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Isolation of Au-, Co-\(\eta^1\)PCO and Cu-\(\eta^2\)PCO complexes, conversion of an Ir-\(\eta^1\)PCO complex into a dimetalladiphosphene, and an interaction-free PCO anion†

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Sodium phosphaethynolate reacts with [MCl(PDI)] (M = Co, Ir; PDI = pyridinediimine) to give metallaphosphaketenes, which in the case of iridium rearranges into a dimetalladiphosphene, via CO migration from phosphorus to the metal. Two different bonding modes of the PCO anion to CAAC-coinage metal complexes [CAAC: cyclic (alkyl)(amino)(carbene)] are reported, one featuring a strong Au–P bond and the other an \(\eta^2\) coordination to copper. The gold complex appears to be mostly unreactive whereas the copper complex readily reacts with various organic substrates. A completely free PCO anion was structurally characterized as the \([\text{Cu}(\text{La})_2]^+\) (OCO\(^-\)) salt. It results from the simple displacement of the PCO unit of the cationic (CAAC)Cu(PCO) complex by a second equivalent of CAAC.

Introduction

Despite their early synthesis in 1992 by Becker, Westerhausen et al., the reactivity of phosphaethynolate salts \(\text{M}^+\)\((\text{PCO})^-\) remained unexplored until the recent development of simple syntheses which allow for the preparation of large quantities of pure material. These salts have been shown to undergo a variety of chemical transformations with organic substrates, including cycloaddition reactions leading to phosphorus containing heterocycles. In contrast, the strong reducing ability of PCO salts has hindered their exploration in transition metal chemistry. In most cases the reactions with metal complexes lead to decomposition products. The only exceptions are the formation of a \(\text{P}_2\text{C}(-\text{O})\text{O}\) ring by reacting Li(OCP) with \(\text{H}_5\text{C}_3\text{R}_2\text{PCO}\text{FeBr}\), the isolation of \([\text{Re(POC)}(\text{CO})_2\text{triphos}]\) \(\text{B}\), and uranium and thorium \(\text{M(OCO)}\text{amid}_3\) complexes \(\text{C}\), in which the phosphaethynolate binds the metal via the oxygen center (Fig. 1). Noteworthy is an extensive computational study, showing that metallaphosphaketene complexes such as \(\text{D}\) may rearrange via CO migration into molecular metal phosphides \(\text{E}\). The limited number of studies concerning the coordination chemistry of PCO is in marked contrast with the large number of reports dealing with the lighter analogue, namely the cyanate anion (NCO\(^-\)).

Herein we describe salt metathesis reactions leading to both unstable and stable terminal PCO transition metal complexes, featuring different coordination modes, and reactivity. We also report the experimental demonstration of the predicted conversion of \(\text{D}\) to \(\text{E}\), and the displacement of the PCO unit of the copper complex by a CAAC, which leads to a PCO anion with no coordinating solvents or binding agents.

Results and discussion

Because of the strongly reducing character of Na(OCP)\(^-\), we targeted complexes bearing pyridinediimine (PDI) ligands and...
cyclic (alkyl)(amino)carbenes (CAACs) which are known to efficiently stabilize metals in low oxidation states.\textsuperscript{14}

When the [CoCl(PDI)\textsuperscript{2+}] complex 1 was reacted with Na(OCP) in THF at –30 °C the color changed from pink to deep purple, and a single broad resonance in the \textsuperscript{31}P NMR spectrum at δ = –226 ppm [vs. δ = –392 ppm for Na(OCP)] indicated quantitative conversion. The metallaphosphaketene 3 was isolated in 61% yield and fully characterized. The IR spectrum showed the asymmetric stretching frequency of the phosphaketene unit at ν\textsubscript{asym} = 1851 cm\textsuperscript{−1}, intermediate between Na(OCP) (ν\textsubscript{asym} = 1755 cm\textsuperscript{−1}) and Ph\textsubscript{3}Sn=Pa=O (ν\textsubscript{asym} = 1946 cm\textsuperscript{−1})\textsuperscript{24} indicating a cobalt phosphaketene structure, Co-P=O=C=O. This is confirmed by a single crystal X-ray diffraction analysis (Fig. 2). The P–C\textsubscript{1} 1.633(4) Å and C–O\textsubscript{1} 1.179(6) Å bond distances, the rather large Co–P–C angle [116.2(1)\textdegree] and long Co–C distance [3.325(4) Å] indicate a σ\textsuperscript{1}-coordination via the phosphorus atom of the OCP\textsuperscript{−} anion.\textsuperscript{6} The structural parameters confirm that neither the cobalt center nor the PDI ligand are reduced by OCP\textsuperscript{−}.

