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Group 8 Transition Metal Complexes of the Tripodal Triphosphino Ligands $PhSi(CH_2PR_2)_3$ (R = Ph, *i*Pr)

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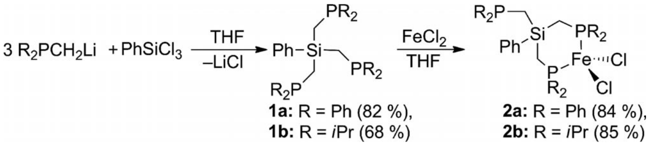
A series of group 8 transition metal complexes of new tridentate phosphine ligands with Fe, Ru, and Os were prepared. The new complexes were characterized by multinuclear NMR spectroscopy and X-ray crystallography.

Introduction

Tripodal ligands have played important roles in coordination chemistry and catalysis.[1] Generally, such ligands are used to enforce specific coordination geometries or to function as crucial ancillary ligands in metal-mediated chemistry. For four-coordinate complexes, such ligands may occupy three coordination sites, thereby leaving one reactive site free to engage in chemical transformations. For octahedral complexes, tripodal ligands may bind in *facial* manner to provide rigorously defined coordination geometries. Tripodal triphosphine ligands designed to bind in this way include $[PhB(CH_2PPh_2)_3]^-$,[2] $MeC(CH_2PPh_2)_3$ (triphos),[3] *t*$BuSi(CH_2PMe_2)_3$,[4] and $MeSi(CH_2PMe_2)_3$.[5] These latter neutral tridentate tripodal phosphine ligands were previously employed to stabilize highly reactive iron(0) complexes for vicinal dichlorine elimination at dichloroalkenes[6,7] or heterodinuclear trihydride complexes of rhodium and iron for hydrogenations and C–H activation reactions.[8] For ruthenium, they have also been used in mechanistic studies of C–C and C–H bond activations.[9–11] In this contribution we report new triphosphines $PhSi(CH_2PPh_2)_3$ (**1a**) and $PhSi(CH_2P\textit{i}Pr_2)_3$ (**1b**). For comparative purposes these were used as ligands to prepare complexes of the group 8 metals iron, ruthenium, and osmium.

Results and Discussion

Following established procedures, diphenylmethylphosphine (Ph_2PCH_3) and diisopropylmethylphosphine (*i*Pr_2PCH_3) were deprotonated[12,13] and then treated with three equivalents of trichlorophenylsilane to give neutral tridentate ligands **1a** and **1b** (Scheme 1).



Scheme 1. Synthesis of **1a** and **1b**, and reactions with iron dichloride to give **2a** and **2b**.

Complex **1a** is a colorless solid, whereas **1b** is a viscous colorless oil. Phenyl-substituted compound **1a** exhibits a $^{31}P\{^1H\}$ NMR shift (–23.59 ppm) that is significantly upfield of that for the corresponding isopropyl derivative **1b** (–5.14 ppm).

Reaction of **1a** with iron dichloride suspended in THF gave iron(II) complex **2a** as a colorless solid in good yield (Scheme 1). NMR spectroscopic data were not obtainable because of the paramagnetic nature of the compound. By Evans' method,[14] **2a** is a high-spin iron(II) complex ($S = 2$, $\mu_{eff} = 4.83\ \mu_B$). Complex **2a** possesses a tetrahedral iron(II) center as determined by X-ray crystallography (see Supporting Information).

Only two phosphorus atoms are bound to the metal center, resulting in Fe–P distances of 2.480(1) and 2.449(1) Å, and one phosphorus atom remains unbound to the metal center. Interestingly, the less sterically demanding triphosphine $MeSi(CH_2PMe_2)_3$ forms the diiron ionic compound $\{[MeSi(CH_2PMe_2)_3]_2Fe_2(\mu\text{-}Cl)_3\}Cl$ with octahedral metal centers.[15] The Fe–Cl bond lengths in **2a** are 2.207(1) and 2.245(1) Å. Also, the pseudo-tetrahedral geometry in **2a** results in a relatively large Cl–Fe–Cl bond angle of 117.30(4)°, which is similar to the value reported in a related four-coordinate iron(II) dichloride complex.[16] The chelation of the phosphine ligand results in a small P–Fe–P bond angle of 94.05(4)°.

