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Synthesis and Reactivity of an Unusual Ferrocenophane Bis(carbene complex)

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Dedicated to the memory of Professor Herbert Schumann

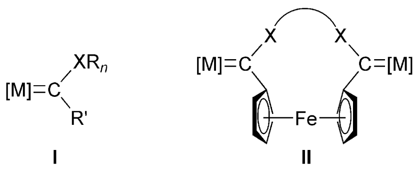
Keywords: 2*H*-Azaphosphirenes / Ferrocenophanes / Ring opening / Carbene complexes / Phosphorus heterocycles

Selective macrocyclization of 1,1′-ferrocenediylbis(aminocarbene complex) **1** was achieved by its reaction with chloro(methylene)phosphane **2** and triethylamine at ambient temperature, thus yielding the novel diaminophosphane-bridged [5]ferrocenophane bis(carbene complex) **3**. This trimetallic species, which combines the structural features of both ferrocenophane and Fischer carbene complex functional groups, is prone to undergo facile ring opening under mild conditions with formation of bis(2*H*-azaphosphirene complexes) **6a**,**b** and 2,3-dihydro-1,2,3-azadiphosphete complex **7**. The single-crystal X-ray structures of **3** and **7** as well as the reaction courses are discussed.

Introduction

Fischer-type metal carbene complexes[1] **I** (Scheme 1) are of great importance in synthetic organic chemistry,[2] which might be illustrated by, e.g., the Dötz benzannulation[3] or the Hegedus (carbene)metal-based photochemistry,[4] which provide facile access to a wide range of products that are otherwise difficult to obtain.[2] Fischer carbene complexes have also found use in phosphorus heterocyclic chemistry, i.e., in the synthesis of 2*H*-azaphosphirene complexes,[5] which themselves are versatile precursors for a large number of acyclic, cyclic and polycyclic compounds.[5] More recently, we developed new synthetic methodologies based on 2*H*-azaphosphirene complexes that provide facile access to four-[6] and five-membered[7,8] heterocycles under mild oxidative[7] or protic[8] conditions, thus introducing the “click-chemistry” concept to the field of phosphorus heterocyclic chemistry. We demonstrated that this new synthetic concept can be easily extended to oxaphosphirane[9] and azaphosphiridine[10] complex chemistry.

In addition, di- and polymetallic transition metal complexes have attracted considerable interest in recent years.[11–16] Incorporation of further metal centers into Fischer carbene complexes[14–16] led in many instances to a significant modulation of their reactivity patterns.[15] For example, ferrocenyl groups, either attached directly to the carbene carbon atom or linked by a π-tether, can behave as internal electron carriers.[16] Very recently, Lotz and coworkers presented a macrocyclic bis(carbene) complex, $[\{Cr(CO)_5\}_2\{\mu_2\text{-}C_2(O_2TiCp_2\text{-}O,O')[Fe(C_5H_4)_2\text{-}C,C']\}]$,[14d] which is the first example of a ferrocenophane of type **II** (Scheme 1) having two (carbene)metal centers that electronically communicate with the iron center. However, no reaction of this novel compound was reported, so far. Ferrocenophanes, in general, have found various applications. Small, ring-tilted derivatives are effectively employed in ring opening polymerizations (ROP),[17–21] resulting in linear or cyclic[19] metallopolymers, which have potential for the usage as multifunctional materials in various fields of application;[20] incorporation of phosphorus centers[21] is of interest for the development of polymeric materials that serve as carriers for transition metal catalysts.[17] 2-Aza[3]ferrocenophanes showed intriguing electro- and photochemical behavior due to electronic communication between the amino group of the ligand and the iron center in the oxidized state.[22] Recently, a [7]ferrocenophane with N- and P-donor centers has attracted special interest, as transition metal complexes thereof showed exceptional coordination geometries.[23]



Scheme 1. Fischer carbene complexes **I** ([M]: transition metal fragment; X: heteroatom; R: organic substituent), and novel 1,1′-ferrocenophane bis(carbene complexes) **II**.

