Coordination Chemistry of \( \text{P}_2\text{S}_3 \) and \( \text{P}_2\text{Se}_3 \) towards the Iron Fragments \( [	ext{Fe}(\text{Cp})(\text{CO})_2]^+ \) and \( [	ext{Fe}(\text{Cp})(\text{PPh}_3)(\text{CO})]^- \)

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Abstract: The complexes \( \text{Ag}(\text{L})_2[\text{WCA}] \) (\( \text{L} = \text{P}_2\text{S}_3, \text{P}_2\text{Se}_3, \text{As}_2\text{S}_3, \) and \( \text{As}_2\text{Se}_3; \) \( \text{WCA} = [\text{Al}(\text{OR})_3]_3^2^- \) and \( [\text{Al}(\text{OR})_3]_3^2^-; \) \( R^2 = \text{C}(\text{CF}_3)_2; \) \( \text{WCA} = \text{weakly coordinating anion} \)) were tested for their performance as ligand-transfer reagents to transfer the poorly soluble nortricyclane cages \( \text{P}_2\text{S}_3, \text{P}_2\text{Se}_3, \) and \( \text{As}_2\text{S}_3 \) as well as realgar \( \text{As}_2\text{Se}_3 \) to different transition-metal fragments. \( \text{As}_2\text{S}_3 \) and \( \text{As}_2\text{Se}_3 \) with the poorest solubility did not yield complexes. However, the more soluble silver-coordinated \( \text{P}_2\text{S}_3 \) and \( \text{P}_2\text{Se}_3 \) cages were transferred to the electron-poor \( \text{P}^+ \) moiety \( ([\text{CpFe}(\text{CO})_2]_3^-) \). Thus, reaction of the silver salt in the presence of the ligand with \( \text{Fp}^-\text{Br} \) yielded \( [\text{Fp}^-\text{P}_2\text{S}_3]([\text{Al}(\text{OR})_3]_3^2^-) \) \( (1a) \), \( [\text{Fp}^-\text{P}_2\text{Se}_3][([\text{Al}(\text{OR})_3]_3^2^-)^2 \) \( (1b) \), and \( [\text{Fp}^-\text{P}_2\text{Se}_3]([\text{Al}(\text{OR})_3]_3^2^-) \) \( (2) \). Reactions with \( \text{P}_2\text{S}_3 \) also yielded \( [\text{Fp}^+\text{P}_2\text{S}_3][([\text{Al}(\text{OR})_3]_3^2^-) \) \( (3) \), a complex with the more electron-rich monophosphine-substituted \( \text{P}^+ \) analogue \( [\text{Fp}^+\text{P}_2\text{S}_3]_3^2^- \) \( ([\text{CpFe}(\text{PPh}_3)(\text{CO})]_-) \). All complex salts were characterized by single-crystal XRD, NMR, Raman, and IR spectroscopy. Interestingly, they show characteristic blueshifts of the vibrational modes of the cage, as well as structural contractions of the cages upon coordination to the \( \text{Fp}^-\text{P}_2\text{S}_3 \) moieties, which oppose the typically observed cage expansions that lead to redshifts in the spectra. Structure, bonding, and thermodynamics were investigated by DFT calculations, which support the observed cage contractions. Its reason is assigned to \( \sigma \) and \( \pi \) donation from the slightly \( \text{P}^-\text{P} \) and \( \text{P}^-\text{E} \) antibonding \( \text{P}_2\text{E}_3^-\text{C} \) HOMO (\( \text{symmetry} \)) to the metal acceptor fragment.

Introduction

To the known examples of neutral complexes of \( \text{P}_2\text{E}_3 \) \( (\text{E} = \text{S}, \text{Se}) \) cages with \( \text{BX}_3 \) \( (\text{X} = \text{Br}, \text{I}) \), \( \text{NbCl}_3 \), \( \text{Ni}^{(np3)} \) \( (np3 = \text{tris}(2\text{-diphenylphosphino})\text{thiophosphino})\text{ethylamine} \), \( \text{M}([\text{CO}]_3) \) \( (\text{M} = \text{Mo}, \text{W}) \), \( \text{CuX}([\text{PR}_3]_2) \) \( (\text{X} = \text{Cl}, \text{Br}, \text{I}; \text{R} = \text{Me}, \text{Et}, \text{iPr}, \text{Cy}) \), and \( \text{Cp}^*(\text{CO})_3 \) \( (1) \) cationic complexes that use these cages as ligands include electron-rich transition-metal fragments, mostly \( 16 \) valence electron iron or ruthenium. The presence of electron-rich phosphines or additionally the pentamethycyclopentadienide \( \text{(Cp)}^* \) ligand is hitherto paramount for stability; typical examples include \( [\text{Fe}^\text{II}\text{Cp}][\text{dppe}][\text{P}_2\text{S}_3]_3^2^- \) and \( [\text{Ru}(\text{Cp})^*(\text{dppe})][\text{P}_2\text{Se}_3]_3^2^- \) \( (\text{dppe} = \text{bis}(\text{diphenylphosphino})\text{ethane}) \) \( (\text{Figure} \, 1) \). In such complexes, the basal phosphorus atoms of the cage coordinate to the metal atom, or as in dimeric \( [\text{Ru}(\text{Cp})\text{(PPh}_3)_2][\text{P}_2\text{S}_3]_3^2^- \) \( , \) the nortricyclane cage interacts with the metal fragments through the apical as well as one of the basal phosphorus atoms.\( ^{2-3,5} \) Complexes of these transition-metal fragments with other inorganic cages as ligands, such as \( \text{P}_2\text{As}_2 \) and \( \text{As}_2\text{P}_2 \) also exist; for example, \( [\text{Cp}^\text{II}\text{Fe}(\text{dppe})][\text{P}_2\text{As}_2]_3^2^- ; [\text{Cp}^\text{II}\text{Fe}(\text{dppe})][\text{P}_2\text{As}_2]_3^2^- \), and \( [\text{Cp}^\text{II}\text{Ru}(\text{dppe})][\text{As}_2\text{S}_3]_3^2^- \) \( ^{6,7} \) These complexes can enable interesting degradation chemistry of the otherwise inert cages under standard conditions. The hydrolysis of \( [\text{CpRu}(\text{PPh}_3)_2][\text{P}_2\text{S}_3]_3^2^- \) and \( [\text{CpRu}(\text{PPh}_3)_2][\text{P}_2\text{Se}_3]_3^2^- \) \( + \) salts, for example, yield complexes of diphenosphate and thiophosphinic acid.\( ^{[9]} \)