Reaction of **1b** and iron dichloride gave the related complex **2b**. The structural and metrical parameters of **2b** are similar to those of **2a** (Figure 1). The Fe–P as well as the

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Fe–Cl bond lengths are nearly identical in comparison to **2a** (within 0.02 Å). A notable difference corresponds to larger Cl–Fe–Cl [122.72(2)°] and P–Fe–P [97.86(2)°] angles for **2b**, apparently the result of more sterically demanding phosphino groups in the latter complex.

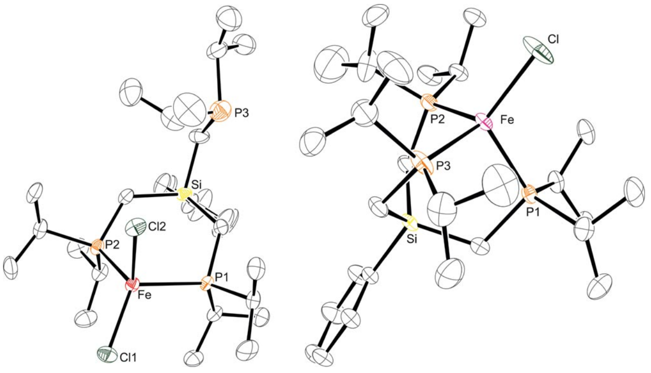
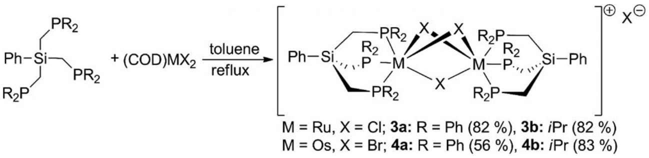


Figure 1. ORTEP diagram of **2b** (left) and **5** (right) with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2b**: Fe–Cl1 2.2239(6), Fe–Cl2 2.2589(5), Fe–P1 2.4233(6), Fe–P2 2.4403(5); Cl1–Fe–Cl2 122.72(2), P1–Fe–P2 97.86(2). **5**: Fe–Cl 2.271(1), Fe–P1 2.297(1), Fe–P2 2.305(1), Fe–P2 2.304(1); P1–Fe–P2 101.54(4), P1–Fe–P3 102.76(4), P2–Fe–P3 101.63(4), P1–Fe–Cl 114.85(5), P2–Fe–Cl 115.89(5), P3–Fe–Cl 117.85(5).

Complex **2b** was reduced by KC_8 to green iron(I) complex $PhSi(CH_2P\mathit{i}Pr_2)_3FeCl$ (**5**). While the Fe–Cl bond length [2.271(1) Å] remains unchanged in comparison to that in compound **2b**, the Fe–P bond lengths are shortened by slightly more than 0.1 Å [to an average value of 2.302(4) Å, Figure 1]. This Fe–P bond length is approximately 0.1 Å shorter than those found in iron(II) complexes featuring the tripodal $[PhB(CH_2PPh_2)_3]^-$[17] and $[PhB(CH_2P\mathit{i}Pr_2)_3]^-$ ligands.[18] The Fe–P bonds in **5** are also similar in length (within 0.02 Å) to Fe–P bonds in iron(I) compounds with the $[PhB(CH_2PPh_2)_3]^-$ ligand.[17] The P–Fe^I–P bond angles in **5** [102.0(7)°] are significantly greater than those in iron(II) complexes of $[PhB(CH_2PPh_2)_3]^-$ [92(2)°][17] or $[PhB(CH_2P\mathit{i}Pr_2)_3]^-$ [93.9(6)°].[18] These differences may be caused by the larger size of silicon relative to boron, which allows ligand **1b** to accommodate a larger bite angle for the phosphorus atoms bound to iron, thus forming a more tetrahedral complex.

