dicular to that of the drawing. Explicitly represented in Figure 3b are the two d orbitals previously used to form the second π bond, tilted as suggested by the observed geometry of the molecule and with the two electrons uncoupled.

The two fragments shown in parts a and b of Figure 3 can then be combined in an obvious way to result in two W–N single bonds and a three-center two-electron bridge bond extending over the two metal atoms and the carbon atom. Such a bonding picture seems to be consistent with the W–W distance, which is similar to that found in other molecules[11,12] with a σ and π bond as well as bridging ligands between two W^{IV} atoms, and also with the C–N distances, which are in the range of double bonding. The W–C and W–N distances are consistent with the implication from the bonding scheme that bond orders between $^1/_2$ and 1 prevail between these pairs of atoms.

Acknowledgment. We thank the National Science Foundation for support.

Registry No. $[W(OCMe_3)_3]_2(\mu\text{-}C_7H_7NCNC_7H_7)$, 94138-23-5; W2(OCMe$_3$)$_6$, 57125-20-9; $CH_3C_6H_4NCNC_6H_4CH_3$, 1143-91-5.

Supplementary Material Available: A table of observed and calculated structure factors, a table of anisotropic thermal parameters, and complete tables of bond lengths and bond angles (27 pages). Ordering information is given on any current masthead page.

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Preparation, Multinuclear NMR Characterization, and Reactivity of Some *o*-Phenylenebis(dimethylphosphine) Methyl and Acyl Complexes of Iron(II). Steric Effects on Competitive Migratory Carbon Monoxide Insertion and Substitution

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The acyl complex **2** ($[Fe(pdmp)(CO)_2(C(O)Me)(I)]$; pdmp = *o*-phenylenebis(dimethylphosphine)) is prepared by the treatment of $[Fe(pdmp)(CO)_3]$ with excess methyl iodide. Acyl **2** decarbonylates on heating in vacuo to give the corresponding neutral methyl complex **5** ($[Fe(pdmp)(CO)_2(Me)(I)]$ and affords the CO-extruded cationic alkyl **3** (*fac*-$[Fe(pdmp)(CO)_3Me]^+$) in the presence of halide acceptors. Treatment of the alkyl complexes with Lewis bases (L) gives migratory CO insertion in the case of **3** and either migratory CO insertion (L = CO) or sequential substitution (L = $P(OMe)_3$) with final displacement of iodide in the case of **5**. Steric factors are suggested to determine the reaction course followed.

Introduction

Cis-bidentate chelation of *o*-phenylene-based ligands of the type *o*-$C_6H_4L_2$ is highly entropically favored, and thus ligands of this class have been extensively used in transition-metal chemistry.[1] Earlier,[2,3] as part of a systematic study of migratory carbon monoxide insertion reactions of octahedral transition-metal complexes which recognizes the ability of arsenical *o*-phenylene bidentates to stabilize a wide range of oxidation states, we reported on the stoichiometric migratory CO insertions of *fac*-$[Fe(diars)(CO)_3(Me)]^+$ (diars = *o*-phenylenebis(dimethylarsine)). This paper describes our findings related to the preparation, structural characterization, and reactivity of the new isostructural phosphorus analogue *fac*-$[Fe(pdmp)(CO)_3(Me)]^+$ (**3**, pdmp = *o*-phenylenebis(dimethylphosphine)) which extend our earlier stereochemical conclusions[3] and rationalize, on the basis of steric effects, competitive migratory carbonyl insertion and simple substitution previously observed[3-5] for a number of octahedral d^6 complexes.

Results and Discussion

Treatment of $[Fe(pdmp)(CO)_3]$, prepared by thermal reaction of iron pentacarbonyl and pdmp[6-8] at 410 K, with an excess of methyl iodide in the dark at 273 K affords[2,9] an isomeric mixture of octahedral neutral acyl–iodo complexes **2** (cf. Scheme I). ^1H NMR of the chromatographed product showed three isomeric acyls **2a** (2.51 ppm), **2b** (3.00 ppm), and **2c** (3.13 ppm) in a ratio of 100:18:19, respectively. Two strong ν_{CO} infrared stretches ((CH_2Cl_2) 2006, 1968 cm^{-1}) and a singlet (($CDCl_3$) 53.4 ppm) in the $^{31}P\{^1H\}$ NMR spectrum of samples enriched in the major isomer indicate a *trans*-(acyl, I) geometry for **2a**. Definitive assignments of the remaining isomers could not be made. The reaction presumably proceeds via an initial attack of Fe at carbon to give a six-coordinate cationic methyl complex followed by iodide promoted migratory CO insertion.[2,10,11]