Herein, we present the synthesis of a diaminophosphane-bridged [5]ferrocenophane bis(carbene complex) and preliminary studies on ring opening reactions that afforded the

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first bis(2*H*-azaphosphirene complex) together with a trinuclear 1,1′-ferrocenediyl-bridged complex bearing a 2,3-dihydro-1,2,3-azadiphosphete and a nitrile ligand.

Results and Discussion

The reaction of 1,1′-ferrocenediylbis(aminocarbene complex) **1**[24] with chloro(methylene)phosphane **2**[25] in the presence of triethylamine in a dilute CH_2Cl_2 solution at ambient temperature selectively yielded [5]ferrocenophane bis(carbene complex) **3** (Scheme 2), which was isolated in 62% yield by using low-temperature column chromatography. Its formation can be explained by a base-induced condensation of one carbene complex unit and the chloro(methylene)phosphane (i) and subsequent 1,2-addition of the pending NH functionality in intermediate **4** to its P=C bond (ii). Alternatively, a 1,2-NH addition to the P=N bond in **5** (iv), formed by a [1,3]-H shift from **4** (iii), could be envisaged.

The molecular structure of **3** was unambiguously established by multinuclear NMR experiments, mass spectrometry, IR spectroscopy, and a single-crystal X-ray diffraction study (Figure 1).

Although C–N bonds of aminocarbene complexes generally have enhanced bond orders, thus leading to (*E*)/(*Z*)-isomeric forms,[1b] complex **3** was formed as a single diastereomer with (*E*,*E*) configuration; **3** shows a ^{31}P NMR resonance at $\delta = 66$ ppm. The ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic data are consistent with a C_S-symmetric molecule, as the two half units give rise to identical sets of resonances. The carbene carbon atom resonates at $\delta = 279.5$ ppm, thus being significantly deshielded compared to aminocarbene complex **1** ($\delta = 253.5$ ppm),[24] but in the same range as the carbene centers of acyclic *N*,*N*′-λ^3-P-bridged (carbene)tungsten complexes.[26] The molecular structure in the crystal shows that the Cp–Fe–Cp axis is slightly folded (174.7°), and the tilt angle (α) is 5.1°, whereas the Cp rings are tilted away from the comparatively large linking bridge. The carbene carbon centers do not deviate significantly from the planes of the attached Cp rings [0.017 (C8) and 0.196 Å (C19)]. This is also indicated by the ^{13}C NMR chemical shift of the ferrocenediyl *ipso*-carbon centers, which resonate at $\delta = 92.0$ ppm and, thus, not upfield from complex **1** ($\delta = 90.3$ ppm), as it would be expected if the ferrocenophane **3** were heavily tilted.[18c,27] As in the structure of the titanadioxy-bridged [5]ferrocenophane bis[(carbene)chromium complex], presented by Lotz and co-workers,[14d] the planes of the trigonal-planar carbene moieties of **3** are out of the adjacent Cp ring planes, here with twist angles of 22.2 and 49.6°.

