energies due to the overall stronger ionic bonding forces. Excited-state methyl → chain CT could effectively weaken or neutralize such ionic bonding contributions, thus facilitating easy scission as observed experimentally.[16]

In summary, CNDO/2 (Cl) minimal basis set computations on trans H–$(SiMe_2)_5$–H were shown to yield transition energy and intensity profiles paralleling the observed optical spectrum. The likely importance of d orbital contributions to higher lying excitations of hydrogenated and methylated silane chains has been most recently addressed computationally by Halevi and co-workers.[17]

Registry No. *trans*-H(S;Me$_2$)$_5$H, 7514-96-7.

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Synthesis and Substitution Reactions of Tris- and Tetrakis(trimethyl phosphite)-Substituted Carbyne Complexes of Chromium, Molybdenum, and Tungsten

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Summary: Methods for the synthesis of X(CO)[P(OMe)$_3$]$_3$M$\equiv$CPh (M = Cr, X = Br; M = Mo, W, X = Cl) and Cl[P(OMe$_3$)]$_4$M$\equiv$CPh (M = Mo, W) starting from the acyl complexes [NMe$_4$][(CO)$_5$M–C(O)Ph]are described. Substitution of two or all four trimethyl phosphite ligands in Cl[P(OMe)$_3$]$_4$W$\equiv$CPh by bis(diphenylphosphino)ethane is demonstrated. The crystal structure of Cl[P(OMe)$_3$]$_4$Mo$\equiv$CPh is reported.

Disubstituted carbonylmetal carbyne, or alkylidyne, complexes X(CO)$_2$L$_2$M$\equiv$CR[1a] (X = halide; L = donor ligand; M = Cr, Mo, W; R = alkyl, aryl) have become easily accessible through recently developed synthetic methods.[2] The chemistry of these compounds is strongly influenced by the presence of the two carbonyl ligands. For example, reaction of Cl(CO)$_2$(py)$_2$W$\equiv$CR (py = pyridine) with anionic bidentate ligands leads to carbonyl–carbyne coupling,[3] a process which has also been observed for other carbonylmetal carbyne complexes.[4] With alkenes Cl(CO)$_2$(py)$_2$W$\equiv$CR reacts to give stable tungsten alkene carbyne complexes but only when the alkenes are highly activated.[5] Presumably, the two carbonyl ligands stabilize the occupied metal d orbitals to such an extent that normal olefins cannot compete effectively for π-bonding. For a general investigation of the reactivity of carbyne ligands it therefore seemed desirable to have access to systems containing only one or no carbonyl ligand. However, such compounds are not easily available. The first monocarbonyl derivatives of *trans*-halotetracarbonylmetal carbyne complexes, such as Cl(CO)(maleic anhydride)(py)$_2$W$\equiv$CPh, have been prepared only recently.[5] Cyclopentadienyl-substituted monocarbonyl carbyne complexes (η^5-C$_5$H$_5$)(CO)(PMe$_3$)M$\equiv$CC$_6$CH$_3$-(4) had been described previously as byproducts in the formation of ketenyl complexes.[6] Carbonyl-free derivatives have been prepared only by routes other than carbonyl substitution. The complex Cl(PMe$_3$)$_4$W$\equiv$CCMe$_3$ has been synthesized by reduction of Cl$_3$(PMe$_3$)$_3$W$\equiv$CCMe$_3$ in the presence of trimethylphosphine and Cl(PMe$_3$)$_4$W$\equiv$CH by reaction of Cl$_2$W(PMe$_3$)$_4$ with Al(CH$_3$)$_3$.[7] Reaction of the dinuclear molybdenum complex Br(Me$_3$SiCH$_2$)$_2$Mo$\equiv$Mo(CH$_2$SiMe$_3$)$_2$Br with phosphines leads to formation of Br(PR$_3$)$_4$Mo$\equiv$CSiMe$_3$.[8] Me(PMe$_3$)$_4$W$\equiv$CMe resulted from the reaction of WMe$_6$ with PMe$_3$.[9] Complexes of the type (η^5-C$_5$H$_5$)[P(OMe)$_3$]$_2$M$\equiv$CCH$_2$R (M = Mo, W; R = CMe$_3$, SiMe$_3$) have been generated by isomerization of η^2-vinyl complexes.[10] Thermolysis of the ketenyl complex (η^5-C$_5$H$_5$)(CO)(Me$_2$PCH$_2$CH$_2$PMe$_2$)W[C(CO)C$_6$H$_4$CH$_3$-(4)] led to (η^5-C$_5$H$_5$)(Me$_2$PCH$_2$CH$_2$PMe$_2$)W$\equiv$CC$_6$H$_4$CH$_3$-(4).[11] Since tetracarbonyl carbyne complexes X(CO)$_4$M$\equiv$CR are very easily accessible,[2] facile routes for their conversion into monocarbonyl and carbonyl-free derivatives would be of considerable interest. Here we describe simple methods for the synthesis of tris- and tetrakis(trimethyl phosphite)-substituted carbyne complexes of Cr, Mo, and W and demonstrate further substitution of the phosphite ligands.