A novel approach towards complexes of weak ligands, like the group \( 15/16 \) cages, is ligand-transfer reactions. Thus, Scheer et al. succeeded in the synthesis of complexes of yellow arsenic \( ([\text{PPh}_3\text{Au}(\text{As}_2\text{S}_3)]^2^- \) and \( [\text{Cp}^\text{II}\text{Ru}(\text{dppe})][\text{As}_2\text{S}_3]_3^2^- \) ) through the
reaction of the corresponding transition-metal halide with Ag[As₄]_₄[Al(OR)]₄. This acts as a stable storage form of yellow arsenic that releases the As₄ cluster upon removal of the Ag⁺ cation with a well-soluble halide complex.[7,4]

In this realm, the electron-poor complex [CpFe(CO)]₄⁺ (Fp⁺) and monophosphine-substituted complex [CpFe(CO)(PPh₃)]⁺ ([FpPPh₃]⁺) units are not known for coordination chemistry that uses such weak ligands. However, they readily yield complexes with strongly coordinating ligands, such as phosphines.[9] Only recently, [Fp−P₃]⁺ and monophosphine-substituted [FpPPh₃−P₃]⁺ that include dynamically bound P₄ cages, which are visible on the NMR timescale, were synthesized.[10] The formation of these complexes showed that it is possible to use the ligand-transfer reaction to bind weak ligands to these metal fragments through halide abstractions given that the ligand is immediately present in the reaction environment by coordination to the silver ion. With this precaution, the reactivity of the metal fragment is not quenched by competing reactions, such as the formation of the adduct [Fp−Br−Fp]⁺ with residual Fp−Br or the dismutation product [CpFe(CO)PPh₃]⁺. Interestingly, characteristic blueshifts of the breathing modes of the P₄ ligand accompanied by a considerable shrinkage of the P−P bond lengths were observed in these complexes. Thus, apparently, the relatively electron-poor fragments Fp⁺ and FpPPh₃⁺ induced a novel bonding situation of the P₄ ligand: The carbonyl-substituted metal fragments prevent π back-bonding, and the Fe−P interaction is reduced mainly to π donation from the P₄ cluster to the metal. As the HOMO of P₄ has some antibonding character, this results in a structural contraction of the cages. By contrast, the known examples with the more electron-rich metal fragments, such as [CpFe(dppel)]⁺, form stable and NMR-static complexes with these ligands owing to a considerable amount of π back-bonding that cancels out this cage contraction.[10]

Yet, quite a number of complexes of weak and often poorly soluble ligands with the silver ion of Ag[Al(OR)]₄ are accessible; that is, those with inorganic rings, such as S₄P₄Se₄ (n = 6, 12), and the cages P₅, P₅S₅, P₅Se₅, As₅S₅, and As₅Se₅.[11,12–14] Hence, the concept of ligand-transfer chemistry can be tested by reacting easily accessible representatives of these compounds with suitable, soluble transition-metal halides. Herein, we present complexes of P₅S₅ and P₅Se₅ with the electron-poor iron fragments Fp⁺ and FpPPh₃⁺. They are the first examples of such complexes that do not rely on bidentate phosphine and the electron-rich Cp⁺ ligands. These complexes show similar blueshifts of their vibrational modes and cage contractions upon coordination to the metal, as in [Fp−P₃]⁺ and [FpPPh₃−P₃]⁺.

Results and Discussion

Synthesis of the complexes

Generally, the synthesis of the complexes was achieved by weighing one equivalent of Ag[WCA] (WCA = weakly coordinating anion) together with one equivalent of the ligand on one side of a double-bulb vessel that was separated by a glass frit plate and condensing CH₂Cl₂ onto the solids. After stirring for 1 h at room temperature, the solids were dissolved, and a solution of one equivalent of [M]X (X = Fp−Br, FpPPh₃−Br, or PPh₃AuCl) in CH₂Cl₂ was added to the reaction mixture (Scheme 1). Immediately, a precipitate of AgBr formed and a color change of the yellow-orange solution to deep red occurred (not for PPh₃AuCl). After stirring for several hours to ensure a complete reaction and removal of AgBr by filtration, the obtained deep red solutions were reduced in volume to around half and layered with pentane. Storage of these mixtures at room temperature or at 6°C led to the formation of crystals after several days. For P₅S₅ and P₅Se₅, this procedure led to complexes 1, 2, and 3 (Scheme 1, Reaction 1). The synthesis of complex 1 was done with the [Al(OR)]₄⁺ (1a) as well as the [F(Al(OR)]₃)_n⁺ anion (1b) to tackle problems with the structural characterization. Syntheses of the potential [Fp(As₄S₄)]⁺, [Fp(As₄Se₄)]⁺, and [PPh₃Au(As₄S₄)]⁺ complex salts were futile with all conditions tested (Scheme 1, Reactions 2–4); instead, the reactions led to a precipitate of free ligand and crystals of Au(PPh₃)[Al(OR)]₄ (4) or Fp−Br−Fp[Al(OR)]₄ (5). The cations [Fp−Br−Fp]⁺ as well as [Au(PPh₃)]⁺ are already known.[15]

NMR spectra of the complexes

The NMR spectra of isolated crystals of complexes 1a, 2, and 3 dissolved in CD₂Cl₂ show that the used [Al(OR)]₄⁺ anion stays intact over the course of the reactions because only the typical ¹⁹F and ²⁷Al NMR signals are visible (see the Supporting Information, Figures S4–S24). Owing to their dynamic nature in solution, the known silver complexes Ag(P₅S₅)[WCA][12,13] and Ag(P₅Se₅)[WCA] (n = 1, 2, 3)[14] show only two distinct signals of the ligands in the ³¹P NMR spectra. Complexes 1 and 2 show three distinct signals of the apical phosphorus atom P₅, the coordinated basal phosphorus atom P₅coord, and the noncoordi-
nated phosphorus atoms P$_{b/noncoord}$. This demonstrates that the P$_{5}$S$_{4}$ and P$_{6}$S$_{5}$ cages are firmly bound to the Fp moiety through one of their basal phosphorus atoms, similar to the more electron-rich analogues [Cp*Ru(L$_{2}$)(P$_{5}$S$_{4}$)]$^{+}$ and [Cp*Ru(L$_{2}$)(P$_{6}$S$_{5}$)]$^{+}$ ($L_2$ = bidentate phosphine) but unlike the more weakly bound P$_4$ ligand in [Fp-P$_{4}$]$^{+}$.[8,10] Complex 3 shows five different phosphorus signals, one for the PPh$_3$ ligand and four for the P$_{5}$S$_{4}$ cage. An apical coordination of the cages would exhibit less cage signals, as known from studies of ruthenium 16 electron fragments coordinated to P$_{5}$S$_{4}$ that include a mixture of isomers. Isomer formation did not occur for P$_{5}$Se$_{4}$.[3] However, apical coordination of P$_{5}$S$_{4}$ was observed to a low extent in complexes 1 (<1%) and 3 (5%). All $^{31}$P NMR spectra are summarized in Figure 2.