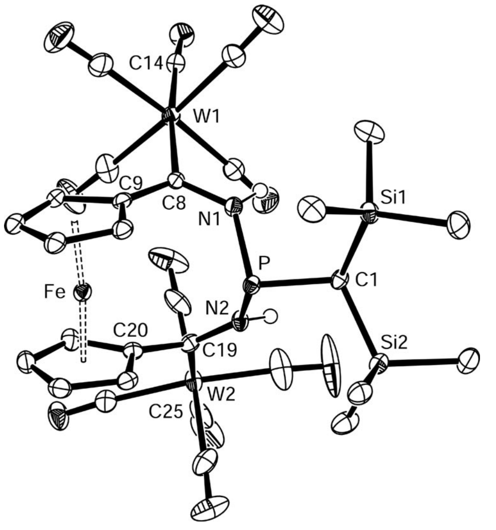
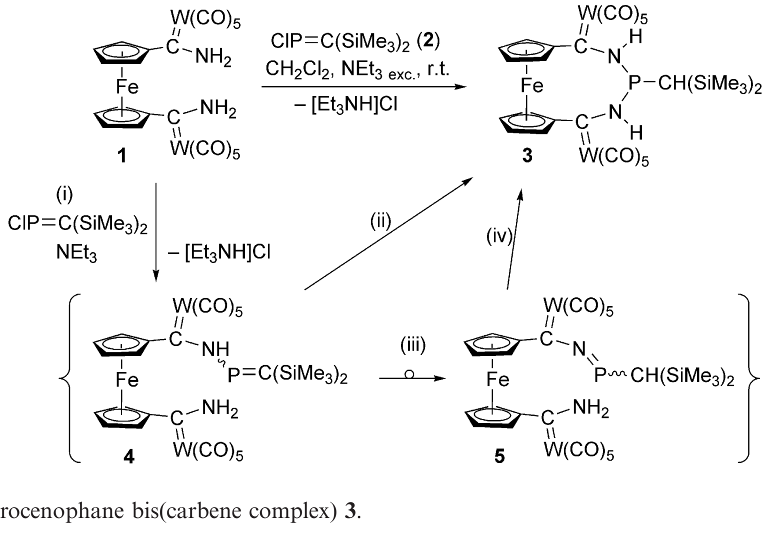
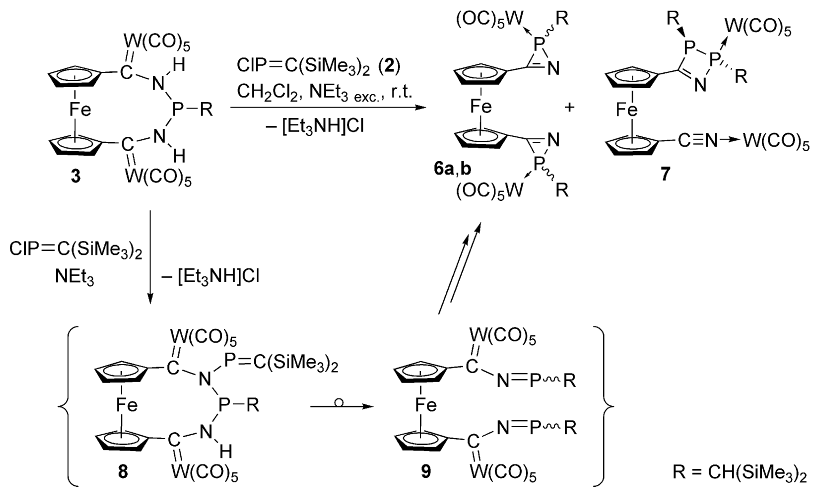


Figure 1. Molecular structure of complex **3** in the crystal [50% probability level; except for H at C(1), all other hydrogen atoms are omitted for clarity]. Selected bond lengths [Å] and angles [°]: P–C(1) 1.816(3), P–N(1) 1.769(3), N(1)–C(8) 1.362(4), C(8)–W(1) 2.207(3), C(8)–C(9) 1.462(4); C(1)–P–N(1) 99.04(13), N(1)–P–N(2) 94.25(13), N(1)–C(8)–C(9) 115.0(3), N(1)–C(8)–W(1) 118.4(2).

When **3** was treated with chloro(methylene)phosphane **2** and triethylamine in a concentrated CH_2Cl_2 solution (Scheme 3), cleavage of the ferrocenophane bridge occurred with formation of bis(2*H*-azaphosphirene complexes) **6a**,**b** and complex **7** (ratio 1:1:6).[28] Complexes **6a**,**b** are presumably formed via intermediate **8**, which undergoes ring open-



Scheme 2. Synthesis of [5]ferrocenophane bis(carbene complex) **3**.