The *trans*-chloro(tetracarbonylmetal) benzylidyne complexes of molybdenum and tungsten, Cl(CO)$_4$M$\equiv$CPh, **5** and **6**, react with trimethyl phosphite easily to give the tris(phosphite) complexes Cl(CO)[P(OMe)$_3$]$_3$M$\equiv$CPh, **11** and **12**, respectively. In the presence of excess ligand (5–10-fold) the substitution of three carbonyl ligands proceeds to completion (eq 3) (5 h at room temperature for M = Mo; 24 h at 55 °C for M = W). Since solutions of the tetracarbonylmetal carbyne complexes are conveniently prepared[2] by reaction of the tetramethylammonium salts of the pentacarbonylmetal acyl complexes,[1b] **2** and **3**, with oxalyl halide at low temperatures (eq 1), compounds **11** and **12** are accessible in simple overall procedures (eq 1 and 3) in 85 and 82% yield, respectively.[12]

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[12] Approximately 0.1 M solutions (suspensions) of [NMe$_4$][(CO)$_5$M–C(O)Ph] and oxalyl halide in CH$_2$Cl$_2$ are combined at −78 °C, the reaction mixtures are warmed briefly to −10 °C (M = Cr, W) or −40 °C (M = Mo), and recooled to −78 °C for filtration. (Recooling and filtration can be omitted.) After addition of a five- to tenfold excess of trimethyl phosphite or pyridine, the solutions are allowed to warm to room temperature. The solvent is removed, and the respective products are freed from excess ligand by washing with cold pentane. The bis(pyridine)-substituted complexes (7;[1a] 8, ν_{CO} 1992, 1914 cm^{-1}; 9[2]) are used without further purification.

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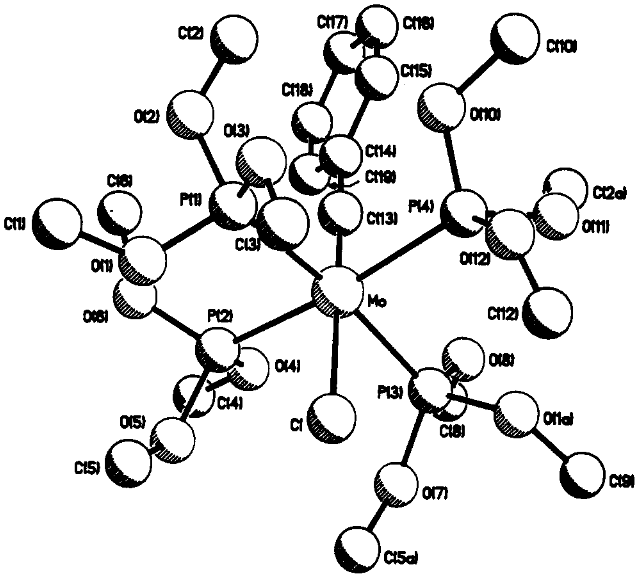

Figure 1. Molecular structure of $\mathrm{Cl[P(OMe)_3]_4Mo{\equiv}CPh}$ (**13**).

Similar yields of these products (**11**, 66%; **12**, 90%) are obtained when the initial tetracarbonylmetal carbyne complexes are first transformed into the bis(pyridine)-substituted complexes $\mathrm{Cl(CO)_2(py)_2M{\equiv}CPh}$ (eq 2) before the reaction with trimethyl phosphite (eq 3).[12] The chromium analogue **10** was prepared in 43% yield only via the bis(pyridine) complex **7**. In this case, the reaction temperature is held at 0 °C. The products are recrystallized from ether. Complex **10** forms red and complexes **11** and **12** form orange crystals.[13]