Equilibration of crude samples of **2** in methylene chloride/benzene (ca. 1/1) at 353 K in a sealed tube under CO

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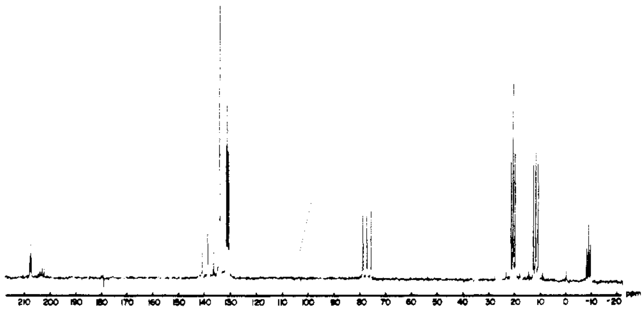
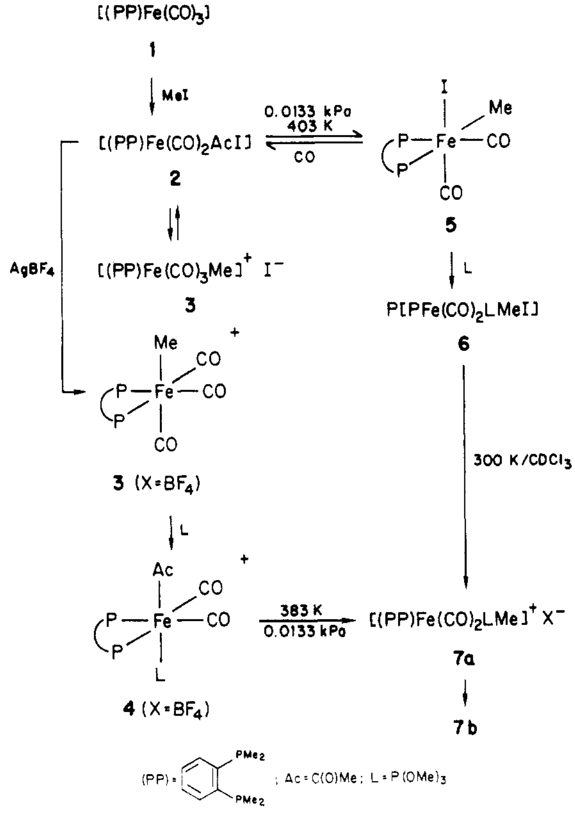


Figure 1. 20.1-MHz $^{13}C\{^1H\}$ NMR spectrum of 3 in $CDCl_3$.

Scheme I

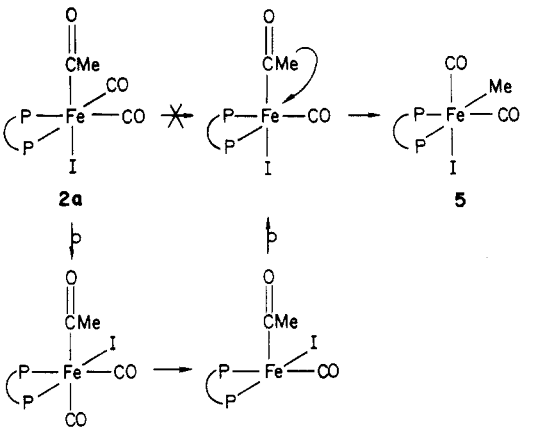


pressure resulted in the formation of all four possible geometric isomers **2a–d**. ^{1}H NMR analysis of equilibrated samples showed four acyl resonances **2a**, **2b**, **2c**, and **2d** (3.16 ppm) in a ratio of 1:1.5:0.25:0.42. Thus the *trans*-(acyl, I) **2a** formed as the major product on reaction of **1** with MeI appears to be kinetically determined in agreement with the strong trans directing effect of η^1-acyl.[3,12-14]

Treatment of isomeric mixture of the acyls **2** with halide acceptors results in CO extrusion to form the cationic methyl **3**. Owing to decreased solubility, halide abstraction with AgBF, proceeds slowly as a two-phase reaction in refluxing dichloromethane but was found to give better yields than when the reaction was carried out in acetone or methanol. Thallium salts proved less attractive for the synthesis of **3** and tended form unidentified side products which were removed with difficulty.