Scheme 3. Reaction of **3** with chloro(methylene)phosphane **2** in the presence of triethylamine.

ing in the presence of a base. The resulting 2-aza-1-phospha-4-metallabutadiene substructure in **9** is the key intermediate in the formation of 2*H*-azaphosphirene complexes.[5a]

Complex **7** features a 2,3-dihydro-1,2,3-azadiphosphete and a nitrile complex unit and constitutes a structural isomer of **6a**,**b** that is formally derived from the latter by intramolecular transfer of a phosphanediyl fragment from one 2*H*-azaphosphirene complex unit to the other one. It was unambiguously identified by multinuclear NMR experiments, mass spectrometry, and a single-crystal X-ray diffraction study (Figure 2). The NMR spectroscopic data of the four-membered ring as well as its structural parameters are best compared to those of a 4-phenyl-substituted 2,3-dihydro-1,2,3-azadiphosphete complex that was obtained in a thermal reaction of a phenyl-substituted mono-2*H*-azaphosphirene complex.[29] The $^{31}P\{^1H\}$ NMR spectrum of **7** shows an AB spin system (δ = 77.5 ppm, $|^1J(W,P)|$ = 254.3 Hz, $|^{1+3}J(P,P)|$ = 115.7 Hz and δ = 90.5 ppm). The ^{13}C resonance of the ring carbon center was found at δ = 197.1 ppm (dd, $|J(P,C)|$ = 41.4 and 7.8 Hz), and the two methine carbon atoms have distinctly different ^{13}C NMR chemical shifts and phosphorus–carbon coupling constant magnitudes (δ = 16.5 ppm, $|J(P,C)|$ = 79.5 and 7.1 Hz; δ = 34.7 ppm, $|J(P,C)|$ = 20.7 and 10.3 Hz). The molecular structure reveals a slightly folded 2,3-dihydro-1,2,3-azadiphosphete ring (mean deviation from least-squares plane: 0.095 Å; torsion angle P1–C1–N1–P2: –18.3°; deviation of P2 from the P1–C1–N1 plane: 0.883 Å), in which the $CH(SiMe_3)_2$ groups adopt a *trans* position at the heterocycle with a CH(P2)–P2–P1–CH(P1) torsion angle of 132.9°.

After complete removal of **7** from the product mixture by Soxhlet extraction, the residue was subjected to low-temperature column chromatography. This afforded a purified mixture of the diastereomers **6a**,**b**, which were characterized by multinuclear NMR spectroscopy and mass spectrometry. Their high-field-shifted ^{31}P resonances with large tungsten–phosphorus coupling constant magnitudes (δ = –113.6 ppm, $|^1J(W,P)|$ = 292.5 Hz; δ = –113.2 ppm, $|^1J(W,P)|$ = 302.6 Hz) are characteristic of (2*H*-azaphosphirene)tungsten complexes, which is also true for the low-field-shifted ^{13}C resonances of the 2*H*-azaphosphirene ring carbon atoms (δ = 189.5 and 189.6 ppm).[5a]

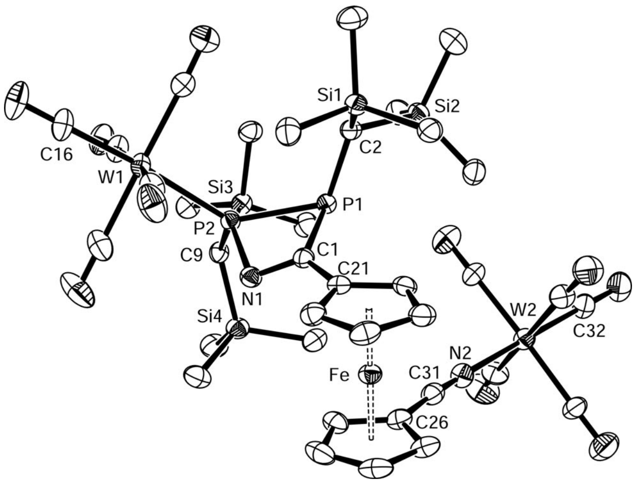


Figure 2. Molecular structure of complex **7** in the crystal (50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]:W(1)–P(2) 2.5188(8), P(2)–P(1) 2.2543(11), P(2)–N(1) 1.751(3), P(2)–C(9) 1.833(3), P(1)–C(2) 1.861(3), P(1)–C(1) 1.841(3), C(1)–N(1) 1.305(4), C(31)–N(2) 1.153(5), N(2)–W(2) 2.177(3); P(1)–P(2)–N(1) 78.43(10), P(2)–P(1)–C(1) 69.74(10), P(1)–C(1)–N(1) 107.8(2), C(1)–N(1)–P(2) 100.4(2).