The corresponding iridium complex [IrCl(PDI\textsubscript{Me})\textsubscript{2}] with the less sterically encumbered PDI\textsubscript{Me} ligand reacts with Na(OCP) at low temperatures to cleanly give product 4. A \textsuperscript{31}P NMR resonance at δ = –316.7 ppm indicates a metallaphosphaketene (Ir–P=O=C=O) featuring a highly covalent metal phosphorus bond. Complex 4 could not be isolated. Keeping a THF solution at 20 °C for about 6 h leads cleanly to complex 5 (δ \textsuperscript{31}P = +682 ppm; ν\textsubscript{max} = 524.1 nm, 732.5 nm), which was isolated as red crystals. A single crystal X-ray structure analysis shows compound 5 to be a dimetalladiphosphene (Fig. 2).\textsuperscript{35} The P–P distance [2.021(1) Å] is short and in the typical range of diphosphenes, R–P=P–R. The iridium centers are bound to a redox-inactive PDI ligand with short C=N bonds [N1–C2 1.340(2) Å; N3–C8 1.335(2) Å] and a carbonyl ligand. The rearrangement of 4 into 5 is the experimental confirmation of the computationally predicted transformation of D to E.\textsuperscript{9} This transformation is also comparable to the conversion of an iridium azido complex, Ir–N\textsubscript{3}, to a transient terminal nitrido complex, Ir≡N, which could be spectroscopically characterized but also dimerizes to an Ir≡N≡Ir complex.\textsuperscript{16}

Monitoring by \textsuperscript{31}P NMR spectroscopy the reaction of gold and copper complexes 6a,b and 7 with Na(OCP) in benzene showed in each case the formation of a single product giving a \textsuperscript{31}P NMR signal (8a: δ = –360; 8b: –364; 9: –387 ppm) slightly up-field shifted compared to that of Na(OCP) (δ = –392 ppm). Single crystals of 8a and 9 were grown and subjected to X-ray diffraction studies (Fig. 3). Only very subtle structural differences between both complexes were observed. The P–C [8a: 1.640(3); 9: 1.636(2) Å] and C–O bond lengths [8a: 1.176(4); 9: 1.184(2) Å] are similar, and the M–P–C angle is slightly more acute for the copper complex 9 [8a: 86.2(1), 9: 79.15(5)\textdegree].

Despite the similarities of the solid state structures, natural bond orbital (NBO) analysis at the M06/6-311++G(2d,p)+SDD//M06/6-31+G(d)+LANL2DZ(+) level of theory shows significant differences between the electronic structures of 8a and 9. The NBO charges of Au and PCO in 8a are +0.39 and –0.56 a.u., respectively, whereas those of Cu and PCO in 9 are +0.58 and –0.68 a.u., suggesting that the PCO anion in 9 is more ionic and “free” than that in 8a. This is in agreement with the different \textsuperscript{31}P NMR chemical shifts of 8a (δ = –360 ppm) and 9 (δ = –387 ppm). The NBOs corresponding to the M(PCO) (M = Au or Cu) fragments are quite different as shown in Fig. 4. The phosphorus center of 8a forms three bonds (Au–P σ, P–C σ and P–C π) (Fig. 4a–c). In contrast, for 9 no Cu–P σ bond could be located. Instead, the phosphorus center of 9 forms one P–C σ
bond and two P–C π bonds (Fig. 4f–h). Moreover, there are two bonds between the C and O atoms (C–O σ and C–O π) in 8a (Fig. 4d and e), while only one C–O σ bond in 9 (Fig. 4i). These computational results suggest that the coordination modes of PCO with gold and copper are \( \eta^1 \) and \( \eta^3 \), respectively.

