  | 0.899963  | 7.288051  | 2.329936 |
| H  | -0.125448 | 6.920190  | 2.327906 |
| C  | -2.544383 | 8.097185  | 3.352947 |
| H  | -2.907144 | 7.136281  | 3.720462 |
| C  | 0.499608  | 15.426002 | 7.220231 |
| H  | 0.560338  | 16.117929 | 8.055468 |
| C  | 3.245323  | 6.988856  | 2.842526 |
| H  | 4.057821  | 6.377796  | 3.237654 |
| C  | 6.741456  | 13.574812 | -0.541113 |
| H  | 7.403768  | 13.163222 | -1.297078 |
| C  | 4.196174  | 12.031408 | 6.321161 |
| H  | 3.597168  | 11.251043 | 6.789076 |
| C  | 5.737353  | 14.040634 | 5.144061 |
| H  | 6.340356  | 14.827057 | 4.687209 |
| C  | 1.936379  | 6.500889  | 2.841215 |
| H  | 1.723415  | 5.507646  | 3.238429 |
| C  | -2.269019 | 6.979780  | 1.538579 |
| H  | -2.421262 | 9.951518  | 0.494380 |
| C  | 4.441093  | 13.806055 | 4.684989 |
| H  | 4.042214  | 14.379550 | 3.843790 |
| C  | 5.502146  | 12.259301 | 6.760275 |
| H  | 5.913585  | 11.650274 | 7.556015 |
| C  | 0.129099  | 9.927086  | 7.304631 |
| H  | -0.568385 | 9.969125  | 8.142129 |
| C  | 6.273403  | 13.268097 | 6.178084 |
| H  | 7.290394  | 13.449728 | 6.527694 |
| C  | -2.725094 | 8.446434  | 2.012450 |
| H  | -3.230729 | 7.761457  | 1.330695 |
### Supporting Information

| Element | X    | Y    | Z    |
|---------|------|------|------|
| C       | 0.641882 | 8.699427 | 6.87955 |
| H       | 0.342894 | 7.778801 | 7.381669 |
| Au      | 1.335025 | 12.127313 | 2.430580 |
| Fe      | 5.801284 | 12.479052 | 0.918588 |
| Fe      | 0.984470 | 15.889683 | 5.277097 |
| Fe      | -1.086695 | 13.570368 | -1.367980 |
| N       | 3.228186 | 15.267652 | 2.058655 |
| N       | 0.986989 | 15.628202 | 1.325500 |
| P       | -0.985867 | 12.186460 | 1.842300 |
| P       | 1.937955 | 12.576398 | 4.706061 |
| P       | 2.787138 | 10.722605 | 1.141710 |

| Triazine+Cu | | | |
| Cu     | 1.33926397356944 | 12.13354784675977 | 2.42667573577746 |
| C      | 3.47134742098076 | 14.69214591315811 | 0.869010264265192 |
| C      | 1.97360532597711 | 15.75200915072574 | 2.22468042287492 |
| C      | 1.33008771432087 | 15.03055238479888 | 0.15857674513461 |
| N      | 3.22681476863506 | 15.2875315638308 | 2.05454365173999 |
| N      | 2.5550495208330 | 14.53163578876876 | -0.10572909577999 |
| N      | 0.98849119806575 | 15.64147615038767 | 1.30979275776982 |
| H      | 0.56330021889960 | 14.93442419401237 | -0.6150441253436 |
| H      | 1.73945880609856 | 16.25486139314124 | 3.16721583673623 |
| H      | 4.48191556676955 | 14.3164402186436 | 0.68650773632939 |

| Triazine+Ag | | | |
| Ag     | 1.36007570263307 | 12.2043369559540 | 2.39154911493072 |
| C      | 3.45604256613390 | 14.63915610785080 | 0.8590649265235 |
| C      | 1.97358776315031 | 15.69739555978449 | 2.25157487940205 |
| C      | 1.30924123898827 | 14.9901166827597 | 0.18557203555339 |
| N      | 3.22371145791428 | 15.22875333694003 | 2.0677828724192 |
| N      | 2.53060047153968 | 14.48642633266197 | -0.09173116770645 |
| N      | 0.97924695031948 | 15.5939202551400 | 1.34435208340459 |
| H      | 0.53482923955519 | 14.89752320942565 | -0.58036716311476 |
| H      | 1.75213911994202 | 16.20619629987658 | 3.19487152556003 |
| H      | 4.46172548982381 | 14.25566174407511 | 0.68489937207617 |

| Triazine+Au | | | |
| Au     | 1.33008666173864 | 12.12596138222222 | 2.43201686396621 |
| C      | 3.46304140084042 | 14.66769914329327 | 0.87295728007915 |
| C      | 1.97708227956843 | 15.7303870787946 | 2.23637048276124 |
| C      | 1.32024074603209 | 15.0148636216286 | 0.17387982308402 |
| N      | 3.22770574838291 | 15.26535530323318 | 2.0593994638000 |
| N      | 2.54223231840860 | 14.51163872281762 | -0.0974398102221 |
| N      | 0.98664019353348 | 15.62683080075094 | 1.32637422761878 |
| H      | 1.75019725323975 | 16.23719457762555 | 3.17996119304853 |
| H      | 4.47288004713670 | 14.29313201746458 | 0.68283613555581 |
| H      | 0.55052246911897 | 14.92394498251332 | -0.59767149147153 |