Complex **3** is assigned a fac geometry on the basis of infrared[2] and $^{13}C\{^1H\}$ NMR data which are uniquely consistent with a symmetry plane bisecting the pdmp ligand.

Scheme II



Thus, two P–Me sites, three *o*-phenylene sites, and two carbonyl sites are observed in the $^{13}C\{^1H\}$ spectrum of **3** (cf. Figure 1). All ^{13}C resonances of complex **3** show appreciable coupling to ^{31}P. Splitting patterns ranging from deceptively simple triplets to "quintets", dependent on the relative magnitudes of $J_{AA'}$, and $[J_{AX} - J_{A'X}]$, are possible[15] for AA′X (more properly ABX: A, B = ^{31}P; X = ^{13}C) spin systems with appreciable $J_{AA'}$. In the present case, $^{13}C\{^1H\}$ NMR spectra reveal symmetrical quintets with weak outer combination lines for the two nonequivalent P–Me resonances as well as the pair of CO groups cis to Fe–Me. Both the unique CO site and the iron–methyl group comprise an A_2X (X = ^{13}C) spin system and therefore appear as triplets (J_{AX} = 15.5 and J_{AX} = 15.5 Hz, respectively).

On the basis of fac geometry, similar symmetrical five-line patterns are expected for the ^{13}C resonances of all the *o*-phenylene carbons; however, owing either to insufficient signal/noise or equalization of J_{AX} and $J_{A'X}$, only the central three strong lines were confidently detected. The ^{1}H NMR spectrum in CD_2Cl_2 shows two overlapping "filled in doublets"[15] for the P–Me groups while the Fe–Me appears as 1:2:1 triplet.

Although slow geometrical isomerization occurs, the yellow neutral iodo acyls **2** are structurally stable in relatively nonpolar media (chloroform, methylene chloride, alkanes). When **2** is dissolved in methanol or acetone, however, the yellow color fades, indicative of iodide dissociation, and a white precipitate forms which slowly redissolves to give a nearly colorless solution. Acyl resonances from **2a–c** and a triplet assigned to Fe–Me of **3** in the ^{1}H NMR spectrum indicate that the ionization equilibrium[5] **2** $\rightleftharpoons$ **3** (X = BF_4) is established. Increasing the solvent dielectric constant by addition of aliquots of water to acetone or methanolic solutions shifted the equilibrium toward the cationic complex **3**.

Unlike its arsenic analogue[2] but similar to the bis-monodentate trans phosphine complex $[Fe(PMe_3)_2(CO)_2(I)(Ac)]$,[5,9] the pdmp acyls **2** readily decarbonylate in the solid state at 403 K (0.0133 kPa) to afford the corresponding neutral iodo–methyl derivative **5**. An all-cis geometry for **5** with Me cis to one P atom and trans to the other is supported by ^{1}H NMR spectroscopy which shows the Fe–Me group as a double doublet and the P–Me groups as four overlapping doublets.[16] Analysis of incompletely decarbonylated samples of **2** by ^{1}H NMR showed that the

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[16] Assignments were confirmed from spectra recorded at 80 and 360 MHz.

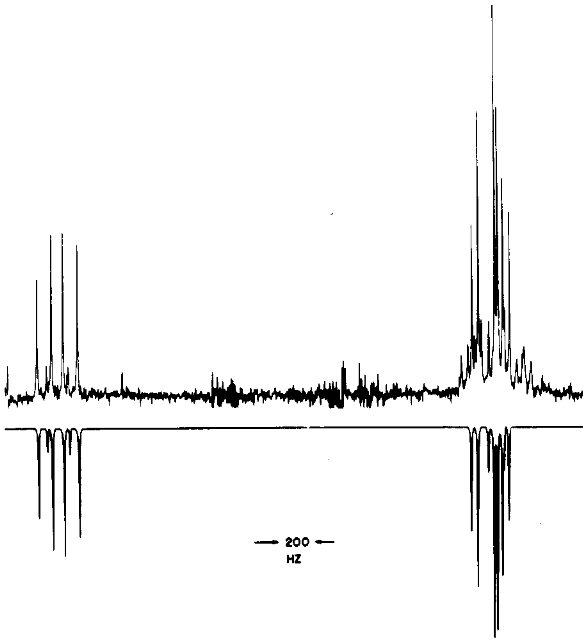


Figure 2. Top: 32.4-MHz $^{31}P\{^1H\}$ NMR spectrum of **7a** in $CDCl_3$. Bottom: simulated spectrum.

major acyl component, assigned a *trans*-(acyl, I) geometry (vide supra), reacts more sluggishly than the other isomers. Careful inspection of the upfield region confirmed **5** as the only Fe–Me species formed. Since decarbonylation followed by methyl migration from *trans*-(acyl, I) **2a** in principle can generate **5** directly (cf. Scheme II), it appears likely that trans effects,[3,12-14] which determine CO lability, control the reaction rate.

