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Reduction Chemistry of $\mathrm{Fe_2(NO)_4(\mu\text{-}PR_2)_2}$ (R = Ph, Cy) and Protonation and Alkylation of Resultant Binuclear Iron Nitrosyl Anions

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Reduction of $\mathrm{Fe_2(NO)_4(\mu\text{-}PPh_2)_2}$ (**1**) with Na, Na/Hg, $\mathrm{LiAlH_4}$, or Red-Al proceeds with cleavage of the Fe–Fe bond to yield $\mathrm{[(NO)_2Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]^{2-}}$ (**2**). By contrast, reduction of **1** or $\mathrm{Fe_2(NO)_4(\mu\text{-}PCy_2)_2}$ with $\mathrm{MBEt_3{}^*H}$ (M = Li, Na, K; *H = H, D (with **1** only)) occurs by transfer of $\mathrm{{}^*H^-}$ to generate $\mathrm{[(NO)_2\overline{Fe(\mu\text{-}PR_2)(\mu\text{-}NO)Fe}(NO)(PPh_2{}^*H)]^-}$ (R = Ph (**3**), Cy). Deprotonation of **3** with *n*-BuLi at –78 °C yields $\mathrm{[(NO)_2\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe}(NO)(PPh_2)]^{2-}}$ (**4**), which isomerizes to **2** at –70 °C. Reaction of **1** with MeLi proceeds analogously to that with $\mathrm{MBEt_3H}$ and results in the formation of $\mathrm{[(NO)_2\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe}(NO)(PPh_2Me)]^-}$ (**5**-Me). The anions **2**–**5** react with $\mathrm{CF_3COOH}$ and alkyl (generally, Me, Et, $\mathrm{CH_2Ph}$, $\mathrm{CH_2CH{=}CH_2}$, $\mathrm{CH_2\overline{CHCH_2CH_2}}$, inter alia) iodides (and bromides and triflates, in some cases) at temperatures of –78 to +25 °C to yield binuclear and mononuclear products. Thus, **2** and **4** are protonated by 1 equiv of acid to **3** and alkylated by 1 equiv of alkylating reagent to **5**. The reaction of **2** with MeI or $\mathrm{MeOS(O)_2CF_3}$ was shown spectroscopically (^{31}P and ^{2}H NMR) at low temperatures to proceed by the intermediacy of a species formulated as $\mathrm{[(NO)_2(Me)Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]^-}$ (**6**), which at –15 °C converts to **5**-Me. The anions **3** and **5** undergo protonation and alkylation with fragmentation of the binuclear framework to give mononuclear complexes $\mathrm{Fe(NO)_2(PPh_2H)_2}$, $\mathrm{Fe(NO)_2(PPh_2H)(PPh_2R)}$, or $\mathrm{Fe(NO)_2(PPh_2R)(PPh_2R')}$ (same or different R and R′), depending on the reaction, and **1**. Probable mechanisms of the foregoing reactions are discussed and compared with those of the corresponding reactions of the binuclear iron carbonyl anions derived from $\mathrm{Fe_2(CO)_6(\mu\text{-}PR_2)_2}$ (R = Ph, Me). The relative propensities of the protonated or alkylated (R′) intermediates to undergo migratory insertion of CO or NO vs. reductive elimination of $\mathrm{Fe(PR_2H)}$ or $\mathrm{Fe(PR_2R')}$ play an important role in determining the course of these reactions of the binuclear anions.

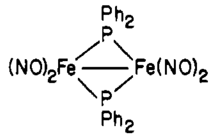
Introduction

Binuclear phosphido-bridged transition-metal complexes represent an important class of inorganic and organometallic compounds. During recent years, these compounds have been the subject of much research activity,[1] particularly with regard to synthesis and structure. In general, considerably less emphasis has been placed on the development of their reaction chemistry.

For the past few years, we have been examining the chemistry of binuclear complexes of the type $\mathrm{L_n\overline{M(\mu\text{-}PR_2)_2M}L_n}$, where L is usually CO or NO.[2] This investigation was initiated with two principal objectives. The first is to employ such compounds as starting materials in the synthesis of various new binuclear complexes, for example, metal hydrides, alkyls, acyls, and methylenes, as well as trinuclear and tetranuclear metal clusters. The second goal is to study mechanisms of reactions at two adjacent metal centers. Of special interest are those reactions that occur in a cooperative fashion.

Early results from this[3] and other[4] laboratories showed that μ-$\mathrm{PR_2}$ ligands in binuclear and polynuclear complexes are not as inert as had previously been believed.[5] In fact, M–(μ-$\mathrm{PR_2}$) bonds sometimes undergo scission under surprisingly mild conditions by coupling reactions of the $\mathrm{PR_2}$ bridge with ligands such as hydride,[3,6–10] alkyl,[9,11] carbene,[9,10] and alkyne,[12] inter alia. The foregoing are representative of those ligands that generally occur during catalysis by organometallic complexes, including clusters. It follows that the use of phosphido-bridged polynuclear compounds in such processes can lead to cluster fragmentation and, therefore, loss of catalytic activity. Thus, mechanistic studies of reactions that disrupt M–(μ-$\mathrm{PR_2}$) bonds are of considerable relevance not only to the chemistry of the compounds in question but also to catalysis in general.

We now report our investigations on the binuclear iron nitrosyl complex $\mathrm{Fe_2(NO)_4(\mu\text{-}PPh_2)_2}$ (**1**) and, to a much lesser extent, its μ-$\mathrm{PCy_2}$ analogue $\mathrm{Fe_2(NO)_4(\mu\text{-}PCy_2)_2}$. Complex **1** was first



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synthesized by Hayter,[13] and its structure was determined by Vahrenkamp.[14] It possesses a planar $\mathrm{Fe_2P_2}$ core with an Fe–Fe bonding distance of 2.70 Å and essentially tetrahedral geometry of the P and N donor atoms at each iron. This complex attracted our attention because of its isoelectronic similarity to the iron carbonyl compounds $\mathrm{Fe_2(CO)_6(\mu\text{-}PR_2)_2}$ (R = Ph, Me), which have been studied in our laboratory.[3,8,15] We were interested in as-

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certaining what effect, it any, the presence of CO and NO would have on the chemistry of the respective systems. Moreover, since metal nitrosyl anions are not common chemical species,[16] we were intrigued by the possibility of synthesizing binuclear iron nitrosyl anions and examining their behavior toward electrophilic reagents. Again, a comparison with the corresponding chemistry of analogous iron carbonyl anions derived from $Fe_2(CO)_6(\mu\text{-}PR_2)_2$ appeared particularly worthwhile.

In this paper are described studies on reduction of $Fe_2(NO)_4(\mu\text{-}PR_2)_2$ (R = Ph, Cy) and on protonation and alkylation of four types of binuclear iron nitrosyl anion derived by reduction of $Fe_2(NO)_4(\mu\text{-}PR_2)_2$. A small part of this investigation was communicated in a preliminary form.[7]

Experimental Section

General Procedures and Measurements. All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of purified N_2 using standard procedures.[17] Chromatographic separations and purifications were effected on columns packed with alumina (ca. 150 mesh, 6% H_2O). Melting points were measured in vacuo on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 337 or 383B spectrophotometer and were calibrated with polystyrene. ^1H NMR spectra were obtained on a Varian Associates EM 360L spectrometer. ^{31}P NMR spectra were recorded on a Bruker HX-90 spectrometer at 36.43 MHz in the Fourier transform mode. Chemical shifts are given with reference to 85% H_3PO_4 and are reproducible to ±0.1 ppm. ^2H NMR spectra were collected on a Bruker WM-300 spectrometer at 46.07 MHz and were standardized against the absolute frequency of the instrument. Mass spectra were obtained by use of the fast atom bombardment (FAB) technique on a Kratos MS-30 spectrometer by C. R. Weisenberger. Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN.