The different bonding modes in 8 and 9 lead to a difference in reactivity. In solution 9 decomposes after a few hours giving a complex mixture, whereas 8b rearranges into complex 10 over the course of a week when left standing in THF at room temperature (Fig. 5). The trinuclear nature of 10 \(([\text{LbAu}]_3\text{P})\), as determined by an X-ray diffraction study, is reminiscent of the rearrangement product of \( \text{Ph}_3\text{Sn}(\text{PCO}) \), namely \((\text{Ph}_3\text{Sn})_3\text{P}\)\(^{9,10}\). Three gold atoms surround a single P atom, leading to a phosphine supported solely by metals. The \(^{31}\text{P}\) NMR spectrum displays a signal at \( \delta = -200 \text{ ppm} \), which is considerably high-field shifted compared to alkyl and aryl phosphines. The electron rich nature as well as the steric crowding around the P center could make 10 an interesting redox active ligand for transition metals.\(^{11}\)

The gold complexes 8a,b are rather inert and do not react with heavier group 14 element halides to give \( R_3\text{E}-\text{PCO} \) derivatives. Equally, no reaction with \( \text{N}^2\text{N}^2\)-dicyclohexylcarbodiimide or with carbene \( \text{L}_3 \) are observed. On the contrary, the copper salt 9 does react with these reagents similarly to Na(OCP) (see the ESI for details).\(^{2b,d}\) Remarkably, 9 reacts with carbene \( \text{L}_3 \) to afford the cationic \( \text{bis(CAAC)}\text{Cu} \) complex 11, in which the PCO fragment is the anionic counterpart. The \(^{31}\text{P}\) NMR signal appears at \( \delta = -400 \text{ ppm} \), which is more downfield shifted than Na(OCP) (\( \delta = -392 \text{ ppm} \)), implying that PCO\(^-\) is less coordinated. The IR spectrum showed the asymmetric stretching frequency of the PCO unit at \( \nu_{\text{asym}} = 1791 \text{ cm}^{-1} \), suggesting a more cumulenic nature than in the two crystalline forms of Na(OCP) (\( \nu_{\text{asym}} = 1780 \text{ or } 1755 \text{ cm}^{-1} \)).\(^{6,13a,b}\) Lastly, although a disorder precludes accurate determination of the geometric parameters, the X-ray diffraction study revealed that the PCO anion has no close contacts with the cationic part of the complex (Fig. 6). This is the first time that the PCO anion has been structurally observed without any binding agents or coordinating solvents.

On the basis of DFT calculations, the HOMOs of 8a and 9 are mainly localized on the PCO fragments (see ESI) and the oxygen atoms carry the largest negative charge (\(-0.56 \text{ a.u.} \) in 8a).

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**Fig. 4** NBOs corresponding to M(PCO) fragments of 8a and 9 (isovalue = 0.05). NBOs of 8a: (a) \( \text{Au} – \text{P} \sigma \); (b) P–C \( \sigma \); (c) P–C \( \pi \); (d) C–O \( \sigma \); (e) C–O \( \pi \). NBOs of 9: (f) P–C \( \sigma \); (g) P–C \( \pi \); (h) P–C \( \sigma \); (i) C–O \( \sigma \).

**Fig. 5** Conversion of 8b to \((\text{L}_3\text{Au})_3\text{P} \) 10, and solid state structure of 10 (50% thermal ellipsoids are shown with hydrogen atoms omitted for clarity).

**Fig. 6** Solid-state structure of 11 showing the free PCO anion. 50% thermal ellipsoids are shown and hydrogen atoms are omitted for clarity.

**Fig. 7** Reaction of 8b,9 with B(C\(_6\)F\(_5\))\(_3\) and two resonance structures of 12 and 13: solid state-structure of the gold complex 12 (50% thermal ellipsoids are shown with hydrogen atoms omitted for clarity).
and −0.59 a.u. in 9). Thus, we were curious to see if the terminal oxygen atom could react with a Lewis acidic borane. Indeed, adding one equivalent of B(C6F5)3 to either 8b or 9 led to the same type of heterocycle 12 and 13, respectively (Fig. 7). In the case of gold, the corresponding product immediately crystallized out and became insoluble in the tested solvents. However, for copper the product was soluble and the 31P NMR spectrum showed two broad peaks at δ = 261 and δ = 137 ppm. Single crystal X-ray diffraction studies of 12 and 13 revealed a four-membered P2C2 heterocycle that arose from borane coordination to oxygen followed by a dimerization and lastly a migration of a LM fragment from one phosphorus center to the other. The four-membered P2C2 heterocycles have a planar geometry and, as expected, the bond lengths of the PCO fragments become elongated compared to 8b and 9 as a result of the delocalization over the ring. This small ring represents a novel bonding mode for the rapidly growing field of molecular polyphosphorus clusters and cages.20

Conclusions

PCO complexes with electron rich metal centers such as copper, gold and also cobalt can be prepared and are relatively stable. On the other hand, the iridium phosphaketene 4 rapidly rearranges via CO migration to give a genuine dimetalladiphosphine. The copper complex features an n2 coordination mode, which leads to an active PCO fragment that can undergo further mechanisms leading to them merit further exploration.