This line of reasoning suggests that *trans*-(CO, CO) **2** and/or *trans*-(Ac, CO) **2** represent the labile species leading to **5**. Support for this hypothesis derives from the reverse reaction, carbonylation of **5**, which gives the acyls **2a–d** in a ratio of 1:4.2:0.4:0.5 when carried out in methylene chloride at 273 K. Allowing for a minor amount of isomerization under the conditions of the experiment, microscopic reversibility fixes acyl **2b** as the labile species with respect to decarbonylation. The strong trans effect of the η^1-acyl ligand observed in this (vide infra) and the related diars series[3] allows a tentative assignment of the *trans*-(Ac, CO) geometry to **2b**.

Methylene chloride solutions of the cationic methyl complex **3** readily "insert" carbon monoxide in the presence of excess trimethyl phosphite at 273 K to afford the cationic acyl **4**. Under these conditions the promoting base enters trans[3] to the acyl group to give a single isomer **4**; however, partial rearrangement and decarbonylation occur (viz., ^1H NMR) at higher temperatures. The stereochemical assignment follows from a consideration of the $^{31}P\{^1H\}$ NMR spectrum of isolated samples of **4** which shows an A_2X spin system assigned as $P(OMe)_3$ coupled to two magnetically equivalent P atoms of pdmp.

In contrast with the cationic methyl **3**, treatment of the neutral methyl complex **5** with excess trimethyl phosphite in chloroform solution leads to substitution rather than "insertion". ^1H NMR time profiles at 304 K (cf. Figure 2) provide direct evidence for the formation of a transient intermediate methyl complex followed by a slower conversion to a new methyl species which subsequently isomerizes. The Fe–Me region shows an initial rapid formation of a "triplet" (0.20 ppm (J = 7.8 Hz)) presumably due to similar coupling with $P(OMe)_3$ and one P atom of unidentate pdmp in **6**. Coordinated phosphite appears as a doublet (3.79 ppm (J = 10.6 Hz)); however, the complex P–Me region did not yield to analysis. A second, slower substitution follows in which I^- is displaced as pdmp again becomes bidentate. The second substitution is marked by the appearance of a distinctive 8-line pattern, assigned as Fe–Me of cationic **7a** coupled to three nonisochronus P atoms (X part of $ABMX_3$, –0.46 ppm (J_{AX} = 8.7 Hz, J_{BX} = 7.2 Hz, J_{MX} = 10.3 Hz)) which grows at the expense of the original "triplet".

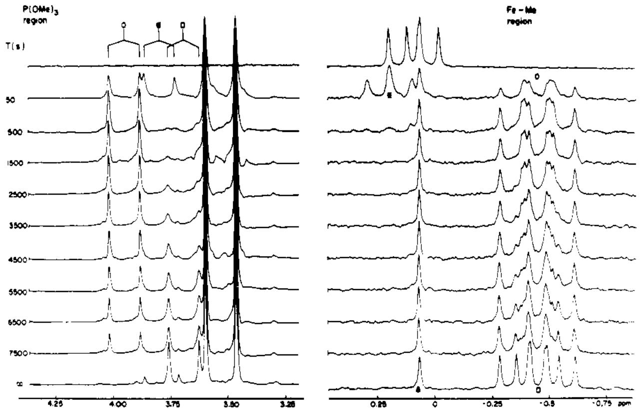
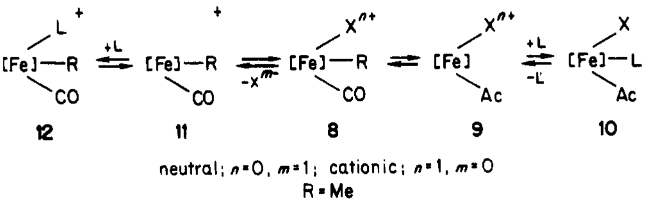


Figure 3. Time-dependent, 80-MHz NMR spectra for **5–7**: *, **6**; ○, **7a**; □, **7b**; A, impurity.