Materials. THF was distilled from Na and benzophenone under an atmosphere of N_2 immediately before use. Other solvents were purified according to procedures described by Perrin, Armarego, and Perrin.[18]

Trialkylborohydride reagents were obtained as 1.0 M solutions in THF from Aldrich. Sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al, 3.4 M solution in toluene), *n*-butyllithium (1.6 M solution in hexanes), and methyllithium (1.4 M solution in diethyl ether) were also purchased from Aldrich. Other reagents were obtained from various commercial sources and used as received. $\overline{CH_2CH_2CH}CH_2I$ was prepared from $\overline{CH_2CH_2CH}CH_2Cl$ and NaI in acetone.[19]

$Fe_2(NO)_4(\mu\text{-}PPh_2)_2$ (**1**) was synthesized in 85% yield as described by Rauchfuss.[20] A strictly analogous procedure was employed to obtain $Fe_2(NO)_4(\mu\text{-}PCy_2)_2$ in 89% yield as orange crystals, mp 304 °C. $^{31}P\{^1H\}$ NMR (THF): δ 329.7 (s). IR (THF): $\nu(N{\equiv}O)$ 1770 (s), 1750 (s) cm^{-1}. Mass spectrum, *m/e*: 626 (P^+).

Reduction of $Fe_2(NO)_4(\mu\text{-}PR_2)_2$ (R = Ph, Cy). To a stirred suspension of the title iron complex (generally, ca. 0.5 g) in THF (50 mL) at or below room temperature was added 1.0 or 2.0 molar equiv of the desired reducing agent in solution. The suspended material gradually dissolved to afford a dark brown solution within ca. 30 min. When solid reducing agents (e.g., Na, Na/Hg) were employed, a much longer reaction time, up to 12 h, was sometimes required. At the end of this time, the reaction solution was examined by ^{31}P NMR and IR spectroscopy.

The reduction product $Na_2[(NO)_2Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]$ ($(Na^+)_2$**2**) was isolated as follows. A mixture of **1** (0.50 g, 0.83 mmol) and Na powder (0.038 g, 1.66 mmol) in 50 mL of THF was stirred at room temperature for 10 h. The resulting solution was filtered under nitrogen, and the filtrate was evaporated to dryness to yield 0.42 g (78%) of a dark brown solid. Elemental analyses for C and H were high, suggesting the presence of THF in the product; this was confirmed by ^1H NMR spectroscopy.

Attempts at isolation of $[(NO)_2\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe}(NO)(PPh_2H)]^-$ (**3**) suitable for analysis have been unsuccessful. For example, a solution of Li^+**3** was generated by treatment of **1** (0.10 g, 0.17 mmol) in THF (2 mL) with 1.0 M $LiBEt_3H$ (0.17 mL of solution in THF, 0.17 mmol) at room temperature. A $^{31}P\{^1H\}$ NMR spectrum of this solution revealed only signals attributable to **3**. Filtration and removal of the solvent under reduced pressure afforded a very air-sensitive material that showed extraneous signals in its $^{31}P\{^1H\}$ NMR spectrum in THF solution. Likewise, addition of $(Ph_3P)_2NCl$ to a solution of Li^+**3** followed by workup furnished impure $(Ph_3P)_2N^+$**3**.

Reactions of Binuclear Anionic Complexes with CF_3COOH and Alkylating Reagents. (i) $Na_2[(NO)_2Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]$ ($(Na^+)_2$2). A weighed amount of the title complex was dissolved in 2.0 mL of THF in an NMR tube, and the resulting solution was cooled to −78 °C and treated with a measured amount of the desired electrophilic reagent. $^{31}P\{^1H\}$ NMR spectra of the reaction mixture were periodically recorded as the temperature gradually increased to ca. 25 °C. Generally, neutral complexes were separated and/or purified by chromatography (vide infra).

(ii) $Li[(NO)_2\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe}(NO)(PPh_2H)]$ (Li^+3). A solution of Li^+**3** generated in an NMR tube as described above was cooled to −78 °C in a dry ice–acetone bath. To this solution was then added the desired electrophilic reagent (1 molar equiv or excess), and $^{31}P\{^1H\}$ NMR spectra of the resulting solution were periodically recorded as the temperature gradually increased to ca. 25 °C. The mixture was evaporated to dryness, and the brown residue was chromatographed on a 10 × 1 cm column. Elution first with diethyl ether and then with CH_2Cl_2 afforded the mononuclear product(s) and **1**, respectively, which were identified by a combination of elemental analyses, IR and ^{31}P NMR spectroscopy, and mass spectrometry.

(iii) $Li_2[(NO)_2\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe}(NO)(PPh_2)]$ ($(Li^+)_2$4). A solution of Li^+**3** in THF, prepared as in (ii) and cooled to −78 °C, was treated first with 1.6 M *n*-BuLi in hexanes (0.10–0.11 mL of solution, 0.17 mmol) and then with a measured amount of the desired electrophilic reagent. $^{31}P\{^1H\}$ NMR spectra were recorded as the temperature of the mixture increased to ca. 25 °C. Neutral complexes were separated and/or purified by chromatography.

(iv) $Li[(NO)_2\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe}(NO)(PPh_2R)]$ (Li^+5; R = Me, Et, $(CH_2)_2CH{=}CH_2$). A solution of $(Li^+)_2$**4**, prepared as in (iii) at −78 °C, was treated with MeI (10 μL, 0.17 mmol), EtI (13 μL, 0.17 mmol), or $CH_2{=}CH(CH_2)_2Br$ (17 μL, 0.17 mmol). The resulting solution was allowed to warm to room temperature and was then cooled back to −78 °C. The desired electrophilic reagent (1 molar equiv or excess) was added, and $^{31}P\{^1H\}$ NMR spectra of the resulting solution were periodically recorded as the temperature slowly increased to ca. 25 °C. The mixture was evaporated to dryness, and the brown residue was chromatographed on a 10 × 1 cm column. Diethyl ether eluted the mononuclear product(s), and then CH_2Cl_2 eluted **1**. The products were identified by a combination of elemental analyses, IR and ^{31}P NMR spectroscopy, and mass spectrometry.

Results

Reduction of $Fe_2(NO)_4(\mu\text{-}PR_2)_2$ (R = Ph, Cy). Complex **1**, the principal starting material for the studies described in this paper, was prepared by the method of Rauchfuss[20] and characterized by comparison of its spectroscopic properties with those reported in the literature.[13] Its $^{31}P\{^1H\}$ NMR spectrum in THF solution exhibits a signal at δ 261.5, consistent with the presence of an Fe–Fe bond[21] as established by X-ray crystallography.[14] An analogue of **1**, $Fe_2(NO)_4(\mu\text{-}PCy_2)_2$, was synthesized by the appropriate adaptation of the foregoing procedure[20] and characterized spectroscopically (Experimental Section). Its solutions in THF show a single $^{31}P\{^1H\}$ NMR signal at δ 329.7 also to indicate the occurrence of metal–metal bonding.[21]

Four types of binuclear iron nitrosyl anion, **2**–**5**, have been obtained by various reduction processes starting with **1**. The preparation, characterization, and some properties of these anions are presented next. The various transformations involving binuclear iron nitrosyl species that were examined in this study are set out in Scheme I.