All $^{31}$P chemical shifts as well as the coupling constants are given in Table 1. Complexes 1 and 2 exhibit an ABX$_3$ spin system with slightly higher order effects in their $^{31}$P(H) NMR spectra. In the non-decoupled $^{31}$P spectra, P$_{b/coord}$ shows further splitting, which is due to the coupling of the five protons of the Cp ring to P$_{b/coord}$ with $^4$J(P$_{b/coord}$H) = 2 Hz in both cases. The resonance of the apical phosphorus atoms P$_a$ in complexes 1 and 2 manifests as a triplet of doublets. The signals of the coordinated basal phosphorus atoms P$_{b/coord}$ show a signal that resembles a triplet of doublets, but it includes further splitting of the central line of the triplet owing to slightly higher order effects. The noncoordinated basal phosphorus atoms P$_{b/noncoord}$ also show a signal that resembles a doublet of doublets, but this shows further splitting owing to slightly higher order effects.

Owing to the loss of the chemical equivalency of the two P$_{b/noncoord}$ atoms in complex 3, the $^{31}$P[H] NMR spectra of this compound show an ABFMX spin system with ddd splits for each phosphorus atom, with the coupling constants $^1$J(P$_{b/coord}$P$_{b/noncoord}$) = 236, $^2$J(P$_{a}$P$_{b/coord}$P$_{b/noncoord}$) = 233, $^3$J(P$_{a}$P$_{b/coord}$P$_{b/noncoord}$) = 75, $^2$J(P$_{a}$P$_{b/noncoord}$P$_{b/noncoord}$) = 73, $^1$J(P$_{b/noncoord}$P$_{b/coord}$P$_{b/noncoord}$) = 56, $^2$J(P$_{b/coord}$P$_{b/noncoord}$P$_{b/noncoord}$) = 44, $^1$J(P$_{b/coord}$P$_{b/noncoord}$P$_{b/noncoord}$) = 47, $^3$J(P$_{b/noncoord}$P$_{b/noncoord}$P$_{b/noncoord}$) = 4, and $^3$J(P$_{b/coord}$P$_{b/noncoord}$P$_{b/noncoord}$) = 1 Hz, as well as the $^3$J(P$_{a}$P$_{b/coord}$P$_{b/noncoord}$) coupling, which is below 1 Hz. The two P$_{b/noncoord}$ atoms are not chemically equivalent in complex 3; therefore, the two atoms P$_{b/noncoord1}$ and P$_{b/noncoord2}$ can be found at two different chemical shifts of −133.6 and −139.2 ppm, respectively. Again, further splittings of the signals are notable in the non-decoupled $^{31}$P spectra, because the protons of the Cp ligand couple to the phosphorus atoms in the P$_{5}$S$_{4}$ cage.

The coordination of Fp$^+$ and FpPPh$_3$$^+$ moieties to the P$_{5}$S$_{4}$ and P$_{6}$S$_{5}$ cages significantly alters their chemical shifts: The apical phosphorus atoms P$_a$ are shifted slightly downfield upon coordination of one of the basal phosphorus atoms to the metal. The noncoordinated basal phosphorus atoms P$_{b/noncoord}$ are only moderately shielded with respect to P$_b$ of free P$_{5}$S$_{4}$ and P$_{6}$S$_{5}$ (shifted upfield, $\delta$ = 7 to 10.5 ppm). The coordinated basal phosphorus atoms P$_{b/coord}$ experience a strong downfield shift to $\delta$ = 139.3 (1a), 157.8 (2), and 126.6 ppm (3). It is notable that this shift is larger in the phosphine-substituted example. This is consistent with other complexes of P$_{5}$S$_{4}$ and P$_{6}$S$_{5}$ with the metal fragments [(Cp*Ru(L$_1$))]$^+$ (L$_1$ = dppe, dppm, dppe, dpadpppe) that have shown similar trends of the chemical shifts. The shift of P$_{b/coord}$ is stronger in the examples with bishosphine ligands. In contrast to complexes 1, 2, and 3, which are firmly bound at room temperature, the recently synthesized complex [Fp-P$_{4}$]$^+$ [Al(OR)$_4$]$_{12}$ shows fluctuating behavior at room temperature that can be frozen out at temperatures below 263 K.[10]

The $^{77}$Se spectra (see the Supporting Information, Figure S16) of complex 2 shows that the multiplet of the P$_{5}$Se$_{4}$ cages in Ag$_4$(P$_{5}$Se$_{4}$)$_4$[Al(OR)$_4$]$_{12}$, which can be found at $\delta$ $\approx$ 800 ppm,[14] splits into two distinct signals at $\delta$ = 775 and 622 ppm, with the high-field shifted signal at $\delta$ = 622 ppm...
Table 1. $^{31}P$ chemical shifts as well as coupling constants and multiplicities of the signals of complexes 1, 2, and 3 alongside free ligands $P_S$ and $P_Se$ in $CDCl_3$ at room temperature.\(^{26}\)

| Spin system | $P_S$ | $P_{b/coord}$ | $P_{b/truncate}$ | $PPh_3$ |
|-------------|-------|---------------|-----------------|---------|
| $P_{S1}$    | $AB_3$ | 62.6 ppm (q)  | $P_{b/coord}$   | $P_{b/truncate}$ |
| 1a          | $ABX_3$ | 93.2 ppm (td) | $P_{b/coord}$   | $P_{b/truncate}$ |
| 3           | $ABFMX$ | 94.7 ppm (ddddd) | $P_{b/coord}$   | $P_{b/truncate}$ |
| $P_{S2}$    | $AB_3$ | 30.5 ppm (q)  | $P_{b/coord}$   | $P_{b/truncate}$ |
| 2           | $ABX_3$ | 71.4 ppm (td) | $P_{b/coord}$   | $P_{b/truncate}$ |