Ruthenium analogues **3a** and **3b** were prepared by refluxing a toluene suspension of dichloro(1,5-cyclooctadienyl)ruthenium(II) ([COD]$RuCl_2$) with **1a** or **1b** (Scheme 2). Both complexes were isolated as orange solids. These complexes exhibit a single resonance in the $^{31}P\{^1H\}$ NMR spectrum, at 29.44 (**3a**) and 39.19 ppm (**3b**). A single crystal of **3a** was obtained by layering diethyl ether on a concentrated solution of **3a** in dichloromethane. As determined by single-crystal X-ray diffraction analysis, **3a** possesses a dimeric structure in which each ruthenium core has an octahedral environment. Three chlorine atoms are bridging between the ruthenium centers, while one remaining chloride is outer-sphere (see Supporting Information). The average Ru–Cl and Ru–P bond lengths are 2.478(9) and 2.31(1) Å, respectively. Ruthenium is in a slightly distorted octahedron with *trans* P–Ru–Cl bond angles of about 170(2)°, and the *cis* P–Ru–Cl bond angles average 95(2)°.



Scheme 2. Synthesis of ruthenium and osmium complexes by using **1a** and **1b**.

Following a similar synthetic procedure, dimeric osmium bromide complexes **4a** and **4b** containing ligands **1a** and **1b** were prepared. The $^{31}P\{^1H\}$ NMR spectra for **4a** and **4b** exhibit a single resonance, at –30.00 and –21.67 ppm, respectively. The crystal structure of **4a** (Figure 2) reveals a dimer with slightly distorted octahedra for both osmium centers, as found for the ruthenium analogue **3a**. For this structure, the mean Os–Br bond length is 2.61(2) Å, the mean Os–P bond length is 2.314(8) Å, and the Os–Os separation is 3.603(1) Å. The crystal structure of **4b** (see Supporting Information) reveals slight elongations of the mean Os–Br [by 0.02(1) Å], Os–P [by 0.011(7) Å], and Os–Os [by 0.085(1) Å] distances, with respect to comparable parameters in **4a**. This can be attributed to the higher steric demand of the isopropyl groups, which enforce a greater separation between the osmium centers.

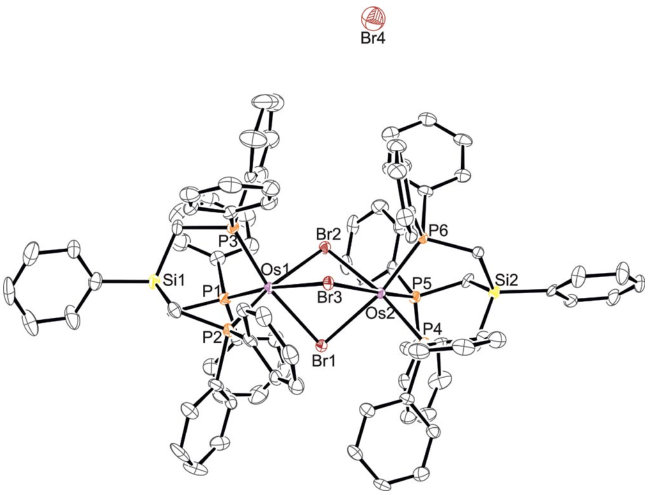


Figure 2. ORTEP diagram of **4a** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–Br1 2.6320(6), Os1–Br2 2.5844(8), Os1–Br3 2.6231(7), Os1–P1 2.326(2), Os1–P2 2.303(2), Os1–P3 2.318(2); P2–Os1–Br2 167.82(5), P3–Os1–Br1 168.80(5), P2–Os1–P3 92.28(6).

The Os–Os distances in **4a** and **4b** [3.603(1) and 3.688(1) Å] are longer in comparison with those in related diosmium complexes presumed to lack metal–metal bonding, such as $[H_4(P\mathit{i}Pr_3)_4Os_2(\mu\text{-}Cl)_3]CF_3SO_4$ [3.539(1) Å],[19] $[(PEt_3)_6Os_2(\mu\text{-}Cl)_3]PF_6$ [3.474(1) Å],[20] and $[(PEt_2Ph)_6Os_2$-

(μ-Cl)$_3$]Cl [3.465(1) Å].[21] These differences might correspond to the larger bromine atoms bridging between the osmium centers.