(i) $[(NO)_2Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]^{2-}$ (2). Treatment of **1** in THF with 2 molar equiv of Na dispersion or amalgam quantitatively (determined by ^{31}P NMR spectroscopy) affords a brown solution of the reduced species **2**. This dianion can also be obtained by reduction of **1** with $LiAlH_4$ or Red-Al (1–2 molar equiv) in THF. **2** was previously reported[22] to arise by electrochemical reduction

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Table I. $^{31}P\{^1H\}$ NMR and IR Spectroscopic Data for Binuclear Anionic Iron Nitrosyl Complexes in THF Solution^a

compd	$^{31}P\{^1H\}$ NMR,^{b} δ	IR, cm^{-1} ν(N≡O)	IR, cm^{-1} ν(N=O)
$(Li^+)_2$**2**	−34.6 (s)	1673 (vs, br)	
$(Na^+)_2$**2**	−32.9 (s)	1673 (vs, br)	
Li^+**3**	164.6 (d), 43.4 (d, J_{PP} = 20 Hz)^c	1704 (st), ~1670 (sh), 1660 (vs)	1420 (m)
Na^+**3**	161.4 (d), 44.0 (d, J_{PP} = 20 Hz)	1696 (st), ~1665 (sh), 1656 (vs)	1435 (m)
K^+**3**	161.5 (d), 43.3 (d, J_{PP} = 20 Hz)	1696 (st), ~1670 (sh), 1660 (vs)	1435 (m)
$(Li^+)_2$**4**	159.6 (d), 20.5 (d, J_{PP} = 50 Hz)^d		
Li^+**5**-Me	164.4 (d), 43.1 (d, J_{PP} = 15 Hz)	1710 (st), ~1660 (sh), 1650 (vs)	1430 (m)
Li^+**5**-Et	163.7 (d), 54.9 (d, J_{PP} = 14 Hz)	1708 (st), ~1670 (sh), 1660 (vs)	1435 (m)
Li^+**5**-CH_2Ph	158.8 (d), 60.8 (d, J_{PP} = 15 Hz)		
Li^+**5**-Cy	161.9 (d), 63.0 (d, J_{PP} = 12 Hz)		
Li^+**5**-$(CH_2)_2CH{=}CH_2$	163.1 (d), 52.2 (d, J_{PP} = 15 Hz)		
Li^+**5**-$CH_2\overline{CHCH_2CH_2}$	163.1 (d), 51.3 (d, J_{PP} = 15 Hz)		
Na^+**5**-$CH_2CH{=}CH_2$	159.5 (d), 49.8 (d, J_{PP} = 15 Hz)^e		

^{a}Abbreviations: st = strong, vs = very strong, m = medium, sh = shoulder, br = broad, s = singlet, d = doublet. ^{b}At 25 °C unless otherwise indicated. ^{c} $^1J_{PH}$ = 338 Hz. ^{d}At −78 °C. ^{e}At −58 °C.

of **1** in two successive one-electron steps, but its chemical and spectroscopic properties were not given. We find that **2** is rapidly and quantitatively reconverted to **1** upon contact with air in THF solution. Thus, reduction of **1** to **2** followed by oxidation back to **1** results in virtually complete recovery of **1**. **2** was isolated as a brown, air-sensitive solid by using Na^+ as the counterion.

Solutions of **2** in THF show one $^{31}P\{^1H\}$ NMR signal, the position of which varies somewhat with the counterion and temperature. Accordingly, for $(Li^+)_2$**2**, the resonance at δ −34.6 at 25 °C shifts to higher field with decreasing temperature and occurs at δ −42.2 at −73 °C. For $(Na^+)_2$**2**, the ^{31}P resonance is observed at δ −32.9 at 25 °C. These spectra remain unchanged when the proton decoupling is not applied. The observed chemical shifts are consistent with a structure in which equivalent PPh_2 ligands bridge across two Fe atoms with no metal–metal interaction.[21]

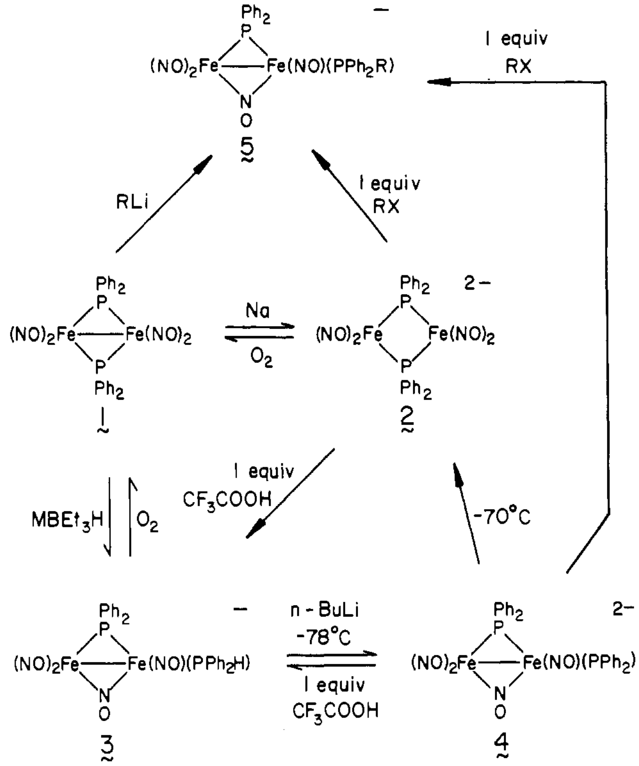
The IR spectrum of $(Li^+)_2$**2** in THF solution shows a strong, broad, and unsymmetrically shaped ν(N≡O) band at 1673 cm^{-1}. This frequency represents a shift of 82 cm^{-1} to lower values from the average position of the IR ν(N≡O) absorptions of **1** (1762, 1748 cm^{-1}) and is consistent with the dianionic nature of **2**. On the basis of its almost certain D_{2h} molecular symmetry, **2** is expected to show two IR-active ν(N≡O) modes. However, the separation of the bands is probably small (as for **1**), and it is likely that they overlap in polar THF.

(ii) $[(NO)_2\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe}(NO)(PPh_2H)]^-$ (3). Reaction between **1** and 1 or 2 equiv of $MBEt_3H$ (M = Li, Na, K) in THF at room temperature or ca. −23 °C (dry ice–CCl_4 bath) yields a brown solution of **3**. Surprisingly, use of $MB(sec\text{-}Bu)_3H$ (M = Li, K) in place of $MBEt_3H$ gave a dark brown solution that apparently contained a paramagnetic species, since no ^{31}P NMR signal could be detected in the range δ +200 to −100. This reaction was not studied further. Solutions of **3** generated by use of 1 equiv of $MBEt_3H$ are stable at ambient temperatures in the absence of air. However, when 2 equiv of $MBEt_3H$ were employed, a gradual conversion of **3** to **2** occurred on storage, with the rate of this conversion increasing as a function of M in the order M = Li < Na < K. In THF at reflux, the formation of **2** was complete within 2 min for all three $MBEt_3H$ reagents. This reaction apparently proceeds via deprotonation of **3** by a second equivalent of $MBEt_3H$; it will be considered later in the paper.

Solutions of **3** in THF rapidly react with oxygen to give **1**. Attempts at isolation of **3** as M^+**3** or $(Ph_3P)_2N^+$**3** invariably resulted at least in some decomposition of the anion.