$$\begin{array}{ccc} [\mathrm{NMe_4}][(\mathrm{CO})_5\mathrm{M{-}C(O)Ph}] & \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{C_2O_2X_2}} & \mathrm{X(CO)_4M{\equiv}CPh} \\ \mathbf{1},\ \mathrm{M = Cr} & \mathrm{X = Cl,\ Br} & \mathbf{4},\ \mathrm{M = Cr} \\ \mathbf{2},\ \mathrm{M = Mo} & & \mathbf{5},\ \mathrm{M = Mo} \\ \mathbf{3},\ \mathrm{M = W} & & \mathbf{6},\ \mathrm{M = W} \end{array} \tag{1}$$

$$\begin{array}{ccc} \mathrm{X(CO)_4M{\equiv}CPh} & \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{pyridine}} & \mathrm{X(CO)_2(py)_2M{\equiv}CPh} \\ & & \mathbf{7},\ \mathrm{M = Cr} \\ & & \mathbf{8},\ \mathrm{M = Mo} \\ & & \mathbf{9},\ \mathrm{M = W} \end{array} \tag{2}$$

$$\begin{array}{ccc} \mathbf{5}\text{–}\mathbf{9} & \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{P(OMe)_3}} & \mathrm{X(CO)[P(OMe)_3]_3M{\equiv}CPh} \\ & & \mathbf{10},\ \mathrm{M = Cr} \\ & & \mathbf{11},\ \mathrm{M = Mo} \\ & & \mathbf{12},\ \mathrm{M = W} \end{array} \tag{3}$$

Substitution of the remaining carbonyl ligand by trimethyl phosphite proved successful for the molybdenum and tungsten compounds simply by heating **11** and **12** in neat trimethyl phosphite to 70 and 110 °C for 8 and 48 h, respectively. The *trans*-chlorotetrakis(trimethyl phosphite)metal carbyne complexes $\mathrm{Cl[P(OMe)_3]_4M{\equiv}CPh}$ (**13**, M = Mo; **14**, M = W) are obtained as orange and yellow crystals in 86 and 79% yield, respectively, after recrystallization from ether.[14] We have not yet been able to isolate the analogous chromium compound using similar reaction conditions.

$$\begin{array}{ccc} \mathrm{Cl(CO)[P(OMe)_3]_3M{\equiv}CPh} & \xrightarrow[\Delta]{\mathrm{P(OMe)_3,\ neat}} & \\ & & \mathrm{Cl[P(OMe)_3]_4M{\equiv}CPh} \\ & & \mathbf{13},\ \mathrm{M = Mo} \\ & & \mathbf{14},\ \mathrm{M = W} \end{array} \tag{4}$$

The molecular structure of $\mathrm{Cl[P(OMe)_3]_4Mo{\equiv}CPh}$ (**13**) is shown in Figure 1.[15] It contains an essentially linear Cl—Mo$\equiv$C axis, 179.6 (3)°, with a short Mo$\equiv$C distance, 1.793 (8) Å, and a long Mo–Cl distance, 2.585 (3) Å.[16] The arrangement of the four equatorial phosphite ligands is puckered with P(1) and P(3) being bent toward chloride by 5.4° and P(2) and P(4) being bent toward the carbyne ligand by 3.6° (average). The average Mo–P bond distance is 2.451 Å.[16]

The phosphite ligands in the new carbyne complexes are coordinatively labile and can be substituted by other ligands. For example, reaction of $\mathrm{Cl[P(OMe)_3]_4W{\equiv}CPh}$ (**14**) with an equivalent amount of dppe (bis(diphenylphosphino)ethane) in $\mathrm{CH_2Cl_2}$ at 55 °C for 2 h affords orange-red $\mathrm{Cl[P(OMe)_3]_2(dppe)W{\equiv}CPh}$ (**15**).[17] Further reaction of **15** with a second equivalent of dppe in refluxing toluene for 24 h provides $\mathrm{Cl(dppe)_2W{\equiv}CPh}$ (**16**).[17]

The tris- and tetrakis(phosphite)-substituted metal carbyne complexes possibly will form a useful starting point for the investigation of the chemistry of carbyne complexes containing only one or no carbonyl ligand. This paper is the fourth in a series describing new syntheses of transition-metal carbyne, or alkylidyne, complexes.[5,18,19] With the developed methods the major types of group 6 transition-metal complexes containing metal–carbon triple bonds are now easily accessible.