Experimental section

General considerations

All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk techniques or an MBraun dry-box under argon. THF was distilled over sodium benzo-phenone-ketyl before use. THF-d8, CD2Cl2, and C6D6 were purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves. (19PDI)CoCl2 1, (16PDI)IrCl2 2, L4AuCl6a,b20 and L4CuOTBu 2d were synthesized according to literature procedures. 1H, 13C, 11B, 19F, and 31P NMR spectra were recorded on a Varian VX 500, Bruker 300, Bruker 500 and Jeol 500 spectrometer at 25 °C. All 1H and 13C NMR chemical shifts are given relative to SiMe4 using the 1H (residual) and 13C chemical shifts of the solvent as a secondary standard. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad signal. Chemical shifts are given in ppm and coupling constants J are given in Hz. Peak widths at half heights (in Hz) are given for broad signals. Infrared spectra were collected on a Perkin-Elmer-Spectrum 2000 FT-IR-Raman and Bruker ALPHA FT-IR spectrometer. Elemental analyses were performed at the Mikrolabor of ETH Zürich. Single crystals suitable for X-ray diffraction were coated with polysobutylene oil in a dry-box, transferred to a nylon loop and then transferred to the goniometer of a Bruker X8 APEX2 diffractometer equipped with a molybdenum X-ray tube (λ = 0.71073 Å) or on a Bruker Apex II-CCD detector using Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.5418 Å). The data were processed using the Bruker SAIINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by Fourier synthesis and refined by full-matrix least-squares procedures. Mass spectra were performed at the UC San Diego Mass Spectrometry Laboratory. Melting points were measured with an electrothermal MEL-TEMP apparatus.

Preparation of [(19PDI)Co(PCO)] 3. In the glove box, a 20 mL scintillation vial was charged with 0.200 g (0.347 mmol) of [(19PDI)CoCl2 1] and 10 mL of THF. The solution was cooled to −35 °C and Na(OCP) (0.130 g, 0.355 mmol) was added portion-wise over the course of 5 minutes, eliciting a color change from pink to dark purple. The reaction was placed in the freezer at −35 °C for one hour then filtered through Celite. The solution was concentrated, layered with hexane and placed at −35 °C. This gave 0.152 g (48%) of a purple crystalline solid identified as [(19PDI)Co(PCO)] 3. The mother liquor was placed back in the freezer to obtain another 42 mg (13%) of product. X-Ray quality crystals were grown from the second fraction. Analysis for C47H43CoN3OP, 599.64 g mol−1, calc.: C, 68.10; H, 7.23; N, 7.01 found: C, 66.05; H, 7.35; N, 6.85. IR (powder): ν CO = 1851 cm−1. 1H NMR (C6D6, 500 MHz): δ = 9.66 (t, J = 7.6 Hz, 1H, CHpyr), 7.47 (t, J = 7.7 Hz, 2H, CHacrom), 7.35 (d, J = 7.7 Hz, 4H, CHacrom), 7.05 (d, J = 7.6 Hz, 2H, CHpyr), 3.32 (sept, J = 6.7 Hz, 4H, 19Pr(CH)), 1.13 (dd, J = 2.4 Hz, J = 6.7 Hz, 24H, 19Pr(CH)), −0.19 (s, 6H, CH−CH3), 13C NMR (C6D6, 125 MHz): δ = 181.2 (d, JPC = 98.8 Hz, CO), 168.1, 153.4, 150.5, 140.0, 125.1, 124.0, 116.4, 28.6 (Ar-CH3), 24.0 (Ar-CH3), 23.3, 21.8; 31P NMR (C6D6, 202 MHz): δ = −225.8 ppm (lb = 634 Hz).