The proposed structure of **3** has been deduced from spectroscopic data, which are given in Table I for this and other binuclear anionic complexes derived from **1**. The $^{31}P\{^1H\}$ NMR spectrum of Li^+**3**, unlike that of the analogous iron carbonyl complex $Li[(CO)_3\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe}(CO)_2(PPh_2H)]$,[3] is temperature-invariant in the range −75 to +25 °C. It shows two doublets (J_{PP} = 20 Hz) at δ 164.6 and 43.4, which are assigned to a bridging PPh_2 ligand supported by an Fe–Fe bond[21] and to a terminal PPh_2H ligand, respectively. Consistent with this assignment, the latter signal is further split into a doublet ($^1J_{PH}$ = 338 Hz) when the proton decoupling is not applied. The origin of the PH hydrogen in **3** was ascertained by carrying out the reduction of **1** with $LiBEt_3D$. The resulting solution of $[(NO)_2\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe}(NO)(PPh_2D)]^-$ (**3**-d_1) shows the higher field $^{31}P\{^1H\}$ NMR signal as a 1:1:1 triplet ($^1J_{PD}$ = 50 Hz) of doublets to reveal the presence of PPh_2D and demonstrate that the PH hydrogen comes from the reducing agent. The presence of deuterium in Li^+**3**-d_1 is corroborated by the ^2H NMR spectrum, which shows a doublet ($^1J_{PD}$ = 50 Hz) at δ 6.0. In the IR spectrum of Li^+**3**, both terminal ν(N≡O) bands at 1704, ca. 1670, and 1660 cm^{-1} and a bridging ν(N=O) band at 1420 cm^{-1} are observed. The latter shifts to 1435 cm^{-1} for Na^+**3** and K^+**3**, consistent with a less tight ion pair between **3** and Na^+ or K^+ than between **3** and Li^+.

Scheme I



The reaction between $Fe_2(NO)_4(\mu\text{-}PR_2)_2$ and $LiBEt_3H$ was investigated by low-temperature ^{31}P NMR spectroscopy with a view to observing intermediate species. Because of its higher

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Table II. $^{31}P\{^1H\}$ NMR Spectroscopic Data for Mononuclear Iron Nitrosyl Complexes in THF Solution[a,b]

compd	δ	$^2J_{PP}$, Hz	$^1J_{PH}$,[c] Hz
$Fe(NO)_2(PPh_2H)_2$	32.3 (s)[c]		210
$Fe(NO)_2(PPh_2H)(PPh_2Me)$	41.8 (d), 35.9 (d)[c]	21	168
$Fe(NO)_2(PPh_2Me)_2$	42.2 (s)		
$Fe(NO)_2(PPh_2Me)(PPh_2Et)$	55.5 (d), 41.6 (d)	22	
$Fe(NO)_2(PPh_2Et)_2$	55.0 (s)		
$Fe(NO)_2(PPh_2Et)(PPh_2CH_2Ph)$	56.8 (d), 54.6 (d)	25	
$Fe(NO)_2(PPh_2CH_2Ph)_2$	56.7 (s)		
$Fe(NO)_2(PPh_2H)(PPh_2(CH_2)_2CH{=}CH_2)$	52.5 (d), 35.6 (d)[c]	21	169
$Fe(NO)_2(PPh_2Me)(PPh_2(CH_2)_2CH{=}CH_2)$	55.3 (d), 42.7 (d)	22	
$Fe(NO)_2(PPh_2(CH_2)_2CH{=}CH_2)_2$	55.0 (s)		
$Fe(NO)_2(PPh_2Me)(PPh_2CH_2CHCH_2CH_2)$	51.7 (d), 41.4 (d)	22	
$Fe(NO)_2(PPh_2(CH_2)_2CH{=}CH_2)(PPh_2CH_2CHCH_2CH_2)$	54.8 (d), 52.0 (d)	19	
$Fe(NO)_2(PPh_2CH_2CHCH_2CH_2)_2$	51.8 (s)		

[a] Abbreviations: s = singlet, d = doublet. [b] At 25 °C. [c] $^1J_{PH}$ observed when the proton decoupling is not applied.

solubility in THF, $Fe_2(NO)_4(\mu\text{-}PCy_2)_2$ was used in place of **1** for this study. Raising the temperature gradually from −33 to +20 °C revealed no signals other than that of $Fe_2(NO)_4(\mu\text{-}PCy_2)_2$ at δ 329.7. At 20 °C, resonances appeared at δ 220.4 (d, J_{PP} = 2.4 Hz) and 48.4 (d, J_{PP} = 2.4 Hz; $^1J_{PH}$ = 296 Hz in the absence of proton decoupling), which indicate the formation of $[(NO)_2Fe(\mu\text{-}PCy_2)(\mu\text{-}NO)Fe(NO)(PCy_2H)]^-$. No other resonances were observed.

(iii) $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]^{2-}$ (4). Treatment of a THF solution of Li^+**3** with 1 equiv of *n*-BuLi at −78 °C results in the formation of a bright red solution containing the dianion **4**. This deprotonated product possesses very low thermal stability and at ca. −70 °C begins to irreversibly isomerize to **2**. The sequence deprotonation of **3** followed by rearrangement of **4** to **2** is no doubt responsible for the conversion of **3** to **2** by $MBEt_3H$ at or above room temperature (vide supra).

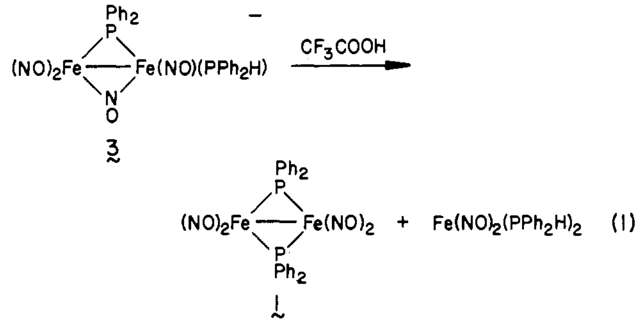
The structural assignment to **4** is based on the ^{31}P NMR spectrum, the chemical behavior to be considered later, and an analogy to the related binuclear anionic carbonyl species. The $^{31}P\{^1H\}$ NMR spectrum of $(Li^+)_2$**4** shows two doublet (J_{PP} = 50 Hz) signals at δ 159.6 and 20.5, the position of the former signal suggesting the presence of metal–metal bonding.[21] The latter signal remains essentially unchanged in the absence of proton decoupling to confirm that the PPh_2H group had been deprotonated. Although we have no direct evidence for the presence of a bridging NO group in **4**, we favor it over a single-bridge structure such as $[(NO)_2Fe(\mu\text{-}PPh_2)Fe(NO)_2(PPh_2)]^{2-}$. Our preference derives from similar constitutions of **4** and **3** or **5** (vide infra), the last two of which possess bridging NO, and from the presence of a CO bridge in each of $[(CO)_3Fe(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe(CO)_2(PPh_2H)]^-$ and the product of its deprotonation.[3,15]

(iv) $[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2R)]^-$ (5). When a red suspension of **1** and a slight excess of MeLi in THF is stirred at room temperature, a dark brown solution of **5**-Me results. The $^{31}P\{^1H\}$ NMR spectrum after ca. 30 min of reaction time shows doublet (J_{PP} = 14.6 Hz) signals at δ 165.4 and 42.9, which are very similar to those of **3**. However, the absence of P–H bonding is indicated by the unchanged nature of the resonance at δ 42.9 when the proton decoupling is not applied. The IR $\nu(N{\equiv}O)$ and $\nu(N{=}O)$ bands of **5**-Me (Table I) are also comparable with those of **3**, indicating a close similarity in structure of the two species.

A series of binuclear anions **5** containing various PPh_2R ligands, including PPh_2Me, was prepared by alkylation of **2** and **4**. These complexes will be considered later in the paper.