[a] All values of chemical shifts are given in ppm. Couplings to the protons are omitted in this list (see the Supporting Information). In the case of complex 3, the coupling constants in the higher order spin systems are given in the Supporting Information (Table S3). [b] These spin systems show additional splittings owing to higher-order effects. Hence, the affected signals are marked as multiplets (m).

being caused by the single selenium atom next to $P_{b/coord}$. This signal shows a ddt splitting with the coupling constants $J(Se, P_{b/coord}) = 463$, $J(Se, P_J = 273$, and $J(Se, P_{b/truncate} = 20$ Hz). The resonance at $\delta = 775$ ppm is caused by the isotopeomer that has one $^{77}Se$ atom in a position between $P_J$ and $P_{b/truncate}$ and shows a multiplet of higher order (see the Supporting Information, Table S3 for coupling constants). It should be noted that the coupling constant between the two $P_{b/truncate}$ is exceptionally small for a $J(P, P)$ coupling. $^{77}Se$ NMR spectra of previously characterized similar compounds, such as $[(Cp*)Ru(dppe)P_{Se}]$ (BPH$_3$) and other analogues were not reported owing to the limited solubility of the compounds.\(^{31}\)

The $^{13}C$ NMR spectra of complexes 1, 2, and 3 show signals for the Cp ligands at around $\delta = 88$ ppm. The CO ligands of complexes 2 and 3 are visible at $\delta = 205.4$ and 213.1 ppm, respectively, which is consistent with the data recorded for $[Fe-P_J[WCA]$ and $[FePPh_3-P_{J}][WCA]$.\(^{10}\) $^{13}C$ NMR signals of the CO ligands in complex 1a could not be obtained within a reasonable timeframe, and thus, are not given (but IR and Raman spectroscopy data are available).

**Single-crystal structures**

The crystals of compounds 1 to 3 were obtained as yellow to red blocks. We were not able to obtain a data set of complex 1a because the crystals crack in the cooling stream of the diffractometer. Thus, complex 1b was synthesized, which contains the same cation.\(^{16}\) The crystal structures of complexes 4 and 5 were also determined and deposited\(^{16}\) (see the Supporting Information, Table S1), but they are not discussed because they contain known cations. The asymmetric unit of all structures only contains one cation. All cations show the $Fp$ or $FpPPh_3$ moieties bound to one of the basal phosphorus atoms of the nortricyclane cage, which supports the findings from the NMR spectroscopy. The molecular structures of all cations are shown in Figure 3.

A summary of all relevant bond lengths is given in Table 2. All nortricyclane cages show slight contractions of the $P_{b/coord}^b$-$P_{b/truncate}^b$ bonds of up to 4.1 pm in complex 3 compared with...
the uncoordinated cage. All $P_{b/noncoord}$–$P_{b/noncoord}$ bonds are elongated by up to 2.5 pm (in complex 3). This is in accordance with the very small $\nu(P-P)$ coupling observed between these two atoms in the 31P NMR spectra. The $P_{b/coord}$–$E$ and $P_{b/noncoord}$–$E$ are also shortened by up to 4.1 pm (in complex 1b) in the complexes, but typically, the $P_{b/E}$ bonds are less affected by coordination of the cage. However, even here, slight changes are noticeable: the $P_{b/E}$ bond nearest to $P_{b/noncoord}$ are shortened by up to 0.6 pm in complex 1b and the $P_{b/E}$ bonds further away from the coordinated phosphorus atom are elongated by up to 1.0 pm (in complex 1). The Fe–$P_{b/coord}$ bond is shorter in the phosphine-substituted complex 3 than in 1b, which is consistent with the findings in our studies on $[Fp–P_{b}^{+}]$ and $[FpPh_{3}–P_{b}^{+}]$. It implies a stronger metal–cage bond for the more electron-rich metal fragments.\[a\]

Vibrational spectroscopy

The IR spectra of complexes 1a, 2, and 3 show the anion bands as well as the bands of the CO ligands and several bands of the PPh$_3$ ligand of the cations, whereas the bands of the ligands P$_3$S$_3$ and P$_3$Se$_3$ are only visible in the Raman spectra. These spectra (Figure 4) clearly show that the coordination to the metal lowers the symmetry of the C$_{3v}$-symmetric cages because some degenerate bands of the ligands split upon coordination and show slightly different vibrational patterns. Generally, the experimental Raman spectra are in good agreement with the calculated spectra (see the Supporting Information, Figures S1–S3) that were used for further evaluation and band assignment.

![Figure 4](image-url)

**Table 2.** Comparison of the structural parameters of complexes 1b (100 K), 2 (100 K), and 3 (170 K) with the free ligands P$_3$S$_3$ and P$_3$Se$_3$ at 100 K. E denotes the chalcogen atoms of the ligand (S or Se). Calculated bond distances with index “calc.” are given (RIU/B3-LYP(D3BJ)/def2-TZVPP level).

| Distance [pm] | 1b$^{[a]}$ | 3 | $\alpha$-P$_3$S$_3$$^{[b]}$ | 2 | P$_3$Se$_3$$^{[b]}$ |
|--------------|-----------|---|----------------|---|----------------|
| $d(\text{M–P}_{b/noncoord}$) | 219.8(1) | 217.9(1) | – | 221.3(1) | – |
| $d(\text{M–P}_{b/coord}$) | 223.2 | 220.4 | – | 224.0 | – |
| $d(P_{b/noncoord}$–$P_{b/noncoord}$) | 220.0(1), 221.5(1) | 220.1(1), 221.7(1) | 224.1 | 220.7(1), 221.1(1) | 222.8 |
| $d(P_{b/coord}$–$P_{b/coord}$) | 222.6 | 221.8, 223.3 | 225.5 | 221.8 | 224.6 |
| $d(P_{b/noncoord}$–$P_{b/coord}$) | 225.7(1) | 226.0(2) | – | 224.9(1) | – |
| $d(P_{b/noncoord}$–$P_{b/coord}$) | 229.5 | 229.8 | – | 228.2 | – |
| $d(P_{b/coord}$–$E$) | 206.6(1) | 207.5(1) | 210.7 | 221.9(1) | 224.2 |
| $d(P_{b/coord}$–$E$) | 208.4 | 209.3 | 211.0 | 223.7 | 226.2 |
| $d(P_{b/coord}$–$E$) | 207.5(1), 208.1(1) | 207.5(1), 208.0(2) | – | 222.8(1), 223.1(1) | – |
| $d(P_{b/noncoord}$–$E$) | 209.8 | 209.9, 210.2 | – | 224.9 | – |
| $d(P_{b/E}$) | 210.0(1)–211.6(1) | 210.1(1)–211.5(2) | 210.6 | 224.1(1)–225.3(1) | 224.9 |
| $d(P_{b/E}$) | 210.7 | 210.6 | – | 224.9 | – |
| $d(P_{b/E}$) | 213.2–213.6 | 212.9–213.0 | 212.3 | 228.0–228.2 | 227.0 |
| $d(P_{b/E}$) | 213.4 | 213.0 | – | 228.1 | – |