Preparation of [(19PDI)IrCO2(p-F2)] 5. A 20 mL Schlenk flask was charged with 0.100 g (0.167 mmol) of (MePDI)IrCl2 and 5 mL of THF and cooled in a dry-ice/acetone bath. A solution of Na(OCP) (0.060 g, 0.170 mmol) in THF (3 mL) was syringed into the stirring iridium solution, immediately causing a color change to dark purple. The reaction was warmed to room temperature, whereupon the color changed to deep pink, and stirred for an additional hour. The reaction was then filtered through Celite and then concentrated to roughly 3 mL. Storing at −35 °C overnight produced a solid that was collected on a glass frit and dried under reduced pressure, yielding 0.076 g (74% yield) of red crystalline solid 5. X-Ray quality crystals were grown from the slow evaporation of the mother liquor at room temperature overnight. NMR analysis was performed in CD2Cl2 due to the poor solubility of 5 in ethereal or aromatic solvents, but the compound slowly decomposed (if left overnight) in methylene chloride. Analysis for C92H63Ir2N4O2P2, calcd: C 52.16, H 3.02, N 4.67, found: C 52.07, H 3.24, N 4.70. 1H NMR (CD2Cl2, 500 MHz): δ = 8.12 (d, J = 7.8 Hz, 2H, mp), 7.26 (br s, 1H, p-P), 7.07–6.93 (m,
6H), 2.3 (br s, 6H, CN–CH₃), 1.63 (s, 6H, Ar–CH₃); ¹³C NMR (CD₂Cl₂, 125 MHz): δ = 187.50 (CO), 152.66, 149.21, 143.12, 131.89, 130.36, 128.28 (Ar–CH₂), 127.96 (Ar–CH), 126.02, 127.93 (m–Py–CH), 116.16 (m–Py–CH), 20.66 (Ar–CH), 18.31 (Ar–CH₃), 15.51 (CN–CH₃); ¹³P NMR (CD₂Cl₂, 202 MHz): δ = 683.2.

Preparation of (CAAC)Au(PCO) complex 8a. A mixture of (CAAC)AuCl 6a (1.0 g, 1.83 mmol) and [Na(PCO)(dioxane)₂]₃ (0.55 g, 1.83 mmol) was cooled to −78 °C before THF (10 mL) was added. The mixture was stirred for 15 minutes and then warmed to room temperature. After 30 min, the solvent was removed under vacuum and the resulting brown solid was extracted with 15 mL of benzene. After removing the solvent, 8a was obtained as a light yellow solid (0.73 g, yield: 70%). Colorless single crystals of 8a were obtained by vapor diffusion of pentane into a saturated benzene solution of 8a in the dark. IR (CaH₅): ν PCO = 1887 cm⁻¹. M.P. = 193 °C (dec.). ¹H NMR (CD₂Cl₂, 500 MHz): δ = 7.15 (t, 1H, J = 7.3 Hz), 7.00 (d, 2H, J = 7.3 Hz), 2.72 (sept, 2H, J = 6.6 Hz), 1.63 (m, 4H), 1.54 (d, 6H, J = 6.6 Hz), 1.42 (s, 2H), 1.08 (d, 6H, J = 6.6 Hz), 0.85 (m, 12H); ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz): δ = 253.5 (C(carbene) d, JPC = 36.2 Hz), 183.0 (CO = d, JPC = 100.4 Hz), 146.1, 135.3, 130.9, 126.0, 81.0, 63.0, 43.0, 32.4, 20.1, 29.5, 27.7, 23.7, 10.3; ³¹P{¹H} NMR (CD₂Cl₂, 121 MHz) δ = −359.5. HRMS was attempted but a peak corresponding to M⁺ could not be located, probably due to the weak P metal bond.

Preparation of (CAAC)Au(PCO) complex 8b. A mixture of (CAAC)AuCl 6b (1.0 g, 1.63 mmol) and [Na(PCO)(dioxane)₂]₃ (0.49 g, 1.63 mmol) was cooled to −78 °C before THF (10 mL) was added. The mixture was stirred for 15 minutes and then warmed to room temperature. After 30 min, the solvent was removed under vacuum and the resulting brown solid was extracted with 15 mL of benzene. After removing the solvent, 8b was obtained as a light yellow solid (0.70 g, yield: 67%). Colorless single crystals of 8b were obtained by vapor diffusion of (TMS)O into a saturated benzene solution of 8b in the dark. IR (CaH₅): ν PCO = 1889 cm⁻¹. M.P. = 293 °C (dec.). ¹H NMR (CD₂Cl₂, 500 MHz): δ = 7.39 (t, 3H, J = 8.4 Hz), 7.18 (m, 6H), 2.72 (m, 12H), 2.28 (m, 3H), 1.88 (m, 9H), 1.78 (m, 3H), 1.67 (m, 3H), 1.34 (m, 9H), 1.24 (m, 36H), 1.13 (d, 9H, J = 6.6 Hz), 0.98 (m, 18H), 0.90 (d, 9H, J = 6.6 Hz), 0.82 (d, 9H, J = 6.6 Hz); ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz): δ = 260.3 (C(carbene) d, JPC = 84 Hz), 146.3, 145.7, 135.3102, 125.5, 125.2, 79.0, 78.9, 66.5, 66.4, 52.9, 50.5, 36.5, 30.5, 30.4, 30.0, 29.9, 29.5, 28.9, 28.5, 25.2, 25.1, 24.5, 23.3, 23.2, 21.3; ³¹P{¹H} NMR (CD₂Cl₂, 121 MHz) δ = −200.2. HRMS: m/z calculated for [C₈₁H₁₃₀N₃Au₃P]+ (M+H)+ 1766.8999; found 1766.8980.