Scheme III



The assignment of the cationic methyl structure for **7a** is corroborated by its rational preparation from the acyl **4**. Thermal decarbonylation (383 K (0.0133 kPa)) of **4** proceeds readily[4,17] to give **7a** (X = BF_4) which shows a ^1H NMR spectrum identical with that of **7a** (X = I). Its $^{31}P\{^1H\}$ NMR spectrum shows a 14-line ABX (X = $P(OMe)_3$) pattern. Computer simulation (cf. Figure 2) generated all relevant couplings and confirmed one of the two possible all-cis geometries.

Complex **7a** slowly isomerizes (cf. Figure 3) to form the new cationic methyl species **7b** with the alternate all-cis geometry. The conversion is marked by the appearance of a new Fe–Me signal (X part of a $ABMX_3$ pattern, –0.45 ppm (J_{AX} = 9.9 Hz, J_{BX} = 5.7 Hz, J_{MX} = 10.7 Hz)). Related, sterically driven, isomerizations of the cationic complex $[Fe(PMe_3)_2(CO)_2(PMe_2Ph)(Me)]^+$ have recently been reported by Pankowski.[18]

The results reported here, taken together with literature data, show an overwhelming preference for Lewis base promoted migratory insertion in the case of the cationic derivatives $[FeL_2(CO)_3(Me)]^+$ (L = P or As donor)[2,4] while either insertion[4,5,9,19] or substitution[18] results for the neutral derivatives, $[FeL_2(CO)_2(X)(Me)]$ (L = P or As donor, X = halide or pseudohalide). We interpret the data in terms of a predominate steric effect on Scheme III.

When X has moderate to large steric requirements (viz., I^-), halide substitution dominates for the neutral derivatives $[FeL_2(CO)_2(X)(Me)]$. Thus we, as well as others,[18]

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observe exclusive substitution (viz., **5** → **6** → **7** and in general **8** → **11** → **12**) in the presence of sterically demanding bases which fail to intercept the nascent 16-electron intermediate **9**. Treatment of **5** as well as the related bis-monodentate derivatives[5,9,19] with CO gives back the corresponding acyl showing that insertion is possible, but apparently only with ligands of very low steric requirements. For cases where X has a small steric requirement (viz., CN^-), insertion can be observed even for P-donor ligands; however, the acyl products observed in such cases are very labile with respect to dissociation of the promoting P-donor ligand and give rise to methyl ⇄ acyl, **8** ⇄ **10** equilibria.[4]

A similar situation prevails for the cationic derivatives with the added proviso that substitution is more difficult in these positively charged cases. Accordingly, substitution has not been observed and we find that both $[Fe(diars)(CO)_3(Me)]^+$ and **3** insert (**8** → **9** → **10**) with a wide variety of neutral[3] and anionic[2] promoting bases. We have also examined the sterically more congested dicarbonyl cationic derivatives $[FeL_2L'(CO)_2(Me)]^+$ (L, L′ = P or As donors) and find either methyl–acyl, **8** ⇄ **10** equilibria or no reaction with P-donor ligands when L′ has appreciable cone angle.[20]

Experimental Section

General Comments. All operations were carried out by using standard Schlenk techniques under an atmosphere of nitrogen gas which was purified by passage through columns containing heated "De-Ox" catalyst (Alfa), activated (4 Å) molecular sieves, and finally P_4O_{10}. Pentcarbonyliron, -silver, and -thallium salts were purchased from Aldrich Chemical Co. and used as received. Trimethyl phosphite was purchased from Strem Chemicals and was distilled prior to use. Solvents were dried over activated (4 Å or 3 Å) molecular sieves and distilled under nitrogen. Melting points were determined in sealed, nitrogen-filled capillary tubes and are uncorrected. Elemental analyses were determined by Canadian Microanalytical Service Ltd., Vancouver, B.C. ^1H, ^{13}C, and ^{31}P NMR spectra were determined in $CDCl_3$ or CD_2Cl_2 on a Bruker WP-80 or a Nicolet 360 spectrometer. Chemical shifts are reported in parts per million with respect to internal Me_4Si (^1H and ^{13}C) or external 85% H_3PO_4 with downfield shifts assigned positive values. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer.

pdmp was prepared in 26% yield from *o*-difluorobenzene (Aldrich) and potassium dimethylphosphide, obtained by room-temperature reductive cleavage of tetramethyldiphosphine[21] with Na/K alloy in THF, using a modification of literature methods.[6,22] The crude product was distilled at 357–359 K (0.033 kPa).