Protonation of Binuclear Anionic Complexes. (i) $Na_2[(NO)_2Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]$ ($(Na^+)_2$2) and $Li_2[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]$ ($(Li^+)_2$4). Treatment of $(Na^+)_2$**2** with 1 equiv of CF_3COOH in THF at −78 °C followed by a gradual warming of the reaction solution afforded the anion **3**. The formation of **3** commenced at ca. −25 °C and was essentially complete at 25 °C, as observed by ^{31}P NMR spectroscopy. Similarly, **3** formed quantitatively (determined by ^{31}P NMR spectroscopy) when $(Li^+)_2$**4** and 1 equiv of CF_3COOH were allowed to react at −78 °C. These reactions are included in Scheme I.

(ii) $Li[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2H)]$ (Li^+3) and $Li[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2R)]$ (Li^+5; R = Me, $(CH_2)_2CH{=}CH_2$). Protonation of **3** and **5** with 1 equiv of CF_3COOH in THF leads to fragmentation of these binuclear anions to mononuclear species. Accordingly, the reaction between Li^+**3** and CF_3COOH, observable by ^{31}P NMR spectroscopy at −25 °C, affords **1** and $Fe(NO)_2(PPh_2H)_2$ (eq 1). The two products were isolated in 80 and 6% yield (based on **1** from which Li^+**3** was prepared), respectively. The latter complex was principally characterized by ^{31}P NMR spectroscopy; these data together with corresponding data for the other mononuclear compounds $Fe(NO)_2(PPh_2R)_2$ and $Fe(NO)_2(PPh_2R)(PPh_2R')$ (R and R′ may be H) prepared in this study are presented in Table II. The IR spectra of these compounds show two $\nu(N{\equiv}O)$ bands in the region 1735–1660 cm⁻¹, consistent with literature reports.[23] The identity of some mononuclear compounds was further confirmed by ^1H NMR spectroscopy, mass spectrometry, and elemental analyses.



Reactions of Li^+**5**-Me and Li^+**5**-$(CH_2)_2CH{=}CH_2$ with CF_3COOH at −78 to +25 °C resulted in the formation of appropriate complexes $Fe(NO)_2(PPh_2H)(PPh_2R)$ and **1** (eq 2) as the major and minor (5–10% yield based on **1** from which Li^+**5** was prepared) products, respectively.

Alkylation of Binuclear Anionic Complexes. (i) $Na_2[(NO)_2Fe(\mu\text{-}PPh_2)_2Fe(NO)_2]$ ($(Na^+)_2$2) and $Li_2[(NO)_2Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe(NO)(PPh_2)]$ ($(Li^+)_2$4). Alkylation reactions of **2** and **4** with 1 equiv of alkyl halide or triflate afford, as already mentioned, the binuclear anions **5** (Scheme I). These reactions are therefore strictly analogous to the corresponding protonation reactions. They were conducted by mixing $(Na^+)_2$**2** or $(Li^+)_2$**4** and the alkylating reagent at −78 to −60 °C and then examining $^{31}P\{^1H\}$ NMR spectra of the reaction mixture during warming.

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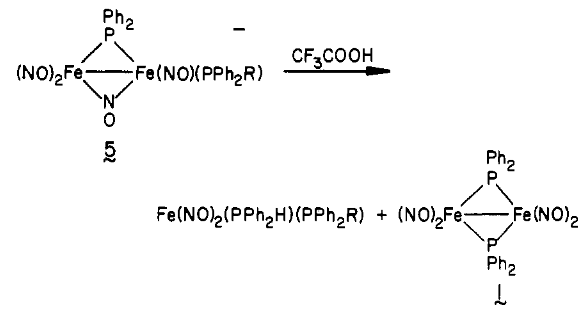
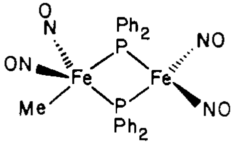
(23) (a) Morris, D. E.; Basolo, F. *J. Am. Chem. Soc.* **1968**, *90*, 2531. (b) Crow, J. P.; Cullen, W. R.; Herring, F. G.; Sams, J. R.; Tapping, R. L. *Inorg. Chem.* **1971**, *10*, 1616.



(2)

With **2**, the reactions generally occurred as the temperature increased to ca. 25 °C, whereas with **4**, they were found to reach completion at the temperature of mixing. The conversions appeared quantitative (determined by ^{31}P NMR spectroscopy) for each of MeI, EtI, $\mathrm{CH_2{=}CH(CH_2)_2Br}$, $\mathrm{PhCH_2I}$, and CyBr reacting with **4** and for $\mathrm{PhCH_2I}$ and $\mathrm{CH_2{=}CHCH_2I}$ reacting with **2**. However, small amounts of $\mathrm{Fe(NO)_2(PPh_2R)_2}$ were observed upon methylation and ethylation of **2**. The binuclear anions **5** were characterized in the same manner as **5**-Me (vide supra) by ^{31}P NMR and IR spectroscopy (Table I).

When the methylation of $\mathrm{(Na^+)_2}$**2** with MeI (and $\mathrm{CD_3I}$) was followed by low-temperature ^{31}P (and ^{2}H) NMR spectroscopy, an intermediate that is assigned structure **6** formed quantitatively upon mixing at −73 °C. This intermediate showed $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR signals as doublets (J_{PP} = 100 Hz) at δ −23.8 and −54.8 to suggest the absence of metal–metal bonding.[21] The spectrum remained unchanged in the absence of proton decoupling. The ^{2}H NMR spectrum of **6**-d_3 showed a $\mathrm{CD_3}$ signal at δ 3.1; this chemical shift is similar to that at δ 2.63 reported[24] for the Me protons of CpCo(NO)Me. The presence of inequivalent μ-$\mathrm{PPh_2}$ groups is rationalized on the basis of a trigonal-bipyramidal arrangement of ligands at one Fe center, with the P atoms being axial and equatorial. Upon warming to ca. −15 °C, **6** underwent conversion to **5**-Me and some $\mathrm{Fe(NO)_2(PPh_2Me)_2}$. Similar results were obtained when $\mathrm{(Na^+)_2}$**2** reacted with $\mathrm{MeOS(O)_2CF_3}$ starting at −60 °C.

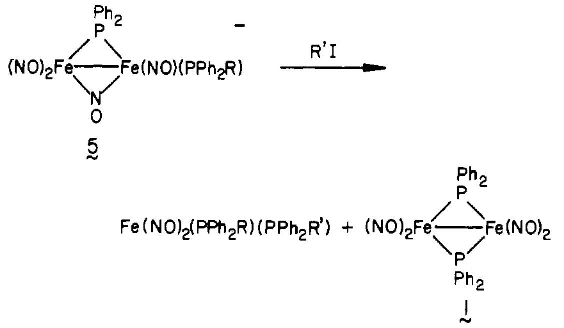


6

The corresponding reaction of $\mathrm{(Na^+)_2}$**2** with EtI afforded **5**-Et and some $\mathrm{Fe(NO)_2(PPh_2Et)_2}$, also at −15 °C; however, no intermediate analogous to **6** was detected. The iodides $\mathrm{PhCH_2I}$ and $\mathrm{CH_2{=}CHCH_2I}$ converted to **2** to **5**-$\mathrm{CH_2Ph}$ and **5**-$\mathrm{CH_2CH{=}CH_2}$, respectively, even at ca. −70 °C. Upon warming in THF solution to ca. −8 °C, **5**-$\mathrm{CH_2CH{=}CH_2}$ completely reacted to give a new species with doublet (J_{PP} = 22 Hz) $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR signals at δ 65.4 and 53.7. Attempts at isolation and characterization of this compound proved unsuccessful. The foregoing reaction temperatures indicate that the rates of the alkylation of **2** by organic iodides decrease in the order $\mathrm{CH_2Ph}$, $\mathrm{CH_2CH{=}CH_2}$ > Me > Et.