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[13] **10**: mp 72–76 °C dec. Anal. Calcd for $\mathrm{C_{17}H_{32}BrCrO_{10}P_3}$: C, 32.86; H, 5.15. Found: C, 33.36; H, 5.40. IR ($\mathrm{cm^{-1}}$, $\mathrm{CH_2Cl_2}$): ν_{CO} 1954. ^{13}C NMR (ppm, $\mathrm{CDCl_3}$): 296.0 (q, $^2J_{\mathrm{CP}} = 47.9$ Hz, *C*Ph), 230.9 (m, CO). ^{31}P NMR (ppm, $\mathrm{CDCl_3}$): 98.5 (t, 1 P, $^2J_{\mathrm{PP}} = 95$ Hz), 90.1 (d, 2 P, $^2J_{\mathrm{PP}} = 95$ Hz). **11**: mp 91–94 °C dec. Anal. Calcd for $\mathrm{C_{17}H_{32}ClMoO_{10}P_3}$: C, 32.89; H, 5.16. Found: C, 33.15; H, 5.24. IR ($\mathrm{cm^{-1}}$, $\mathrm{CH_2Cl_2}$): ν_{CO} 1964. ^{13}C NMR (ppm, $\mathrm{CDCl_3}$): 272.8 (q, $^2J_{\mathrm{CP}} = 22.7$ Hz, *C*Ph), 219.5 (dt, $^2J_{\mathrm{CP(trans)}} = 67.5$ Hz, $^2J_{\mathrm{CP(cis)}} = 15.5$ Hz, CO). ^{31}P NMR (ppm, $\mathrm{CDCl_3}$): 107.6 (t, 1 P, $^2J_{\mathrm{PP}} = 53$ Hz), 101.4 (d, 2 P, $^2J_{\mathrm{PP}} = 53$ Hz). **12**: mp 87–89 °C dec. Anal. Calcd for $\mathrm{C_{17}H_{32}ClO_{10}P_3W}$: C, 28.81; H, 4.52. Found: C, 28.91; H, 4.73. IR ($\mathrm{cm^{-1}}$, $\mathrm{CH_2Cl_2}$): ν_{CO} 1946. ^{13}C NMR (ppm, $\mathrm{CDCl_3}$): 257.9 (q, $^2J_{\mathrm{CP}} = 16.9$ Hz, $^1J_{\mathrm{CW}} = 161.6$ Hz, *C*Ph), 216.2 (dt, $^2J_{\mathrm{CP(trans)}} = 64.6$ Hz, $^2J_{\mathrm{CP(cis)}} = 10.9$ Hz, CO). ^{31}P NMR (ppm, $\mathrm{CDCl_3}$): 117.9 (t, 1 P, $^2J_{\mathrm{PP}} = 40$ Hz, $^1J_{\mathrm{PW}} = 372$ Hz), 115.1 (d, 2 P, $^2J_{\mathrm{PP}} = 40$ Hz, $^1J_{\mathrm{PW}} = 423$ Hz).

[14] **13**: mp 59–61 °C dec. ^{13}C NMR (ppm, $\mathrm{CDCl_3}$): 265.8 (quintet, $^2J_{\mathrm{PC}} = 18.0$ Hz, *C*Ph). ^{31}P NMR (ppm, $\mathrm{CDCl_3}$): 97.8 (s). **14**: mp 103–105 °C dec. Anal. Calcd for $\mathrm{C_{19}H_{41}ClO_{12}P_4W}$: C, 28.35; H, 5.10. Found: C, 28.29; H, 5.31. ^{13}C NMR (ppm, $\mathrm{CDCl_3}$): 251.1 (quintet, $^2J_{\mathrm{CP}} = 17.9$ Hz, *C*Ph). ^{31}P NMR (ppm, $\mathrm{CDCl_3}$): 113.4 (s, $^1J_{\mathrm{PW}} = 215$ Hz).

[15] $\mathrm{C_{19}H_{41}ClMoO_{12}P_4}$: orthorhombic, *Pcmn* (standard, *Pnma*), $a = 10.513$ (3) Å, $b = 14.930$ (4) Å, $c = 20.591$ (6) Å, $V = 3232$ (1) Å^3, $Z = 4$, μ(Mo Kα) = 7.3 $\mathrm{cm^{-1}}$, ρ(calcd) = 1.47 g $\mathrm{cm^{-3}}$. Of the 2965 unique reflections collected, $3 \leq 2\theta \leq 50°$, 2118 were considered observed ($|F_o| \geq 3\sigma(F_o)$) after Lorentz, polarization, and empirical absorption corrections (minimum trans, 0.64; maximum trans, 0.89). The structure was solved by the standard heavy-atom technique and refined by blocked-cascade least-squares procedures. The Mo, Cl, and CPh groups are located on a mirror plane; the four $\mathrm{P(OMe)_3}$ groups are disordered between positions across the mirror plane. The Mo, Cl, CPh carbon, and O atoms refined with anisotropic thermal parameters, the methyl C's refined with isotropic thermal parameters, and the phenyl hydrogens idealized. $R = 0.065$, $R_w = 0.066$, GOF = 1.34, and highest peak in final difference map = 0.58 e^-Å^{-3}.