$[Fe(pdmp)(CO)_2(Ac)(I)]$ (2). A Carius tube of approximate dimensions 20 × 260 mm was charged with *o*-phenylenebis(dimethylphosphine) (2.06 g, 10.4 mmol) and $Fe(CO)_5$ (1.48 mL, 2.16 g, 11.0 mmol). The contents were subjected to three freeze/thaw degassing cycles, sealed in vacuo, and heated in an oil bath set at 453 K for 7 h. The tube was cooled and cautiously opened (CO pressure!), and the resulting golden yellow solid crude $[Fe(pdmp)(CO)_3]$ (**1**) was extracted in benzene and filtered into a 125-mL Schlenk tube through a Celite pad. Benzene and volatiles were removed at oil pump vacuum. Excess freshly distilled methyl iodide (ca. 15 mL) was added, and the reaction vessel was tightly capped and stored in an ice bath protected from light for 48 h. Removal of volatiles at reduced pressure from the resulting deep red solution left a dark oil which slowly solidified. Chromatography on Grade IV alumina eluting initially with benzene followed by benzene/methylene chloride (50:50) moved a red band which was collected to give 2.91 g (6.1 mmol, 58%) of **2** as a mixture of isomers. The isomeric mixture obtained chromatographically was suitable for further reactions. Orange-red crystals of the major acyl isomer, identified as **2a**, were separated by repeated fractional crystallization from *n*-octane: mp 405 K dec; IR (CH_2Cl_2) ν_{CO} 2006, 1968, ν_{acyl} 1617 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) 53.4 ppm (s, pdmp); ^1H NMR ($CDCl_3$) δ 7.57 (m, 4 H, C_6H_4), 2.44 (s, 3 H, $C(O)CH_3$), 2.10 (t, 6 H, PCH_3), 2.04 (t, 6 H, PCH_3). Anal. Calcd for $C_{14}H_{19}FeIO_3P_2$: C, 35.03; H, 3.99. Found: C, 35.25; H, 3.61.

$[Fe(pdmp)(CO)_3(Me)]BF_4$ (3). A slurry of 1.00 g (2.29 mmol) of $[Fe(pdmp)(CO)_2(Ac)(I)]$ (**2**) and 0.445 g of $AgBF_4$ (2.29 mmol) in 50 mL of methylene chloride was stirred at reflux for 12 h. Filtration through Celite gave a straw-colored solution which deposited off-white crystals on concentration and addition of ether. Several recrystallizations from methylene chloride/ether gave **3** as colorless needles: yield 0.471 g (1.33 mmol, 58%); mp 454 K dec; IR (CH_2Cl_2) ν(CO) 2076, 2020 cm^{-1}; $^{13}C\{^1H\}$ ($CDCl_3$) δ 206.8 (q, $(J_{AX} + J_{AX'})$ = 6.6 Hz, CO (cis to Me)), 202.4 (t, J = 15.5 Hz, CO (trans to Me)), 138.6 ("t", $J_{AX} + J_{AX'}$ = 44 Hz, C_6H_4(ipso)), 134.1 ("s", C_6H_4(ortho)), 131.1 ("t", $J_{AX} + J_{AX'}$ = 9.5 Hz, C_6H_4(meta)), 20.9 (q, $J_{AX} + J_{AX'}$ = 32.5 Hz, PMe), 11.9 (q, $J_{AX} + J_{AX'}$ = 36.7 Hz, PMe), −8.6 (t, J = 15.5 Hz, FeMe); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 63.8 (s, pdmp); ^1H NMR (CD_2Cl_2) δ 7.90 (m, 4 H, C_6H_4), 1.97 (m, 12 H, PMe), −0.20 (t, J = 8.5 Hz, 3 H, FeMe). Anal. Calculated for $C_{14}H_{19}FeO_3P_2BF_4$: C, 38.23; H, 4.35. Found: C, 37.86; H, 4.35.

The PF_6^- salt, similarly prepared by using equimolar quantities of $TlPF_6$ and **2**, showed identical ^1H and ^{13}C NMR spectra. Its $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ revealed a septuplet at −144.1 ppm (J = 508 Hz) due to PF_6 in addition to pdmp singlet at 63.6 ppm.