In an attempt to learn more about the mechanism of reaction of **2** with alkyl halides, we examined the behavior of $\mathrm{(Na^+)_2}$**2** toward $\mathrm{\overline{CH_2CH_2CH}CH_2I}$. The free radical derived by the abstraction of the iodine atom in $\mathrm{\overline{CH_2CH_2CH}CH_2I}$ rearranges to the 2-butenyl radical with a very large rate constant of 1.3×10^8 $\mathrm{s^{-1}}$ at 25 °C.[25] Thus, the ratio of products containing the $\mathrm{CH_2\overline{CHCH_2CH_2}}$ and $\mathrm{(CH_2)_2CH{=}CH_2}$ groups is a measure of the extent of radical participation in a given reaction.[26] The alkylation of **2** occurred at ca. −5 °C and resulted in the formation of both **5**-$\mathrm{CH_2\overline{CHCH_2CH_2}}$ and **5**-$\mathrm{(CH_2)_2CH{=}CH_2}$ in an approximate 1:1 ratio. This ratio was determined from the intensities of the appropriate signals in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ and ^{1}H NMR spectra of the reaction mixture, and the assignments were made by comparison with the spectra of authentic **5**-$\mathrm{(CH_2)_2CH{=}CH_2}$ and **5**-$\mathrm{CH_2\overline{CHCH_2CH_2}}$, prepared by reaction of $\mathrm{(Li^+)_2}$**4** with $\mathrm{CH_2{=}CH(CH_2)_2Br}$ and $\mathrm{\overline{CH_2CH_2CH}CH_2I}$, respectively. (Actually, the latter reaction gives a ca. 9:1 mixture of **5**-$\mathrm{CH_2\overline{CHCH_2CH_2}}$ and **5**-$\mathrm{(CH_2)_2CH{=}CH_2}$.) The result of this experiment indicates that there is a significant contribution of a free-radical mechanism to the alkylation of **2** by $\mathrm{\overline{CH_2CH_2CH}CH_2I}$. By way of contrast, alkylation of the related binuclear carbonyl anion $\mathrm{[(CO)_3Fe(\mu\text{-}PPh_2)_2Fe(CO)_3]^{2-}}$ [27] and of the $\mathrm{PPh_2}$ phosphorus in **4** each proceeds with almost complete preservation of the methylcyclopropyl group and therefore involves an ionic ($\mathrm{S_N2}$) mechanism. Furthermore, the facile methylation of $\mathrm{(Na^+)_2}$**2** by $\mathrm{MeOS(O)_2CF_3}$ to yield **5**-Me (vide supra) demonstrates that **2** undergoes alkylation by both radical and ionic paths, depending upon the alkylating reagent.

(ii) $\mathrm{Li[(NO)_2\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe}(NO)(PPh_2H)]}$ ($\mathrm{Li^+}$3) and $\mathrm{Li[(NO)_2\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}NO)Fe}(NO)(PPh_2R)]}$ ($\mathrm{Li^+}$5; R = Me, Et). Treatment of $\mathrm{(Na^+)_2}$**2** or $\mathrm{(Li^+)_2}$**4** with at least 2 equiv of organic iodide (R′I) or of $\mathrm{Li^+}$**5** with 1 or more equiv of R′I (generally 5–10 equiv used) results in the formation of the mononuclear complexes $\mathrm{Fe(NO)_2(PPh_2R)(PPh_2R')}$ (ca. 30% isolated yield based on **1** from which $\mathrm{(Na^+)_2}$**2**, $\mathrm{(Li^+)_2}$**4**, or $\mathrm{Li^+}$**5** was prepared) and, in some cases, small amounts of **1** (less than 10%) (eq 3). This reaction is therefore analogous to the previously described (vide supra) protonation of $\mathrm{Li^+}$**5**. When followed by ^{31}P NMR spectroscopy starting at −78 °C, reactions of $\mathrm{Li^+}$**5**-R (R = Me, Et) with MeI, EtI, $\mathrm{PhCH_2I}$, $\mathrm{\overline{CH_2CH_2CH}CH_2I}$ (R′I), and $\mathrm{(MeO)_2SO_2}$ were observed to commence at ca. 25 °C; upon workup, they afforded $\mathrm{Fe(NO)_2(PPh_2R)(PPh_2R')}$ (Table II) and **1**. Extensive decomposition to uncharacterized insoluble materials was noted in each case. Control experiments showed (^{31}P NMR spectroscopy) that the mixed-phosphine mononuclear complexes result neither from phosphine ligand scrambling (i.e., $\mathrm{Fe(NO)_2(PPh_2Me)_2 + Fe(NO)_2(PPh_2Et)_2 \nrightarrow 2Fe(NO)_2(PPh_2Me)(PPh_2Et)}$; THF, 25 °C, 24 h) nor from phosphine ligand alkylation (i.e., $\mathrm{Fe(NO)_2(PPh_2R)_2 + R'I \nrightarrow Fe(NO)_2(PPh_2R)(PPh_2R') + RI}$; R = Me, R′ = Et; R = Et, R′ = Me; THF, 25 °C, 24 h). Thus, the phosphine $\mathrm{PPh_2R'}$ in $\mathrm{Fe(NO)_2(PPh_2R)(PPh_2R')}$ arises from the alkylation of the μ-$\mathrm{PPh_2}$ ligand in **5** by R′I. The reaction of $\mathrm{Li^+}$**5**-Me with $\mathrm{\overline{CH_2CH_2CH}CH_2I}$ furnished a mixture containing mainly $\mathrm{Fe(NO)_2(PPh_2Me)(PPh_2CH_2\overline{CHCH_2CH_2})}$ and trace $\mathrm{Fe(NO)_2(PPh_2Me)(PPh_2(CH_2)_2CH{=}CH_2)}$ (identified by ^{1}H and ^{31}P NMR spectroscopy in reaction solution), in addition to **1**. This result indicates that the alkylation in question, unlike the corresponding reaction of **2**, is largely an ionic process.



(3)

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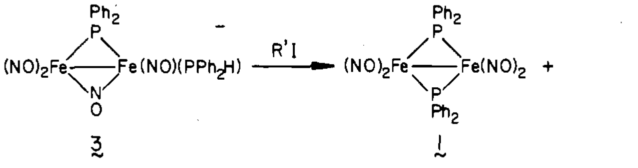
(26) See, for example: San Filippo, J., Jr.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.

(27) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146.

Alkylation reactions of Li^+3, like the corresponding protonation, lead to the formation of the mononuclear iron nitrosyl phosphine complexes (20–30% isolated yield based on **1** from which Li^+3 was prepared) and large amounts (ca. 50% yield) of **1** (eq 4).



$$Fe(NO)_2(PPh_2H)(PPh_2R') \text{ or } Fe(NO)_2(PPh_2R')_2 \qquad (4)$$

When 1 equiv of MeI was employed, the reaction was found by ^{31}P NMR spectroscopy to begin at ca. 25 °C, affording $Fe(NO)_2(PPh_2H)(PPh_2Me)$ as the mononuclear complex. By contrast, when an excess (generally, 4–10 equiv) of the alkylating reagent was used, the reaction with each of MeI, EtI, $PhCH_2I$ (R'I), and $MeOS(O)_2CF_3$ yielded the mononuclear complexes $Fe(NO)_2(PPh_2R')_2$. We do not completely understand how the latter products arise; it appears, however, that their formation is initiated by a radical process. Significantly, reaction of Li^+3 with an excess of $\overline{CH_2CH_2CH}CH_2I$ affords all three complexes $Fe(NO)_2(PPh_2CH_2\overline{CHCH_2CH_2})_2$, $Fe(NO)_2(PPh_2CH_2\overline{CHCH_2CH_2})(PPh_2(CH_2)_2CH{=}CH_2)$, and $Fe(NO)_2(PPh_2(CH_2)_2CH{=}CH_2)_2$ in the approximate 1:2:1 ratios (identified by ^1H and $^{31}P\{^1H\}$ NMR spectra of the unseparated mixture after chromatography). This result implies major involvement of free radicals in the reaction. No further studies were undertaken on this system.