[a] Crystals of complex 1a cracked in the cryostream of the diffractometer. Therefore, 1b was synthesized, which did not pose these problems. [b] For free P$_3$S$_3$ and P$_3$Se$_3$, $d(P_{b–P_{b}})$ and $d(P_{b/E}$) are given, as there are no $d(P_{b/noncoord}$–$P_{b/noncoord}$ and $d(P_{b/coord}$–$E$) or $d(P_{b/noncoord}$–$E$). The average values from refs. [13] and [14] are given. [c] An average distance is only given if there are three or more different bond lengths, including the range of the distances. If there are only two different bond lengths, both bond lengths are given.
| P$_2$S$_3$ Raman | 1a IR | 1a Assignment$^{[b]}$ | 3 IR | 3 Assignment$^{[b]}$ | P$_2$Se$_3$ Raman | 2 IR | 2 Assignment$^{[b]}$ |
|-------|-------|------------------|-----|------------------|-------|-------|------------------|
|       |       |                  | 102 | $\delta$(Fe–CO) |       |       |                  |
|       | 115 (s) | $\delta$(Fe–CO) | 113 | $\delta$(Fe–CO) |       | 111 (m) | $\delta$(Fe–CO) |
|       | 139 (s) | $\delta$(Fe–Cp) | 136 | $\delta$(Fe–Cp) | 135 (vw) | 136 | $\delta$(Fe–Cp)/$\delta$(P–Se$_2$) |
|       | 161 (vw) | $\delta$(Fe–Cp) | 174 | $\delta$(Fe–Cp) |       | 156 | $\delta$(OC–Fe–Cp) |
|       | 189 (m) | $\delta$(OC–Fe–Cp) |       |       | 174 | $\delta$(OC–Fe–Cp) |
| 182 (vw) | A$_2$ | 210 (vw) | $\delta$(P$_2$–S$_2$) | 196 | $\delta$(P$_2$–S$_2$) |       | 214 (m) | A$_1$/E | 192 | $\delta$(P$_2$–Se$_2$)/$\delta$(Fe–P)$_{\text{binder}}$ |
| 220 (vw) | E | 225 (s) | $\delta$(P$_2$–S) | 223 | $\delta$(P$_2$–S) |       | 217 | $\delta$(P$_2$–Se$_2$) |
|       |       |       | 241 | $\delta$(Fe–Cp)/$\delta$(C–H) |       | 225 | $\delta$(P$_2$–Se$_2$) |
|       |       |       | 256 | $\delta$(Fe–Cp)/$\delta$(C–H) |       | 244 | $\delta$(P$_2$–Se$_2$) |
| 285 (vw) | E | 288 (m) | $\delta$(P$_2$–S$_2$) | 285 | $\delta$(P$_2$–S$_2$) | 320 (w) | A$_1$ | 330 | $\delta$(P$_2$–Se$_2$)/[Al(OR)$_3$]$_2^-$ |
|       | 306 (s) | $\delta$(P$_2$–S$_2$) | 310 | $\delta$(P$_2$–S$_2$) | 346 (sh) | E | 358 | $\delta$(P$_2$–Se$_2$) |
|       |       |       | 321 | $\delta$(P$_2$–S$_2$) |       | 367 | $\delta$(Fe–Cp) |
|       |       |       | 330 (vw) | [Al(OR)$_3$]$_2^-$/$\delta$(Fe–Cp) | 330 | $\delta$(P$_2$–S$_2$)/[Al(OR)$_3$]$_2^-$ | 365 (vs) | A$_1$ | 381 | $\delta$(P$_2$–Se$_2$) |
|       |       |       | 344 (m) | $\delta$(Fe–Cp) | 343 | $\delta$(Fe–Cp) |       | 388 | $\delta$(Fe–Cp) |
| 341 (m) | E | 368 (vs) | $\nu$(P$_2$)/$\nu$(C–H) | 362 | $\nu$(P$_2$)/$\nu$(C–H) | 370 (sh) | A$_1$ | 409 | $\nu$(P$_2$–Se$_2$) |
|       | 377 (m) | $\nu$(P$_2$)/$\nu$(C–H) | 373 | $\nu$(P$_2$)/$\nu$(C–H) | 405 (w) | E | 428 | $\nu$(P$_2$–Se$_2$) |
|       |       |       | 384 | $\delta$(C–H) |       | 448 | $\nu$(P$_2$–Se$_2$)/$\delta$(Fe–C–O) |
| 420 (vw) | A$_1$/E | 409 (w) | $\nu$(P$_2$–S$_2$) | 404 | $\nu$(P$_2$–S$_2$)/$\nu$(C–H) |       | 487 | $\nu$(Fe–P)$_{\text{binder}}$//$\delta$(Fe–C–O) |
|       | 425 (m) | $\nu$(P$_2$–S$_2$) | 428 | $\nu$(P$_2$–S$_2$)/$\nu$(C–H) | 484 (w) | A$_1$ | 517 | $\nu$(Fe–P)$_{\text{binder}}$//$\nu$(P$_2$)/$\nu$(Fe–C–O) |
|       |       |       | 437 (vw) | $\delta$(Fe–C–O) | 441 (s) | 443 | $\delta$(C–H) | 517 | [Al(OR)$_3$]$_2^-$/$\delta$(Fe–C–O) |
| 441 (vs) | A$_1$ | 472 (s) | $\nu$(P$_2$–S$_2$) | 472 | 473 | $\delta$(C–H)/$\nu$(P$_2$–S$_2$) | 2040 | 2040 | $\nu$(C–O) asy. |
| 487 (vw) | E | 505 (m) | $\nu$(Fe–P)$_{\text{binder}}$//$\delta$(P$_2$–Se$_2$) | 509 | 504 (m) | $\nu$(Fe–P)$_{\text{binder}}$//$\delta$(P$_2$–Se$_2$) | 2080 | 2081 | $\nu$(C–O) sy. |
|       |       |       | 526 (vw) | $\delta$(Fe–C–O)/ $\nu$(P$_2$–S$_2$) | 528 (s) | 538 | $\delta$(C–H)/$\nu$(P$_2$–S)/$\delta$(Fe–C–O) | 2080 | 2081 | $\nu$(C–O) sy. |
|       |       |       | 571 (vw) | [Al(OR)$_3$]$_2^-$/$\delta$(Fe–C–O) | 555 | 556 | $\delta$(C–H)/$\delta$(Fe–C–O) | 2040 | 2040 | $\nu$(C–O) sy. |
|       |       |       | 595 (w) | [Al(OR)$_3$]$_2^-$/$\delta$(Fe–C–O) |       |       |       |       | $\nu$(C–O) asy. |
|       |       |       | 2045 | $\nu$(C–O) sy. | 1587 | (w) | $\delta$(C–H) |       |       | $\nu$(C–O) sy. |
|       |       |       | 2085 (m) | $\nu$(C–O) sy. | 1984 | 1992 | $\delta$(C–H) |       |       | $\nu$(C–O) sy. |