$[Fe(pdmp)(CO)_2(Ac)(P(OMe)_3)]BF_4$ (4). Excess trimethyl phosphite (0.65 mL, 5.5 mmol) and a solution of **3** (0.50 g, 1.1 mmol) in 10 mL of methylene chloride were stirred at 273 K for 12 h. Removal of volatiles at 318 K (oil pump vacuum) left a gummy pale yellow solid. Repeated trituration with several fresh portions of dry ether follow by recrystallization from methylene chloride/ether gave **4** as an off-white microcrystalline solid: yield 453 mg (0.80 mmol, 73%); mp 326 K dec; IR (CH_2Cl_2) ν_{CO} 2027, 1992 cm^{-1}, ν_{acyl} 1650 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 151.9 (t, J = 55.1 Hz, 1 P, $P(OMe)_3$), 65.8 (d, J = 55.1 Hz, 2 P, pdmp); ^1H NMR (CD_2Cl_2) δ 7.84 (m, 4 H, C_6H_4), 3.81 (d, J = 10.6 Hz, 9 H, $P(OMe)_3$), 2.64 (s, 3 H, C(O)Me), 1.79 (m, 12 H, PMe). Anal. Calcd for $C_{17}H_{28}FeO_6P_3BF_4$: C, 36.20; H, 5.00. Found: C, 36.17; H, 5.17.

$[Fe(pdmp)(CO)_2(Me)(I)]$ (5). $[Fe(pdmp)(CO)_2(Ac)(I)]$ (**2**; 0.125 g, 0.26 mmol) was decarbonylated by heating at 403 K (0.0133 kPa) for 4 h. The crude product was purified by sublimation at 413 K (6×10^{-4} kPa) to give **5** as a dark red solid: yield 0.098 g (85%); mp 459 K dec; IR (CH_2Cl_2) ν_{CO} 2000, 1957 cm^{-1}; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 87.3 (d, J = 51.5 Hz (A part of AB spin system), pdmp) 58.4 (d, J = 51.5 Hz (B part of AB spin system), pdmp); ^1H NMR ($CDCl_3$) δ 7.64 (m, 4 H, C_6H_4), 1.96 (d, J = 8.8 Hz, 3 H, PMe), 1.92 (d, J = 10.3 Hz, 3 H, PMe), 1.66 (d, J = 9.4 Hz, 3 H, PMe), 1.58 (d, J = 10.3 Hz, 3 H, PMe), 0.12 (dd, J_{HP} = 6.3 Hz, $J_{HP'}$ = 11.1 Hz, FeMe). Anal. Calcd for $C_{13}H_{19}FeIO_2P_2$: C, 34.54; H, 4.24. Found: C, 34.48; H, 4.55.

$[Fe(pdmp)(CO)_2(Me)(P(OMe)_3)]^+BF_4$ (7a). A sample of $[Fe(pdmp)(CO)_2(Ac)(P(OMe)_3)]^+BF_4$ (**4**; 200 mg, 0.35 mmol) was decarbonylated by heating at 383 K (0.0133 KPa) for 12 h. The resulting brown gummy solid was triturated with several fresh portions of ether, taken up in methylene chloride, and filtered through a small column (5 × 30 mm) of Florisil. Concentration of the resulting pale yellow solution in a stream of nitrogen and addition of ether deposited pale yellow crystals of **7a**: yield 81 mg (43%); mp 334 K dec; IR (CH_2Cl_2) ν(CO) 2018, 1980 cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$) ABX system, δ 62.4 (A), 65.1 (B), 159.0 (X) (J_{AB} = 45.8 Hz, J_{AX} = +−91.1 Hz, J_{BX} = −+174.3 Hz); ^1H NMR (CD_2Cl_2) δ 7.89 (m, 4 H, C_6H_4), 3.91 (d, J = 10.9 Hz, 9 H, $P(OMe)_3$), 1.88 (m, 12 H, PMe), −0.44 (m, ($ABMX_3$), J_{AX} = 8.7, J_{BX} = 7.2, J_{MX} = 10.3 Hz, 3 H, FeMe). Anal. Calcd for $C_{16}H_{28}FeO_5P_2BF_4$: C, 35.86; H, 5.27. Found: C, 36.15; H, 5.34.

Reaction of Trimethyl Phosphite with $[Fe(pdmp)(CO)_2(Me)(I)]$ (5). To a $CDCl_3$ solution of **5** (2.4 mg of **5** in 0.35 mL of $CDCl_3$) held at 195 K in a 5-mm NMR tube was added 1.5 μL (ca. 2 equiv of $P(OMe)_3$). The contents were subjected to three freeze/thaw degassing cycles and then sealed under nitrogen. Reaction in the NMR probe at ambient temperature (304 K) resulted in a rapid loss of the FeMe ^1H NMR signal from **5**. The

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time course of the initial substitution and subsequent rearrangements was monitored at 500-s intervals; see text and Figure 3 for details.