[16] Comparable bond distances: *trans*-$\mathrm{[(CO)_5Re](CO)_4Mo{\equiv}CPh}$,[16a] Mo$\equiv$C = 1.83 Å; *trans*-$\mathrm{Br(dppe)_2Mo{\equiv}CSiMe_3}$,[8] Mo$\equiv$C = 1.819 Å and Mo—P (av) = 2.514 Å; $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{(CO)_2Mo{\equiv}CC_6H_4CH_3}$-(4),[16b] Mo$\equiv$C = 1.818 Å. (a) Huttner, G.; Frank, A.; Fischer, E. O. *Isr. J. Chem.* **1976/1977**, *15*, 133–142. (b) Uedelhofen, H. Ph.D. Thesis, Technische Universität, Munich, 1979.

[17] **15**: mp 135–138 °C dec. Anal. Calcd for $\mathrm{C_{39}H_{47}ClO_6P_4W}$: C, 49.05; H, 4.93. Found: C, 48.97; H, 5.20. ^{13}C NMR (ppm, $\mathrm{CDCl_3}$): 253.6 (m, $^1J_{\mathrm{CW}} = 186.7$ Hz, *C*Ph). ^{31}P NMR (ppm, $\mathrm{CDCl_3}$): 104.9 (m, $^1J_{\mathrm{PW}} = 507$ Hz, *P*$\mathrm{(OMe)_3}$), 41.0 (m, $^1J_{\mathrm{PW}} = 238$ Hz, $(P\mathrm{Ph_2CH_2})_2$). **16**: mp 207–211 °C dec. Anal. Calcd for $\mathrm{C_{60}H_{55}Cl_3P_4W}$ ($\mathrm{Cl(dppe)_2WCPh{\cdot}CH_2Cl_2}$): C, 60.55; H, 4.63. Found: C, 60.18; H, 4.69. ^{13}C NMR (ppm, $\mathrm{CDCl_3}$): 250.4 (m, *C*Ph). ^{31}P NMR (ppm, $\mathrm{CD_2Cl_2}$, 213 K): 45.2 (s, br).

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Organometallics 1986, 5, 1506–1508

Registry No. **1**, 15975-90-3; **2**, 15975-91-4; **3**, 15975-92-5; **4** (X = Br), 50701-13-8; **5** (X = Cl), 102341-13-9; **6** (X = Cl), 50726-26-6; **7** (X = Br), 62980-43-2; **8** (X = Cl), 102286-21-5; **9** (X = Cl), 99630-91-8; **10** (X = Br), 102286-22-6; **11** (X = Cl), 102306-93-4; **12** (X = Cl), 102286-23-7; **13**, 102286-24-8; **14**, 102286-25-9.

Supplementary Material Available: Crystallographic data for 13. tables of atomic coordinates, bond lengths, bond angles, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Electron Spin Resonance and Molecular Orbital Study of Binuclear Phosphido-Bridged Iron Carbonyl Radicals[†]

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Summary: A new family of 33-electron, paramagnetic phosphido-bridged diiron carbonyl complexes $Fe_2(CO)_7(\mu\text{-}PR_2)$ (I, R = Et, Ph, Cy, *t*-Bu) is reported. These radical species can be isolated in analytically pure form and have been studied by IR and ESR spectroscopy. Studies with ^{13}CO indicate complete CO exchange in seconds in dilute pentane solutions, very rapid scrambling of the CO ligands on the ESR time scale, and reversible addition of a CO molecule to give the 35-electron $Fe_2(CO)_8(\mu\text{-}PR_2)$ adducts (II). Spectroscopic data and EHMO calculations support structures for I and II which differ from those determined previously for the corresponding diamagnetic anions $[Fe_2(CO)_n(\mu\text{-}PPh_2)]^-$ (n = 7, 8). Radicals I react rapidly with 1 equiv of $P(OMe)_3$ to give monosubstituted derivatives $Fe_2(CO)_6[P(OMe)_3](\mu\text{-}PR_2)$.