Conclusions

A series of group 8 transition metal complexes with two new tripodal triphosphine ligands were prepared and characterized. Iron(II) complexes of these ligands possess pseudo-tetrahedral geometries for the iron centers and a "dangling" phosphino group. However, an Fe^{I} analogue exhibits bonding to all three phosphorus donors in an approximate tetrahedral coordination geometry. For the larger ruthenium and osmium atoms, octahedral complexes were obtained. In these cases a cationic, dimeric structure with three halogen atoms bridging between each metal center is observed. Compounds **4a** and **4b** are to the best of our knowledge the first osmium complexes that feature a tripodal triphosphine ligand. Studies of the coordination and organometallic chemistry of the complexes mentioned above is the goal of future work.

Experimental Section

General: Manipulations involving air-sensitive compounds were conducted by using standard Schlenk techniques in a purified nitrogen atmosphere or in a nitrogen glove box. Solvents were dried with a VAC drying system and stored in PTFE-valved flasks. Deuterated solvents (Cambridge Isotopes) were dried with appropriate drying agents and vacuum-transferred before use. NMR spectra were acquired with Bruker AVB-400, AVQ-400, AV-500, or AV-600 spectrometers. Spectra were recorded at room temperature and were referenced to protic impurities.[22] ^{31}P{^{1}H} NMR spectra were referenced to an 85% H$_3$PO$_4$ external standard (δ = 0 ppm).

Tris[diphenylphosphinomethyl]phenylsilane (1a): Ph$_2$PCH$_2$Li·TMEDA[12] (4.47 g, 13.9 mmol) was dissolved in toluene (150 mL), and the resulting solution was cooled to –78 °C. Trichlorophenylsilane (0.92 g, 4.33 mmol) dissolved in toluene (1 mL) was slowly added to the reaction mixture with a syringe. The solution was gradually warmed to room temperature over the course of 20 h. Removing the solvent under reduced pressure gave a cloudy yellow oil. The oil was extracted with pentane (100 mL) and diethyl ether (200 mL). The combined extracts were then filtered through a plug of silica. The solvent was then evaporated under reduced pressure, and the resulting yellow oil was washed with hot methanol (50 mL). The solvent was decanted, and the remaining residue solidified upon drying under vacuum (2.51 g, 3.57 mmol, 82%). ^{1}H NMR (C$_6$D$_6$): δ = 7.59 (dd, *J* = 7.4, 1.6 Hz, 2 H, Ar*H*), 7.43–7.32 (m, 13 H, Ar*H*), 7.12–6.95 (m, 24 H, Ar*H*), 1.57 (s, 6 H, C*H*$_2$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 141.62 (d, J_{PC} = 15.9 Hz), 136.13, 135.26, 133.15 (d, J_{PC} = 20.9 Hz), 132.63, 132.45, 129.40, 128.51, 13.23–12.90 (m) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = –23.59 ppm. HRMS (ESI): calcd. for C$_{45}$H$_{42}$P$_3$Si [M + H]$^+$ 703.2263, found 703.2259.

Tris[diisopropylphosphinomethyl]phenylsilane (1b): *i*Pr$_2$PCH$_2$Li[13] (1.95 g, 14.12 mmol) was dissolved in THF (30 mL), and the resulting solution was cooled to –78 °C. Trichlorophenylsilane (0.94 g, 4.44 mmol) dissolved in THF (2 mL) was slowly added to the reaction mixture with a syringe. The reaction mixture was gradually warmed to room temperature with stirring, over the course of 14 h. Removal of the solvent under reduced pressure gave a brown oil. The oil was extracted into pentane (100 mL), passed through a short column of silica gel (5 cm × 2 cm), and then washed with additional pentane (100 mL) and diethyl ether (100 mL). The solvents were again removed under reduced pressure. A colorless oil was obtained (1.51 g, 3.03 mmol, 68%). ^{1}H NMR (C$_6$D$_6$): δ = 8.01–7.98 (m, 2 H, Ar*H*), 7.27–7.18 (m, 3 H, Ar*H*), 1.64 (sept., *J* = 7.1, 1.1 Hz, 6 H, C*H*), 1.20 (d, *J* = 2.8 Hz, 6 H, C*H*$_2$), 1.09–1.01 (m, 36 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 139.42–139.38 (m), 135.45 (q, J_{PC} = 2.4 Hz), 129.53, 128.35, 127.73, 25.29 (d, J_{PC} = 16.7 Hz), 19.97 (d, J_{PC} = 13.8 Hz), 19.73 (d, J_{PC} = 13.7 Hz), 6.46 (dt, J_{PC} = 38.5, 5.4 Hz) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ = –5.14 ppm. ^{29}Si NMR: δ = –5.1 ppm. C$_{27}$H$_{53}$P$_3$Si (498.7): calcd. C 65.02, H 10.71; found C 64.80, H 10.49.