[a] For reasons of clarity, only the cation bands are shown, and most $\delta$(C–H) and $\nu$(C–H) bands are excluded. A summarizing table showing all vibrational bands is given in the Supporting Information (Table S2). All vibrational bands are given in cm$^{-1}$. [b] From a visualization of the calculated spectra. [c] The symmetry of the vibrational bands was derived from the calculated spectra as well as from ref. [17].

The vibrational frequencies are listed in Table 3. Vibrational bands that are directly affected by the coordination of the Fp and FpPPh$_3$ moieties to the cage, such as the stretching mode $\nu$(P$_2$) ($\delta$), which occurs at 341 cm$^{-1}$ for free P$_2$S$_3$, split distinctly into two bands at $\nu = 368$ and 377 cm$^{-1}$ in complex 1. In complex 2, this splitting was also observed at $\nu = 362$ and 373 cm$^{-1}$. The Raman spectrum of complex 3 also shows further splittings. It is notable that only the degenerate (E) bands of the free ligand show splittings in the complexes, which is due to the previously mentioned desymmetrization of the

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cages upon coordination to the metal. The nondegenerate bands ($A_1$ and $A_2$) are not affected by coordination and show no further splitting.

The vibrational spectra mostly show blue shifts of the vibrational bands of the $P_3S_4$ and $P_3Se_4$ cages. Comparison reveals similar trends for both the calculated gaseous complexes as well as those observed in the solid state; that is, the distortion of the $P_1$ basis, the contraction of the $P_1$--$S$ and $P_1$--Se bonds, and the shorter Fe--P bond in the phosphine-substituted compounds, which were also compared with the calculated gaseous free $P_3S_4$ and $P_3Se_4$ (Table 2). In addition, the calculated electron densities at the bond critical points of those structures agree with this overall bond contraction upon coordination (see below, analysis of the bonding situation with DFT methods, Table 5).

The $C_0$ stretching frequencies indicate the poor donation capability of the cages. Thus, the stretches of the starting material $Fp$--Br (2045 and 1985 cm$^{-1}$) are shifted in complexes 1a and 3 to $\nu=2085/2045$ and 2080/2040 cm$^{-1}$, respectively (IR and Raman). The $C_0$--O stretching frequency of the starting material $Fp$PPh$_3$--Br is at $\nu=1942$ cm$^{-1}$, and that of complex 2 is at $\nu=1980$ (IR)/1992 cm$^{-1}$ (Raman), which corresponds to a slightly smaller blueshift, as in complexes 1a and 3. Similar, but more pronounced, blueshifts were also observed in $[Fp-P_3P]$ and $[Fp$PPh$_3$--$P_3P]^+$, which suggests a weaker coordination of the $P_4$ ligands in comparison to the $P_4$E$_1$ cages.

**DFT-calculated thermodynamics of exchange reactions with other ligands**

Exchange reactions of $[Fp-P_3P]^+$ with the ligands used in this work in both the gas phase and in solution with CH$_2$Cl$_2$, as well as exchange reactions that start from either the side product $[Fp$--Br$]Fp$ or the naked $Fp$ were calculated (Table 4). Although the synthesis of $[Fp$--As$_3S_4]^+$ and $[Fp$--As$_3Se_4]^+$ salts is energetically favored, they could not be isolated; hereby, it was assumed that the ligands are dissolved in CH$_2$Cl$_2$. However, given that the solubility of the silver complexes of the nortricyclane cages decreases in the order $P_3S_4 > P_3Se_4 > A_3S_4$, it is likely that the reactions are inhibited by this issue. By contrast, this does not inhibit reaction with the comparably well-soluble silver--$P_4$ complex, despite being the weakest ligand.

Yet, the most favorable exchange reaction is the formation of the bridged $[Fp$--Br$]$--$Fp$ from residual $Fp$--Br binding the freshly formed $Fp$ cation. Thus, caution needs to be taken upon isolation of the crystalline complexes. This is reinforced by the experimentally verified isolation of the $[Fp$--Br$]$--$Fp$ salt (5). These salts tend to co-crystallize with the products, especially if the reaction mixture was not allowed to stir long enough to ensure a complete reaction. It is notable that the color of the isolated $[Fp$--L$]WCA$ salts indicates whether they are contaminated with salt 5, as red crystals of complex 1b contained salt 5 and pale yellow crystals of complex 1b contained no side products. This also explains the moderate yields of the complexes, because only the good-quality crystals were isolated for further characterization. Most importantly, the calculations suggest that a ligand-transfer reaction takes place. A pre-orientated ligand is necessary for the formation of complexes 1, 2, and 3 to take place. Otherwise the energetically favored formation of the dimer $[Fp$--Br$]$--$Fp$ takes place (Scheme 2). For $Fp$PPh$_3$--Br, the absence of a pre-orientated ligand is followed by CO abstraction of the residual $Fp$PPh$_3$--Br by the freshly generated $Fp$PPh$_3$+, as shown by the reaction of $Fp$PPh$_3$--Br, which yields CpFe(CO)$_3$PPh$_3$[Al(OR)$_3$]$_3$ and was iso-