Preparation of bis(CAAC)Cu(PCO) complex 11. A mixture of 9 (20 mg, 0.046 mmol) and carbene Lb (15 mg, 0.049 mmol) was stirred for 2 min in benzene (0.5 mL). The suspension was filtered and the colorless powder was washed with benzene (1 mL), yielding 11 (30 mg, 86% yield). Single crystals were obtained by slow evaporation of a saturated benzene solution of 11. IR (solid, KBr): ν PCO = 1791 cm⁻¹. M.P. = 158 °C (dec.). ¹H NMR (CD₂Cl₂, 500 MHz): δ = 7.08 (t, 2H, J = 7.8 Hz), 6.97 (d, 4H, J = 7.8 Hz), 2.70 (sept, 4H, J = 6.8 Hz), 1.54 (m, 8H), 1.42 (d, 12H, J = 6.8 Hz), 1.32 (s, 4H), 1.05 (d, 12H, J = 6.8 Hz), 0.84 (t, 12H, J = 7.2 Hz), 0.81 (s, 12H); ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz): δ = 253.3 (C(carbene) d, JPC = 37.1 Hz), 145.8, 135.3, 130.7, 125.5, 80.8, 63.0, 43.6, 31.6, 30.0, 29.4, 28.0, 23.1, 10.2; ³¹P{¹H} NMR (CD₂Cl₂, 121 MHz) δ = −399.5. HRMS: m/z calculated for [C₄₄H₇₀CuN₂]+ 689.4835; found 689.4847.

Preparation of four-membered heterocycle 12. A mixture of 8b (50 mg, 0.078 mmol) and [C₄₃H₉₃CuN₂] (40 mg, 0.078 mmol) was stirred in 2 mL of benzene for 5 minutes. The resulting yellow suspension was filtered and the yellow residue was washed with benzene (0.5 mL), then dried under vacuum, yielding 12 mg (64%) of a bright-yellow powder. Yellow single crystals of 12 were obtained in the filtrate in less than 1 min. M.P. = 230 °C (dec.).

Preparation of four-membered heterocycle 13. A mixture of 9 (50 mg, 0.12 mmol) and [C₄₃H₉₃CuN₂] (59 mg, 0.12 mmol) was stirred in 1 mL of toluene for 5 minutes. The solvent was removed under reduced pressure and the residue was washed with pentane (2 mL), yielding 68 mg (62%) of a light-yellow powder. Colorless single crystals were obtained by vapor diffusion of (TMS)O into a saturated toluene solution of 13. IR (solid): ν PCO = 173°C (dec.). ¹H NMR (CD₂Cl₂, 500 MHz): δ = 7.12 (t, 1H, J = 7.7 Hz), 7.00 (d, 2H, J = 7.7 Hz), 2.75 (sept, 2H, J = 6.8 Hz), 1.68 (m, 4H), 1.43 (d, 6H, J = 6.8 Hz), 1.38 (s, 2H), 1.08 (d, 6H, J = 6.8 Hz), 0.93 (m, 6H), 0.85 (s, 6H); ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz): δ = 251.8 (C(carbene)), 175.2 (C=O), 97.8 Hz, 145.9, 135.5, 130.7, 125.6, 81.2, 63.1, 43.1, 31.9, 29.9, 27.9, 23.1, 10.4; ³¹P{¹H} NMR (CD₂Cl₂, 121 MHz) δ = −387.4. HRMS was attempted but a peak corresponding to M⁺ could not be located, probably due to the weak P metal bond.
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