Carbonylation of 5. A sample of **5** (3 mg) was dissolved in 0.35 mL of CD_2Cl_2, sealed under ca. 200 KPa pressure of carbon monoxide in a 5-mm o.d. NMR tube, and allowed to stand at 273 K for 48 h. ^1H NMR analysis showed 50% unreacted **5** and four isomeric acyls **2a–d** in a ratio of 1:4.2:0.4:0.5, respectively.

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Registry No. 1, 94203-64-2; **2**, 94203-65-3; **2a**, 94292-16-7; **2b**, 94292-17-8; **2c**, 94292-18-9; **2d**, 94292-19-0; **3**·BF_4, 94203-67-5; **3**·PF_6, 94203-68-6; **4**, 94203-70-0; **5**, 94203-71-1; **6**, 94203-72-2; **7a**·BF_4, 94203-74-4; **7a**·I, 94203-75-5; **7b**, 94292-21-4; $Fe(CO)_5$, 13463-40-6.

Correlation of Rate, Spectroscopic, and Structural Data for (Pyridine)- or (Triphenylphosphine)-bis(dimethylglyoximato)organocobalt Complexes

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The crystal and molecular structures of the complexes *trans-bis*(dimethylglyoximato)(R)(triphenylphosphine)cobalt(III) [R = CH_2CH_3 (**1**), 2-C_4H_9 (**2**), $CH_2C(CH_3)(CO_2C_2H_5)_2$ (**3**)] and *trans-bis*(dimethylglyoximato)($CH_2C(CH_3)(CO_2C_2H_5)_2$(pyridine)cobalt(III) (**4**) are reported. Crystal data for **1**: $P2_1/n$; $a = 10.346$ (1) Å, $b = 15.310$ (2) Å, $c = 18.516$ (3) Å, $\beta = 103.10$ (1)°; $Z = 4$; $R = 0.043$ for 4698 independent reflections. Crystal data for **2**: $P2_1/n$, $a = 11.157$ (5) Å, $b = 11.285$ (4) Å, $c = 24.356$ (9) Å, $\beta = 101.86$ (8)°; $Z = 4$, $R = 0.059$ for 2612 independent reflections. Crystal data for **3**: $P\bar{1}$, $a = 10.998$ (5) Å, $b = 10.564$ (5) Å, $c = 16.085$ (8) Å, $\alpha = 104.92$ (4)°, $\beta = 96.25$°, $\gamma = 94.74$ (5)°; $Z = 2$; $R = 0.033$ for 5084 independent reflections. Crystal data for **4**: $P2_1/n$, $a = 13.597$ (9) Å, $b = 22.47$ (1) Å, $c = 8.748$ (5) Å, $\beta = 93.98$ (5)°; $Z = 4$; $R = 0.035$ for 2237 independent reflections. The rate constants, k_1, of PPh_3 dissociation for **1–3** above and other structurally characterized compounds with R = CH_2CN, $CH(CH_3)CN$, CH_2CF_3, CH_2Br, CH_3, i-C_3H_7, and neo-C_5H_{11} were determined. Trends in ^{31}P and ^1H NMR spectra were examined for these and related acido (X = Cl, Br, I, NO_2) complexes. Good correlations were found between Co–P bond length, the sum of the CPC angles, log k_1, and ^1H NMR parameters. The ^{31}P NMR shifts were attenuated by opposing contributions from several different effects and did not correlate with other parameters. Distortions in the planarity of the bis(dimethylglyoximato)cobalt moiety appear to reflect both the bulk of the axial ligands and lattice effects. For **4**, the dihedral angle between the dioximato moieties (12.3°) is toward the pyridine and is the largest such angle in a pyridine complex of this type. No unusual distortions are observed in the alkyl group of **3** or **4**.

Introduction

A large body of structural, spectroscopic, dynamic, and thermodynamic data is now available for the class of organocobalt models of B_{12} coenzymes known as cobaloximes.[1-10] The four corrin ring equatorial N donors in B_{12} compounds are replaced by the four N atoms of a bis(dioximato) moiety in cobaloximes. Although several different dioximes have been employed,[1] the most thoroughly studied group of compounds is of the type $LCo(DH)_2X$, where L and X are neutral and mononegative monodentate axial ligands and DH is a monoanion of dimethylglyoxime.

X-ray structures of compounds of the type $LCo(DH)_2X$ are now more numerous than any other closely related group of organometallic compounds.[6,11-27] Since diverse

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