Discussion

There are two modes of reduction of complex **1** that parallel those of the analogous binuclear iron carbonyl $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$.[3,27] The first occurs by electron transfer and leads to cleavage of the Fe–Fe bond with the formation of dianion **2**. It can be effected electrochemically[22] as well as chemically by use of Na, $LiAlH_4$, and Red-Al. The second mode of reduction affords monoanion **3** when the good hydride-donor reagents $MBEt_3H$ (M = Li, Na, K)[28] are employed. A structurally similar product, **5**, arises when **1** reacts with LiR in place of $MBEt_3H$. By contrast, reaction of $Fe_2(CO)_6(\mu\text{-}PPh_2)_2$ with LiR proceeds to a different type of product (a binuclear iron acyl[27]) than its reaction with $MBEt_3H$.

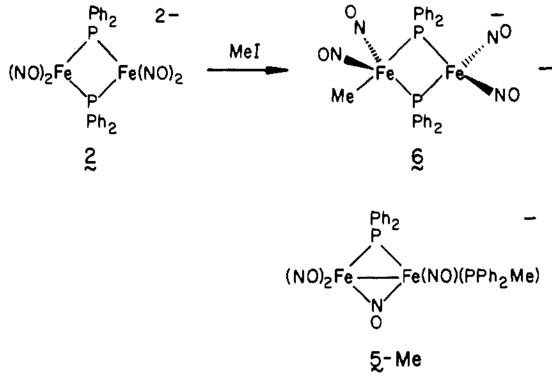
Reaction steps leading to the conversion of $Fe_2(CO)_6(\mu\text{-}PR_2)_2$ (R = Ph, Me) by $MBEt_3H$ to $[(CO_3\overline{Fe(\mu\text{-}PR_2)(\mu\text{-}CO)Fe}(CO)_2(PR_2H)]^-$ have recently been delineated.[8] A similar study here on $Fe_2(NO)_4(\mu\text{-}PR_2)_2$ (R = Ph, Cy) was thwarted by our inability to observe reaction intermediates. We believe, however, that the formation of **3** and **5** from **1** is initiated by attack of H^- ($MBEt_3H$) and R^- (LiR), respectively, at phosphorus, although attack at iron cannot be precluded. Nucleophilic attack at phosphorus has been proposed by Kyba[29] for the corresponding reactions of the linked bis(phosphido) complex $(CO)_3\overline{Fe(\mu,\mu'\text{-}(1\text{-}PPh\text{-}2\text{-}PPhC_6H_4))Fe}(CO)_3$. Addition of R^- (and, probably, H^-) to an NO group of **1**, in analogy with the addition of R^- (and H^-) to a CO group of $Fe_2(CO)_6(\mu\text{-}PR_2)_2$,[8,27] appears to be less probable. This is because the product containing an N(O)R ligand would be expected to exhibit some stability with respect to conversion to **5**.

The anion **3**, like $[(CO)_3\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe}(CO)_2(PPh_2H)]^-$,[15] can be deprotonated by use of *n*-BuLi at −78 °C. The resultant dianion, **4**, is considerably less stable than its carbonyl counterpart $[(CO)_3\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe}(CO)_2(PPh_2)]^{2-}$ and isomerizes to **2** at ca. −70 °C. The binuclear iron carbonyl dianion undergoes the corresponding rearrangement at −40 °C.[15]

Each of the four types of binuclear iron nitrosyl anion prepared in this study, viz. **2**–**5**, undergoes protonation and alkylation reactions. We now consider possible mechanisms of these reactions and compare them with the corresponding reactions of the analogous binuclear iron carbonyl anions.

The dianion **4** is rapidly and cleanly protonated and alkylated to **3** and **5**, respectively, at low temperatures. The latter reaction appears to be a straightforward nucleophilic displacement reaction at carbon by the terminal phosphido phosphorus.

The corresponding reactions of **2** likewise afford **3** and **5**. The methylation of **2** by MeI or $MeOS(O)_2CF_3$ has been observed to proceed via an intermediate that we formulate as a binuclear iron–alkyl complex, **6**. As the reaction temperature is raised, **6** converts to the final product **5**-Me (eq 5). This latter step most likely involves reductive elimination of Me and $Fe(\mu\text{-}PPh_2)$ as $Fe(PPh_2Me)$. Although the alkylation reactions with other organic halides and the protonation reaction with CF_3COOH of **2** have failed to produce spectroscopically detectable intermediates analogous to **6**, it is nevertheless probable that they proceed by parallel pathways. Such a general route has been experimentally delineated for the protonation of $[(CO)_3Fe(\mu\text{-}PR_2)_2Fe(CO)_3]^{2-}$ (R = Ph, Me) to $[(CO)_3\overline{Fe(\mu\text{-}PR_2)(\mu\text{-}CO)Fe}(CO)_2(PR_2H)]^-$ in which binuclear iron carbonyl hydrides, $[(CO)_3(H)Fe(\mu\text{-}PR_2)_2Fe(CO)_3]^-$, were detected as intermediates by NMR spectroscopy.[8] By contrast, the alkylation reactions of $[(CO)_3\overline{Fe(\mu\text{-}PR_2)_2Fe}(CO)_3]^{2-}$ with R'X proceed to $[(CO)_2(C(O)R')\overline{Fe(\mu\text{-}PR_2)_2Fe}(CO)_3]^-$, although similar spectroscopically observable intermediates, $[(CO)_3(R')Fe(\mu\text{-}PR_2)_2Fe(CO)_3]^-$, are involved when R = Me. Hence the intermediates $[(CO)_3(R')Fe(\mu\text{-}PR_2)_2Fe(CO)_3]^-$ react by *migration of R' onto ligated CO*, in contrast to the reaction of **6**, which proceeds by *the coupling of Me and Fe(μ-PPh₂) go give Fe(PPh₂Me)*.



(5)

The monoanions **3** and **5** are protonated and alkylated with extensive fragmentation of their binuclear framework. A possible pathway for these reactions involves protonation or alkylation at the $Fe(NO)_2$ iron followed by the reductive elimination of H or R' and $Fe(\mu\text{-}PPh_2)$ as $Fe(PPh_2H)$ or $Fe(PPh_2R')$, respectively. This sequence of steps would then afford one of the mononuclear complexes $Fe(NO)_2(PPh_2H)_2$, $Fe(NO)_2(PPh_2H)(PPh_2R')$, $Fe(NO)_2(PPh_2H)(PPh_2R)$, or $Fe(NO)_2(PPh_2R)(PPh_2R')$, depending on the reaction, and products of expected decomposition of "$Fe(NO)_2$". Such a behavior has generally been observed. Moreover, the frequently isolated very stable complex **1** appears to be the "thermodynamic sink" in many of these fragmentation reactions.

In this context, it is relevant that the protonation of $[(CO)_3\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe}(CO)_2(PPh_2H)]^-$ by CF_3COOH and the alkylation of $[(CO_3)\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe}(CO)_2(PPh_2R)]^-$ by RI (R = Me, Et, *n*-Pr, *i*-Pr) afford isolable compounds $(CO)_3(H)\overline{Fe(\mu\text{-}PPh_2)Fe}(CO)_3(PPh_2H)$[3] and $(CO)_3\overline{Fe(\mu\text{-}PPh_2)(\eta^2\text{-}(C,O)\text{-}\mu\text{-}C(R)O)Fe}(CO)_2(PPh_2R)$,[15] respectively. These binuclear neutral iron carbonyl products are thus considerably more

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(28) See, for example: Tam, W.; Marsi, M.; Gladysz, J. A. *Inorg. Chem.* **1983**, *22*, 1413 and references therein.