| Exchange reactions of $[M$--Br$]$--$M^+$ with L to $[M$--P$_3P]^+$ and $M$--Br $\Delta H^0$ (gas) $\Delta G^0$ (gas) $\Delta G^0$ (CH$_2$Cl$_2$) |
|---|---|---|
| $[M$--Br$]$--$M^+$ | $+P_3P$ | $[M$--P$_3P]^+$ | $+$M--Br |
| $[M$--Br$]$--$M^+$ | $+P_3S_4$ | $[M$--P$_3S_4]^+$ | $+$M--Br |
| $[M$--Br$]$--$M^+$ | $+P_3Se_4$ | $[M$--P$_3Se_4]^+$ | $+$M--Br |
| $[M$--Br$]$--$M^+$ | $+As_3S_4$ | $[M$--As$_3S_4]^+$ | $+$M--Br |
| $[M$--Br$]$--$M^+$ | $+As_3Se_4$ | $[M$--As$_3Se_4]^+$ | $+$M--Br |

| Exchange reactions of $[Fp$--$Fp]$--$Fp$ with L to $[Fp$--L$]$--$Fp$ $\Delta H^0$ (gas) $\Delta G^0$ (gas) $\Delta G^0$ (CH$_2$Cl$_2$) |
|---|---|---|
| $Fp$--$Fp$ | $+P_3P$ | $[Fp$--$Fp$--$P_3P]^+$ | $-$160 | $-$126 | $-$163 |
| $Fp$--$Fp$ | $+P_3S_4$ | $[Fp$--$Fp$--$P_3S_4]^+$ | $-$205 | $-$164 | $-$221 |
| $Fp$--$Fp$ | $+P_3Se_4$ | $[Fp$--$Fp$--$P_3Se_4]^+$ | $-$214 | $-$173 | $-$236 |
| $Fp$--$Fp$ | $+As_3S_4$ | $[Fp$--$Fp$--$As_3S_4]^+$ | $-$199 | $-$160 | $-$238 |
| $Fp$--$Fp$ | $+As_3Se_4$ | $[Fp$--$Fp$--$As_3Se_4]^+$ | $-$199 | $-$159 | $-$240 |
| $Fp$--$Fp$ | $+P_3P$--$Fp$ | $[Fp$--Br$]$--$Fp^+$ | $-$210 | $-171$ | $-259$ |

[a] Structures of the isomers are shown in the Supporting Information, Figures S25 and S26. Exchange reactions starting from $[M$--P$_3P]^+$ ($M^+$ = $Fp$ and $Fp$PPh$_3$+) (in parentheses) are also given. [b] The COSMO (conductor-like screening model) solvation energies were calculated at the BP86/def-TZVP level.
not show the same structural
case shows an electron density at the
1 2
a
a
1
2
a

Calculated electron density (\(\rho_{\text{BCP}}\)) rises to 0.756 e Å\(^{-3}\), which suggests a stronger, and thus shorter, bond between these atoms. Likewise, \(\rho_{\text{BCP}}\) is lowered to 0.675 e Å\(^{-3}\), which suggests a weaker, and thus longer, bond.

The experimentally determined small distortions of the P\(_3\)E\(_3\) apex of the cage ligands agree with similar \(\rho_{\text{BCP}}\) (P-E) values of the free cages. The monophosphine-substituted analogues show slightly higher \(\rho_{\text{BCP}}\) (Fe-P) and higher ellipticities of the electron density at the BCP (\(\epsilon_{\text{BCP}}\)) than the comp-

**Table 5.** Calculated electron density (\(\rho\)) and ellipticity (\(\epsilon\)) of the electron density at the BCPs of the optimized gas-phase structures (IRUJB3-LYP(D3-BJ)/

| Property | P\(_3\)S\(_3\) | [P\(_3\)P\(_2\)S\(_3\)]\(^+\) | [P\(_3\)P\(_2\)S\(_3\)]\(^+\) |
|----------|----------------|-----------------|----------------|
| \(\rho_{\text{BCP}}\) (Fe–P) | – | 0.601 | 0.614 |
| \(\rho_{\text{BCP}}\) (P–P) | 0.709 | 0.756 | 0.749–0.769 |
| \(\rho_{\text{BCP}}\) (P–P) | – | 0.675 | 0.682 |
| \(\rho_{\text{BCP}}\) (P–S) | 0.864 | 0.925 | 0.904 |
| \(\rho_{\text{BCP}}\) (P–Se) | – | 0.884 | 0.877–0.884 |
| \(\epsilon_{\text{BCP}}\) (Fe–P) | 0.844–0.857 | 0.857 |
| \(\epsilon_{\text{BCP}}\) (P–P) | – | 0.08 | 0.12 |

| Property | P\(_3\)Se\(_3\) | [P\(_3\)P\(_2\)Se\(_3\)]\(^+\) | [P\(_3\)P\(_2\)Se\(_3\)]\(^+\) |
|----------|----------------|-----------------|----------------|
| \(\rho_{\text{BCP}}\) (Fe–P) | – | 0.594 | 0.607 |
| \(\rho_{\text{BCP}}\) (P–P) | 0.715 | 0.756 | 0.749 |
| \(\rho_{\text{BCP}}\) (P–P) | – | 0.682 | 0.682 |
| \(\rho_{\text{BCP}}\) (P–Se) | 0.736 | 0.783 | 0.769 |
| \(\rho_{\text{BCP}}\) (P–Se) | – | 0.746–0.756 | 0.749–0.756 |
| \(\rho_{\text{BCP}}\) (Se–Se) | 0.742 | 0.729 | 0.729–0.736 |
| \(\epsilon_{\text{BCP}}\) (Fe–P) | – | 0.08 | 0.11 |

| Property | P\(_3\) | [P\(_3\)P\(_2\)]\(^+\) | [P\(_3\)P\(_2\)]\(^+\) |
|----------|----------------|-----------------|----------------|
| \(\rho_{\text{BCP}}\) (Fe–P) | – | 0.553 | 0.567 |
| \(\rho_{\text{BCP}}\) (P–P) | 0.722 | 0.783–0.790 | 0.783–0.803 |
| \(\rho_{\text{BCP}}\) (P–P) | – | 0.682–0.688 | 0.682–0.702 |
| \(\epsilon_{\text{BCP}}\) (Fe–P) | – | 0.09 | 0.14 |
plexes of the more electron-poor \( Fp^+ \). This suggests a stronger Fe–P_{b/coord} bond in the more electron-rich complexes, which is in agreement with an increased \( \pi \) back-bonding of the more electron-rich metal fragments. This is also supported by the variety of complexes that are accessible with electron-rich bisphosphine and/or Cp*-substituted metal fragments.