Conclusion

Currently, studies on the synthetic potenial of the trimetallic diaminophosphane-bridged [5]ferrocenophane bis(carbene complex) and the bis(2*H*-azaphosphirene complex) are underway including ring opening and expansion reactions aiming at the construction of novel macrocyclic ligand architectures with redox-active functionalities.

Experimental Section

General: All reactions were carried out under purified and dried argon by using standard Schlenk techniques. Solvents were dried with sodium wire or CaH_2 (CH_2Cl_2) and distilled under argon. NMR spectroscopic data were recorded with a Bruker Avance 300 spectrometer at 30 °C by using C_6D_6, CD_2Cl_2, or $CDCl_3$ as solvents and internal standards; chemical shifts are given relative to tetramethylsilane (^{13}C: 75.5 MHz) and 85% H_3PO_4 (^{31}P: 121.5 MHz). Mass spectra were recorded with an MAT 95 XL Finnigan spectrometer (EI, 70 eV, ^{184}W) or a Bruker Daltonik micrOTOF-Q spectrometer (ESI$^+$). Melting points were determined by using a Büchi apparatus, with samples sealed in capillaries under argon. Selected NMR and MS data are given hereafter. UV/Vis absorption spectra were recorded with a Shimadzu UV-1650 PC spectrometer (λ = 190–1100 nm) from CH_2Cl_2 solutions at ambient temperature. IR spectra were recorded as KBr pellets by using a Thermo Nicolet 380 FT-IR spectrometer. Cyclovoltammetric measurements (CV) were performed by using an EG&G-Potentiostat/Galvanostat M273 in CH_2Cl_2 with 0.1 M [nBu$_4$N][PF$_6$] as supporting electrolyte at a glassy carbon electrode (GCE) with an Ag/AgCl/2 M LiCl reference electrode (Pt wire as counter electrode; scan rate 0.1 V s^{-1}; T = 25 °C).

Synthesis of 3: To a stirred solution of complex **1**[24] (440 mg, 0.50 mmol) in CH_2Cl_2 (30 mL) were added consecutively **2**[25] (140 µL, 0.62 mmol) and NEt_3 (13 mL) at ambient temperature, while the initially red solution turned deep brown. After the mixture had been stirred at ambient temperature for 1.5 h, all volatiles were removed in vacuo (ca. 10^{-2} mbar), and the product was purified by column chromatography on silica (–10 °C; 2 × 8 cm; petroleum ether/CH_2Cl_2, 1:1). Red-brown solid; yield: 328 mg (0.31 mmol, 62%); m.p. 183 °C. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 2.3 [d, $|^3J(P,C)|$ = 5.1 Hz, Si(CH$_3$)$_3$], 20.5 [d, $|^1J(P,C)|$ = 51.4 Hz, *C*H(SiMe$_3$)$_2$], 71.3 [d, $|^4J(P,C)|$ = 2.2 Hz, Cp-C$^{2/5}$], 72.2 (s, Cp-C$^{3/4}$), 75.1 [d, $|^4J(P,C)|$ = 1.5 Hz, Cp-C$^{2/5}$], 77.7 (s, Cp-C$^{3/4}$), 92.0 [d, $|^3J(P,C)|$ = 6.0 Hz, Cp-C^1], 198.4 (s$_{sat}$, $|^1J(W,C)|$ = 127.9 Hz, CO$_{cis}$], 203.0 [d, $|^4J(P,C)|$ = 0.9 Hz, CO$_{trans}$], 279.5 [d$_{sat}$, $|^2J(P,C)|$ = 1.6 Hz, $|^1J(W,C)|$ = 93.8 Hz, C$_{carbene}$] ppm. ^{31}P NMR ($CDCl_3$): δ = 66.0 (s) ppm. IR: $\tilde{\nu}$ = 3305 (ν_{NH}) cm^{-1}. UV/Vis: λ_{max} = 428 (lgε = 4.31) nm. CV: irreversible anodic oxidation wave: E_{pa} = +0.39 V {calcd. vs. $E_{1/2}$([FeCp$_2$]/[FeCp$_2$]$^+$}. MS (EI): m/z (%) = 1076.5 (2) [M]$^{\cdot+}$.