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stable than binuclear products of the corresponding reactions of the iron nitrosyl analogues **3** and **5**, which could not even be detected before undergoing fragmentation. Furthermore, the course of the alkylation reactions of $[(CO)_3Fe(\mu\text{-}PPh_2)(\mu\text{-}CO)Fe(CO)_2(PPh_2R)]^-$ contrasts sharply with that of the alkylation reactions of **3** and **5**, as already mentioned earlier for $[(CO)_3Fe(\mu\text{-}PR_2)_2Fe(CO)_3]^{2-}$ vis-à-vis **2**. The foregoing differences in behavior underscore a much greater propensity of metal–alkyl complexes to undergo migratory insertion of CO compared to that of NO.[24] Also, of the two binuclear iron systems studied in this laboratory, the nitrosyl complexes generally react more readily by the coupling of μ-PR_2 with H or R.

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Registry No. **1**, 14917-04-5; $(Na^+)_2$**2**, 89958-70-3; $(Li^+)_2$**2**, 104034-17-5; Li^+**3**, 89958-71-4; Na^+**3**, 104034-15-3; K^+**3**, 104034-16-4; $(Li^+)_2$**4**, 89958-72-5; Li^+**5**-Me, 104034-18-6; Li^+**5**-Et, 104051-37-8; Li^+**5**-CH_2Ph, 104034-19-7; Li^+**5**-Cy, 104051-38-9; Li^+**5**-$(CH_2)_2CH{=}CH_2$, 104051-39-0; Li^+**5**-$CH_2\overline{CHCH_2CH_2}$, 104034-20-0; Na^+**5**-$CH_2CH{=}CH_2$, 104034-21-1; **6**, 104034-33-5; $Fe(NO)_2(PPh_2H)_2$, 104034-22-2; $Fe(NO)_2(PPh_2H)(PPh_2Me)$, 104034-23-3; $Fe(NO)_2(PPh_2Me)_2$, 33724-83-3; $Fe(NO)_2(PPh_2Me)(PPh_2Et)$, 104034-24-4; $Fe(NO)_2(PPh_2Et)_2$, 85835-68-3; $Fe(NO)_2(PPh_2Et)(PPh_2CH_2Ph)$, 104034-25-5; $Fe(NO)_2(PPh_2CH_2Ph)_2$, 104034-26-6; $Fe(NO)_2(PPh_2H)(PPh_2(CH_2)_2CH{=}CH_2)$, 104034-27-7; $Fe(NO)_2(PPh_2Me)(PPh_2(CH_2)_2CH{=}CH_2)$, 104034-28-8; $Fe(NO)_2(PPh_2(CH_2)_2CH{=}CH_2)_2$, 104034-29-9; $Fe(NO)_2(PPh_2Me)(PPh_2CH_2\overline{CHCH_2CH_2})$, 104034-30-2; $Fe(NO)_2(PPh_2(CH_2)_2CH{=}CH_2)(PPh_2CH_2\overline{CHCH_2CH_2})$, 104034-31-3; $Fe(NO)_2(PPh_2CH_2\overline{CHCH_2CH_2})_2$, 104034-32-4; $[(NO)_2Fe(\mu\text{-}PCy_2)(\mu\text{-}NO)Fe(NO)(PCy_2H)]^-$, 104034-34-6; $Fe_2(NO)_4(\mu\text{-}PCy_2)_2$, 104034-14-2; $LiBEt_3H$, 22560-16-3; $LiAlH_4$, 16853-85-3; $NaBEt_3H$, 17979-81-6; $KBEt_3H$, 22560-21-0; LiB(*sec*-Bu)$_3$H, 63717-73-7; KB(*sec*-Bu)$_3$H, 67940-40-3; *n*-BuLi, 109-72-8; MeLi, 917-54-4; CF_3COOH, 76-05-1; EtI, 75-03-6; $CH_2{=}CH(CH_2)_2Br$, 5162-44-7; $PhCH_2I$, 620-05-3; CyBr, 108-85-0; $CH_2{=}CHCH_2I$, 556-56-9; $MeOS(O)_2CF_3$, 333-27-7; $CH_2CH_2CHCH_2I$, 33574-02-6; Ph_2P^-, 6396-02-7; Na, 7440-23-5; Fe, 7439-89-6; Red-Al, 22722-98-1.

Supplementary Material Available: A listing of analytical data (1 page). Ordering information is given on any current masthead page.

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Electron-Transfer Reactions between Pentaaquo(organo)chromium(2+) and Tris(bipyridyl)ruthenium(3+) Ions[1]

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The ruthenium complex $Ru(bpy)_3^{3+}$, generated by laser flash photolysis, reacts with a wide range of $(H_2O)_5CrR^{2+}$ complexes. The first step in the sequence is attributed to the one-electron oxidation of the organochromium cation. This step is accompanied by formation of $Ru(bpy)_3^{2+}$. The rate constants (*i*-Pr > Et >> Me) correlate with the ionization potentials of the free radicals $R^\bullet$. Values for para-substituted benzylchromium ions follow the Hammett correlation. The immediate product of electron transfer, CrR^{3+}, can undergo homolysis, as found for R = Et by kinetic tests and radical trapping, or in suitably constituted cases it can react by internal electron transfer, e.g., $CrCH_2OCH_3^{3+} + H_2O \rightarrow Cr^{2+} + CH_3OCH_2OH + H^+$.

Introduction

One important question for metal–alkyl complexes is the relation between the lability of a metal–carbon bond and the oxidation state of the metal.[2-4] A better understanding of this relation may assist in synthesis and in homogeneous catalysis, where alkylmetal complexes are often intermediates.[5] One way to labilize metal–carbon bonds is via oxidative homolysis: a one-electron oxidation yields an oxidized species that undergoes homolytic dissociation. This has been well studied for main-group-metal alkyls, e.g., the reaction of SnR_4 with the strong one-electron oxidants such as $IrCl_6^{2-}$ and iron(III) phenanthroline complexes:[6]

$$Sn(CH_3)_4 + Fe(phen)_3^{3+} \rightarrow Sn(CH_3)_4^+ + Fe(phen)_3^{2+} \quad (1)$$

$$Sn(CH_3)_4^+ \rightarrow Sn(CH_3)_3^+ + {}^\bullet CH_3 \quad (2)$$

One characteristic of these reactions is the rate increase in the series Me < Et < *sec*-Bu. This is consistent with rate-limiting electron transfer, rather than with electrophilic substitution, as found for dealkylations by Ag(I), Cu(I), and Cu(II).[2]

Analogous reactions are less well-known for transition-metal alkyls. Among the reactions that have been characterized are the oxidations of $R_2Co(chel)$[7] and RCo(chel)[4,8-10] complexes (where chel = a chelating or macrocyclic ligand system) by $IrCl_6^{2-}$ or iron(III) phenanthroline complexes. These reactions (eq 3) yield

$$RCo^{III}(chel) + IrCl_6^{2-} \rightarrow RCo^{IV}(chel)^+ + IrCl_6^{3-} \quad (3)$$

an oxidized organocobalt complex that can undergo either nucleophilic solvolysis (eq 4a) or homolysis (eq 4b).

When the alkyl cobaloxime complexes $RCo(dmgH)_2$ are oxidized by $IrCl_6^{2-}$, the reaction[8] follows the pathway described by

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