Generally, \( \rho_{\text{BCP}}(\text{Fe–P}_{b/\text{coord}}) \) is higher in complexes 1, 2, and 3 than in the previously reported cations \([Fp_4]^{+}\) and \([FpPPPh_3]^{+}\), which shows that \( P_S \) and \( P_{Se} \) are more strongly bound than \( P_4 \); this is also reflected by the calculated exchange reactions that show the \( P_4 \) complexes to be the least favorable (Table 4). The distances \( \rho_{\text{BCP}} \) are also reflected in the vibrational spectra by showing significant blueshifts of some vibrational modes of the cages owing to the cage contractions. As in our investigations on cations \([Fp_4]^{+}\) and \([FpPPPh_3]^{+}\), computed partial charges as well as Wiberg bond orders have shown no definite trends and partially profound disagreements (Table S4); therefore, they were not used for further discussion.

**MO considerations**

To understand the nature of the cage contractions, we turned to MO investigations. Figure 5 indicates that the interaction of the orbitals of the free \( P_{E} \) cages with those of the iron fragments in \( Fp^+ \) show a modified bonding situation to \([Fp_4]^{+}\). In the latter, the cage contraction was assigned to the removal of electron density from the slightly \( P_4 \) antibonding \( P_4 – P_4 \) bond in \( Fp^+ \). HOMO by \( \pi \) donation into the LUMO of the \( Fp^+ \) fragment. In contrast to \( P_4 \), the HOMO of the \( P_{E} \) cages allows for \( \sigma \) and \( \pi \) donation towards the LUMO (\( \sigma \))/LUMO \(+1 (\pi \) of the metal fragment. Still, the \( P_{E} \) cage HOMO has antibonding character along the \( P_4 – E \) bonds and two of the three \( P – P \) bonds. Therefore, the removal of electron density from these orbitals presumably induces the observed cage contraction. In addition, the third \( P – P \) bond (back side \( P_{b/\text{noncoord}} – P_{b/\text{noncoord}} \) is \( P – P \) bonding in the cage HOMO. Thus, this bond is weakened through the interaction in the molecular structure.

This higher \( \sigma \) character of the Fe–P_{b/coord} bonds in \([Fp_4]^{+}\) compared to \([Fp_4]^{+}\) goes along with the calculated slight decrease of \( \rho_{\text{BCP}}(\text{Fe–P}_{b/\text{coord}}) \) and is the reason for the higher \( \rho_{\text{BCP}}(\text{Fe–P}_{b/\text{coord}}) \) in complexes 1, 2, and 3 than the \( P_4 \) analogues (Table 5). This stronger Fe–P_{b/coord} bond in complexes 1, 2, and 3 manifests itself in the calculated higher thermodynamic stability of these complexes as well as in the static nature of the \( ^{31}P \) NMR signals, compared with the temperature-dependent fluxional nature of \([Fp_4]^{+}\) and \([FpPPPh_3]^{+}\).

**Conclusions**

Investigations towards ligand-transfer reactions of silver complexes with the inorganic cages, such as the almost insoluble nortricyclane cage \( As_4S_3 \) and the realgar cage \( As_4S_4 \), were futile and led to salts of the already known cations \([Fp–Br–Fp]^{+}\) and
In the optimized gas-phase DFT structures and in AIM analyses. The vibrational spectra reflect these observations and show characteristic splittings and blueshifts of the Raman bands of the ligands. Also, the coupling constants observed in the NMR spectra indicate these special binding situations. MO investigations revealed similar reasons for the contraction as in complex \( \text{[P-P-S]}^3 \). However, the herein presented complexes exhibit additional \( \sigma \) donations from the ligand to the metal fragment. In general terms, the prevention of \( \pi \) back-donation by using electron-poor metal fragments may lead to bond contradictions, given that the donating cage orbitals include some antibonding character. In this respect, there is some analogy to the “non-classical” or “\( \sigma \)-only bound” transition-metal/CO complexes.\(^{[10]} \)

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cage compounds · iron · main group elements · transition metals · weakly coordinating anion

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[15] Compound 1b crystallized in the triclinic space group P1 (No.: 2) with \( a = 13.0589(5) \AA, \ b = 14.1991(6) \AA, \ c = 16.6335(3) \AA, \ \alpha = 85.512(2)^\circ, \ \beta = 70.409(2)^\circ, \ \gamma = 79.648(2)^\circ, \ z = 2. \) The anions show disorder; however, there is no disorder in the cation. Compound 2 also crystallized in the triclinic space group P1 (No.: 2) with the cell parameters \( a = 11.7416(5) \AA, \ b = 12.0319(5) \AA, \ c = 16.1237(7) \AA, \ \alpha = 86.314(2)^\circ, \ \beta = 75.701(2)^\circ, \ \gamma = 79.648(2)^\circ, \ z = 2. \) The anions is heavily disordered; however, there is no disorder in the cation. Compound 3 crystallizes in the monoclinic space group P2_1/c (No.: 14) with \( a = 19.0972(4) \AA, \ b = 17.8832(2) \AA, \ c = 18.6942(2) \AA, \ \beta = 117.4534(3)^\circ, \ z = 4. \) The crystal structure of this compound had to be determined at 170 K. Upon further cooling, a splitting of the reflections, which indicated formation of a superstructure, was observed. Again, the anion is heavily disordered, but not the cation.

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[18] CCDC 1890335, 1890336, 1890337, 1890339, and 1890338, 1901739 1b, 2, 3, 4, 5, and [CpFe(CO)2PPh3][Al(ORF)4]), respectively, contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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