Synthesis of 6a,b and 7: To a stirred solution of complex **3** (204 mg, 0.19 mmol) in CH_2Cl_2 (7.6 mL) were added consecutively **2**[25] (0.2 mL, 0.89 mmol) and NEt_3 (2.8 mL) at ambient temperature. After the mixture had been stirred at ambient temperature for 1.5 h, all volatiles were removed in vacuo (ca. 10^{-2} mbar), and the crude product was extracted with n-pentane at –30 °C. Evaporation of the solvent of the second fraction yielded **7**. Red solid; yield: 70 mg (0.06 mmol, 29%). ^{13}C{^{1}H} NMR (C_6D_6): δ = 1.7 {br., σ^4-P–CH[Si(*C*H$_3$)$_3$]$_2$}, 2.8 {br., σ^4-P–CH[Si(*C*H$_3$)$_3$]$_2$}, 3.6 {br., σ^3-P–CH[Si(*C*H$_3$)$_3$]$_2$}, 16.5 {dd, $|J(P,C)|$ = 79.5 Hz, $|J(P,C)|$ = 7.1 Hz, *C*H[Si(CH$_3$)$_3$]$_2$}, 34.7 {dd, $|J(P,C)|$ = 20.7 Hz, $|J(P,C)|$ = 10.3 Hz, *C*H[Si(CH$_3$)$_3$]$_2$}, 70.4 (m$_c$, Cp), 71.9 (m$_c$, Cp), 72.2 (m$_c$, Cp), 73.4 (m$_c$, Cp), 73.7 (m$_c$, Cp), 74.8 (m$_c$, Cp), 75.5 (m$_c$, Cp), 87.4 [dd, $|J(P,C)|$ = 30.4 Hz, $|J(P,C)|$ = 26.5 Hz, Cp-C^1 at dihydroazadiphosphete-C^4], 197.0 [s$_{sat}$, $|^1J(W,C)|$ = 130.0 Hz, CO$_{cis}$ of CN–W(CO)$_5$], 197.1 [dd, $|J(P,C)|$ = 41.4 Hz, $|J(P,C)|$ = 7.8 Hz, PCN], 198.1 [d, $|^2J(P,C)|$ = 7.1 Hz, CO$_{cis}$ of P–W(CO)$_5$], 198.6 [d, $|^2J(P,C)|$ = 29.1 Hz, CO$_{trans}$ of P–W(CO)$_5$], 199.9 [s, CO$_{trans}$ of CN–W(CO)$_5$] ppm. ^{31}P NMR (C_6D_6): δ = 77.5 [ddd$_{sat}$, $|^1J(W,P)|$ = 254.3 Hz, $|^{1+3}J(P,P)|$ = 115.7 Hz, $|^2J(P,H)|$ = 22.3 Hz, $|^{3+5}J(P,H)|$ = 2.5 Hz, σ^4-P], 90.5 [ddd, $|^{1+3}J(P,P)|$ = 117.0 Hz, $|^2J(P,H)|$ = 22.9 Hz, $|^{3+5}J(P,H)|$ = 5.7 Hz, σ^3-P] ppm. HR-MS (ESI$^+$): calcd. for $C_{36}H_{47}FeN_2O_{10}P_2Si_4W_2$ 1265.0150; found 1265.0118; dev. 0.0032. Subsequently, the residue was subjected to Soxhlet extraction with n-pentane for 3 d. Then, the product was purified by column chromatography on silica (–15 °C; 1 × 10 cm; petroleum ether/Et$_2$O, 10:1). Evaporation of the solvents of the first fraction yielded a mixture of diastereomers **6a**,**b**. Red solid; yield: 33 mg (0.31 mmol, 14%); m.p. 119 °C (decomp.). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ = 1.1 [d, $|^3J(P,C)|$ = 3.9 Hz, Si(CH$_3$)$_3$], 1.9 [d, $|^3J(P,C)|$ = 2.6 Hz, Si(CH$_3$)$_3$], 28.9 [d, $|^1J(P,C)|$ = 22.0 Hz, *C*H(SiMe$_3$)$_2$], 71.5 (s, Cp), 71.9 (s, Cp), 72.0 (s, Cp), 72.4 (s, Cp), 75.0 (s, Cp), 75.1 (s, Cp), 75.4 (s, Cp), 75.5 (s, Cp), 189.5 (s, PCN), 189.6 (s, PCN), 196.5 [d, $|^2J(P,C)|$ = 9.1 Hz, CO$_{cis}$], 209.6 [d, $|^2J(P,C)|$ = 32.3 Hz, CO$_{trans}$] ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = –113.6 [s$_{sat}$, $|^1J(W,P)|$ = 292.5 Hz], –113.2 [s$_{sat}$, $|^1J(W,P)|$ = 302.6 Hz] ppm. HR-MS (ESI$^+$): calcd. for $C_{36}H_{47}FeN_2O_{10}P_2Si_4W_2$ 1265.0150; found 1265.0165; dev. 0.0015.