The cooperative effects of two transition-metal centers held together by a bridging phosphido ligand are of great interest in organometallic chemistry.[1] Such adjacent metal centers offer modes of bonding and reaction pathways which are not possible at single metal centers and which may produce enhanced activity and selectivity in homogeneous catalysis. With few exceptions,[2] the vast majority of binuclear phosphido-bridged systems studied so far have been diamagnetic. We now report the preparation, characterization, and ESR studies of a new family of paramagnetic phosphido-bridged binuclear iron carbonyl complexes $Fe_2(CO)_7(\mu\text{-}PR_2)$ (I, R = Et (A), Ph (B), cyclohexyl, *t*-Bu).

Scheme I

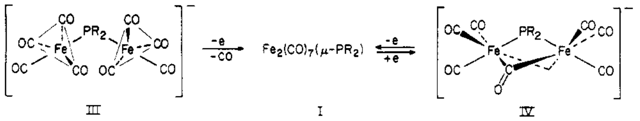

Table I. ESR Parameters for $Fe_2(CO)_7(\mu\text{-}PR_2)$ Radicals[a]

	PEt_2	PPh_2	PCy_2	P-*t*-Bu_2
g_1	2.0990	2.0978	2.0958	2.0826
g_2	2.0323	2.0309	2.0317	2.0426
g_3	2.0263	2.0259	2.0255	2.0130
g_{av}	2.0525	2.0515	2.0510	2.0461
g_{iso}	2.0526	2.0520	2.0508	2.0469
$A_1(P)$	22.1	21.5	20.6	19.0
$A_2(P)$	28.2	28.7	28.6	23.8
$A_3(P)$	20.7	20.7	19.7	21.8
$A_{av}(P)$	23.7	23.6	23.0	21.5
$A_{iso}(P)$	23.16	23.39	22.65	20.51

[a] Anisotropic parameters at −173 °C in 3-methylpentane; isotropic parameters at −70 °C in pentane. The hyperfine splittings are in gauss.

One-electron oxidation of the anions III and IV[3] with [ferrocenium][BF_4] yields the 33e binuclear radicals I, isolated as sublimable, air-sensitive, dark green crystals (Scheme I).[4] Complexes I were characterized by elemental analysis, MS, IR, and ESR spectroscopy. The IR spectra of I showed no absorption bands due to bridging carbonyls and are strikingly similar to the IR spectrum of the structurally characterized 34e complex $FeCo(CO)_7(\mu\text{-}PMe_2)$ (V).[5,6] We conclude that I and V are isostructural, with one six-coordinate, pseudooctahedral metal center and one five-coordinate, distorted trigonal-bipyramidal metal center (Scheme II).

The ESR spectra of I in dilute pentane solutions are doublets (Figure 1A), appropriate for a weak hyperfine interaction with a phosphorus atom (Table I). The pow-

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[†] Contribution no. 3785.

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(4) In a typical preparation, a solution of 956 mg (4.32 mmol) of PPh_2Cl in 50 mL of THF was added dropwise to a suspension of 1.65 g (4.32 mmol) of $Na_2Fe_2(CO)_8$ in 100 mL of THF over 30 min. After being stirred for 1 h, the solution was concentrated in vacuo to 20 mL and filtered through Celite and the solvent evaporated. The residue was washed with 2 × 15 mL of hexane and dissolved in 50 mL of CH_2Cl_2, and a solution of 1.18 g (4.32 mmmol) of $[Cp_2Fe]$ $[BF_4]$ in 50 mL of CH_2Cl_2 was added dropwise over 30 min. The resulting dark green solution was stirred for 18 h and evaporated to dryness. Extraction of the residue with 250 mL of hexane and cooling to −30 °C for 14 h afforded 1.60 g of green-black crystals of $Fe_2(CO)_7(\mu\text{-}PPh_2)$ (75%), mp 90–93 °C. Anal. Calcd for $C_{19}H_{10}Fe_2O_7P$: C, 46.29; H, 2.04; Fe, 22.66; P, 6.28. Found: C, 46.24, 46.00; H, 2.21, 2.14; Fe, 22.7, 22.8; P, 6.14, 6.16.

(5) IR for IA in hexane: 2029 (m), 1994 (m), 1978.5 (vs), 1958 (s), 1950 (s, sh), 1922.5 (s), 1908 (s) cm^{-1}.

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