PhSi(CH$_2$PPh$_2$)$_3$FeCl$_2$ (2a): A suspension of iron dichloride (13.8 mg, 0.11 mmol) in THF (5 mL) was stirred for 30 min. A solution of **1a** (75.0 mg, 1.06 mmol) in THF (1 mL) was then slowly added to the light orange-brown suspension of FeCl$_2$. The resulting mixture was stirred for 24 h, and then the solvent was removed under reduced pressure. The remaining residue was extracted into toluene (10 mL) and filtered through a plug of Celite. The solvent was again removed under reduced pressure. A colorless solid was obtained, which was then washed with pentane (2 × 5 mL). The isolated product was dried under vacuum to give colorless **2a** (76 mg, 0.09 mmol, 84%). μ_{eff} (C$_6$D$_6$) = 4.83 μ$_B$. EI MS: *m*/*z* = 828 [M]$^+$. C$_{45}$H$_{41}$Cl$_2$FeP$_3$Si (829.6): calcd. C 65.15, H 4.98; found C 65.54, H 5.04.

PhSi(CH$_2$P*i*Pr$_2$)$_3$FeCl$_2$ (2b): The same procedure used for the synthesis of **2a** was employed, starting from **1b**. Yield: 1.60 g, 2.56 mmol, 85%. μ_{eff} (C$_6$D$_6$) = 4.90 μ$_B$. EI MS: *m*/*z* = 624 [M]$^+$. C$_{27}$H$_{53}$Cl$_2$FeP$_3$Si (625.5): calcd. C 51.85, H 8.54; found C 51.70, H 8.53.

{[PhSi(CH$_2$PPh$_2$)$_3$]$_2$Ru$_2$(μ-Cl)$_3$}Cl (3a): [(COD)RuCl$_2$]$_n$ (67 mg, 0.24 mmol) was placed in a Teflon-sealed NMR tube, and to this solid was added **1a** (174 mg, 0.25 mmol) in toluene (1 mL). The resulting suspension was heated to 125 °C for 21 h. The red-orange suspension was extracted into dichloromethane (2 × 2 mL) and then filtered through a plug of Celite. After evaporation of the solvent, the resulting orange powder was washed with diethyl ether (2 mL) and then dried under vacuum to give **3a** (178 mg, 0.10 mmol, 82%). Crystals suitable for X-ray diffraction were obtained by layering a concentrated solution of **3a** in dichloromethane with diethyl ether. ^{1}H NMR (CD$_2$Cl$_2$): δ = 7.65–7.62 (m, 4 H, Ar*H*), 7.56–7.47 (m, 6 H, Ar*H*), 7.36–7.23 (m, 36 H, Ar*H*), 6.92 (t, *J* = 7.5 Hz, 24 H, Ar*H*), 1.95–1.93 (m, 12 H, C*H*$_2$) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 138.67–138.23 (m), 134.3, 133.92, 131.7, 130.03, 129.34, 128.03, 11.39–11.28 (m) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 29.44 ppm. C$_{90}$H$_{82}$Cl$_4$P$_6$Ru$_2$Si$_2$·CH$_2$Cl$_2$ (1749.6 + 84.9): calcd. C 59.58, H 4.62; found C 59.28, H 4.75.