X-ray Crystallographic Analysis of 3 and 7: Suitable red single crystals of **3** and **7** were obtained from concentrated Et$_2$O solutions upon decreasing the temperature from ambient temperature to +4 °C. Data for **3** were collected with a Nonius KappaCCD diffractometer, and data for **7** were collected with a STOE-IPDS2T diffractometer, each equipped with a low-temperature device (Cryostream, Oxford Cryosystems) at 123 K by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by Patterson methods (SHELXS-97)[30a,30c] and refined by full-matrix least squares on F^2 (SHELXL-97).[30b,30c] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included isotropically by using the riding model on the bound atoms. Absorption corrections were carried out semi-empirically from equivalents [min./max. transmissions: 0.46064/0.63328 (**3**) and 0.1765/0.4163 (**7**)]. Crystal-structure data for complex **3** ($C_{29}H_{29}FeN_2O_{10}PSi_2W_2$): Crystal size 0.20 × 0.08 × 0.07 mm, monoclinic, $P2_1/n$, a = 12.6934(2), b = 13.5261(2), c = 20.7751(3) Å, β = 98.1493(6)°, V = 3530.90(9) Å^3, Z = 4, $\rho_{calcd.}$ = 2.025 Mg m^{-3}, $2\theta_{max}$ = 57.5°, collected (independent) reflections = 38919 (9154), R$_{int}$ = 0.0568, μ = 7.073 mm^{-1}, 439 refined parameters, 0 restraints, R_1 [for $I > 2\sigma(I)$] = 0.0241, wR_2 (for all data) = 0.0465, max./min. residual electron density = 1.973/–1.642 e Å^{-3}. Crystal-structure data for complex **7** ($C_{36}H_{46}FeN_2O_{10}P_2Si_4W_2$): Crystal size 0.50 × 0.30 × 0.20 mm, triclinic, P$\bar{1}$, a = 11.9658(2), b = 14.4371(3), c = 14.6344(3) Å, α = 84.768(2), β = 72.406(2), γ = 84.245(2)°, V = 2392.76(8) Å^3, Z = 2, $\rho_{calcd.}$ = 1.755 Mg m^{-3}, $2\theta_{max}$ = 58°, collected (independent) reflections = 45553 (12724), R_{int} = 0.0453, μ = 5.312 mm^{-1}, 527 refined parameters, 0 restraints, R_1 [for $I > 2\sigma(I)$] = 0.0319, wR_2 (for all data) = 0.0823, max./min. residual electron density = 1.394/–1.796 e Å^{-3}. CCDC-766006 (for **3**) and -766007 (for **7**) 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.

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