{[PhSi(CH$_2$P*i*Pr$_2$)$_3$]$_2$Ru$_2$(μ-Cl)$_3$}Cl (3b): The same procedure used for the synthesis of **3a** was employed, starting from **1b**. Yield: 120 mg, 0.09 mmol, 82%. ^{1}H NMR (CD$_2$Cl$_2$): δ = 7.57–7.53 (m, 4 H, Ar*H*), 7.49–7.43 (m, 6 H, Ar*H*), 2.58–2.38 (m, 12 H, C*H*$_2$), 1.64–1.49 (m, 32 H, *i*Pr*H*), 1.38–1.26 (m, 40 H, *i*Pr*H*), 1.19–1.13 (m, 12 H, *i*Pr*H*) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 134.14, 129.11, 33.2, 22.23, 21.61, 21.41, 4.34 ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 39.19 ppm. C$_{54}$H$_{106}$Cl$_4$P$_6$Ru$_2$Si$_2$ (1341.4): calcd. C 48.35, H 7.97; found C 47.97, H 7.97.

{[PhSi(CH$_2$PPh$_2$)$_3$]$_2$Os$_2$(μ-Br)$_3$}Br (4a): The same procedure used for the synthesis of **3a** was employed, starting from **1a** and [(COD)-

OsBr$_2$]$_n$, and this resulted in a yellow-green solid. Yield: 810 mg, 0.39 mmol, 56%. ^{1}H NMR (CD$_2$Cl$_2$): δ = 7.66 (d, J = 7.0 Hz, 4 H, ArH), 7.57–7.51 (m, 6 H, ArH), 7.34–7.24 (m, 36 H, ArH), 7.11 (t, J = 7.4 Hz, 24 H, ArH), 2.2 (d, J = 8.0 Hz, 12 H, CH_2) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 138.51–138.18 (m), 134.43, 133.43, 131.71, 130.08, 129.41, 128.07, 10.11–9.97 (m) ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = –30.00 ppm. C$_{90}$H$_{82}$Br$_4$Os$_2$P$_6$Si$_2$ (2105.7): calcd. C 51.34, H 3.93; found C 50.80, H 4.23.

{[PhSi(CH$_2$P*i*Pr$_2$)$_3$]$_2$Os$_2$(μ-Br)$_3$}Br (4b): The same procedure used for the synthesis of **3a** was employed, starting from **1b** and [(COD)-OsBr$_2$]$_n$, to give a green solid. Yield: 155 mg, 0.09 mmol, 83%. ^{1}H NMR (CD$_2$Cl$_2$): δ = 7.59–7.55 (m, 4 H, ArH), 7.51–7.42 (m, 6 H, ArH), 2.64–2.42 (m, 12 H, CH_2), 1.60–1.45 (m, 32 H, *i*PrH), 1.36–1.12 (m, 52 H, *i*PrH) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 133.69, 130.46, 128.49, 34.29–34.02 (m), 22.23, 21.55, 21.21, 4.8 ppm. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = –21.67 ppm. C$_{54}$H$_{106}$Br$_4$Os$_2$P$_6$Si$_2$ (1697.5): calcd. C 38.21, H 6.21; found C 38.52, H 6.12.

PhSi(CH$_2$P*i*Pr$_2$)$_3$FeCl (5): Compound **2b** (153 mg, 0.25 mmol) was dissolved in toluene (1.5 mL), and the resulting solution was cooled to –35 °C. This solution was added to a suspension of KC$_8$[23] (49 mg, 0.37 mmol) in toluene (1 mL). The mixture was allowed to stand for 30 min at –35 °C before being allowed to gradually warm to room temperature. It was then stirred for 16 h. The dark reaction mixture was then filtered through Celite to give a dark red solution. The solution was concentrated to approx. 0.5 mL and then pentane (3 mL) was added, whereupon green solids precipitated. The mixture was stored for 16 h in the freezer. The red solution was decanted from the green solids, which were washed with cold pentane (2 × 1 mL) and then dried under vacuum (80 mg, 0.14 mmol, 55%). UV/Vis (THF): $\lambda_{\max}$ (ε, $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) = 741 (607), 312 (5157), 265 (6071), 210 (26458) nm. μ_{eff} (C$_6$D$_6$) = 4.50 μ_{B}. C$_{45}$H$_{41}$ClFeP$_3$Si (794.1): calcd. C 54.96, H 9.05; found C 54.46, H 8.71.

CCDC-951146 (for **2a**), -951142 (for **2b**), -951144 (for **3a**), -951143 (for **4a**), -951145 (for **4b**), and -951141 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ORTEP diagrams of **2a**, **3a** and **4b**, and further details of the X-ray crystallographic structure determination.

Acknowledgments

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