# New Chemistry Based on Reduction of Homobinuclear Bis($\mu$-phosphido) Metal Complexes

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## Abstract

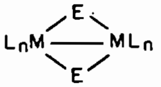
Studies are reported on the chemical reduction of the homobinuclear bis($\mu$-phosphido) metal complexes $(CO)_3\overline{Fe(\mu\text{-}PR_2)_2Fe}(CO)_3$ (R = Ph or Me), $(NO)_2\overline{Fe(\mu\text{-}PPh_2)_2Fe}(NO)_2$ and $(CO)_4\overline{M(\mu\text{-}PPh_2)_2M}(CO)_4$ (M = Mo or W). Two reduction pathways have been observed which result in different two-electron transformations: (1) with Na or $LiAlH_4$, electron transfer to yield the corresponding symmetric dianions of the type $L_nM(\mu\text{-}PR_2)_2ML_n^{2-}$ without metal–metal bond and (2) with $M'BR'_3H$ (M′ = Li, Na, or K; R′ = Et or sec-Bu), hydride transfer to give monoanionic complexes of the type $L_n\overline{M(\mu\text{-}PR_2)(\mu\text{-}L)M}L_{n-1}(PR_2H)^-$ or $L_n\overline{M(\mu\text{-}PR_2)M}L_n(PR_2H)^-$ (M = Fe, Mo, or W; L = CO or NO; R = Ph or Me). The monoanionic complexes can be deprotonated with n-BuLi at −78 °C to the corresponding unsymmetric dianions $L_n\overline{M(\mu\text{-}PR_2)(\mu\text{-}L)M}L_{n-1}(PR_2)^{2-}$ (M = Fe; L = CO or NO; R = Ph) or symmetric dianions $L_nM(\mu\text{-}PR_2)_2ML_n^{2-}$ (M = Mo or W; L = CO; R = Ph). The unsymmetric dianions isomerize on slight warming to the symmetric dianions, which undergo protonation by $CF_3COOH$ to yield the aforementioned monoanions. Reactions of several members of these three classes of binuclear anions with $CF_3COOH$, alkylating reagents, 1,1-diiodohydrocarbons and metal diiodo complexes have resulted in the synthesis of new binuclear and trinuclear compounds. Examples include $(CO)_3(H)\overline{Fe(\mu\text{-}PPh_2)Fe}(CO)_3(PPh_2H)$, $(CO)_3\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}C(R)O)Fe}(CO)_2(PPh_2R)$ (R = Me, Et, n-Pr, or i-Pr), $(CO)_4\overline{M(\mu\text{-}PPh_2)_2M}(CO)_3(C(R)OMe)$ (M = Mo or W; R = Me or Ph), $(CO)_2(\eta^3\text{-}C_3H_5)\overline{Fe(\mu\text{-}PPh_2)Fe}(CO)_3(PPh_2C_3H_5)$, $(NO)_2\overline{Fe(\mu\text{-}PPh_2)(\mu\text{-}CH_2PPh_2)Fe}(NO)_2$, $(NO)_2\overline{Fe(\mu\text{-}CH_2)(\mu\text{-}Ph_2PPPh_2)Fe}(NO)_2$, and $Fe_2Co(\eta^5\text{-}C_5H_5)(CO)(NO)_4(\mu\text{-}PPh_2)_2$. Synthetic and mechanistic studies on these reactions are presented.

## Introduction

Binuclear transition metal complexes with metal–metal bonds, especially metal carbonyls, serve as useful starting materials for the synthesis of a variety of organometallic compounds. The metal–metal bond in such complexes can be cleaved reductively [1], oxidatively [2], or homolytically [3] and the resultant species provide valuable reagents for organometallic synthesis. An excellent example is furnished by the chemistry of the metal–metal bonded $Mn_2(CO)_{10}$. This complex can be reduced (*e.g.*, with Na) to $Mn(CO)_5^-$ [4], oxidized with halogens ($X_2$) to $Mn(CO)_5X$ [5] and cleaved symmetrically under photochemical conditions to $Mn(CO)_5\cdot$ [6]. The former two species have been used extensively and with considerable success in preparative organometallic chemistry [1, 7].

$$(CO)_5Mn{-}Mn(CO)_5 \begin{cases} \xrightarrow{2\,Na} 2\,Na[Mn(CO)_5] \\ \xrightarrow{X_2} 2\,Mn(CO)_5X \\ \xrightarrow{h\nu} 2\,Mn(CO)_5\cdot \end{cases}$$

We can envisage a novel and a potentially useful extension of this chemistry if the starting binuclear complex contains strong bridging ligands in conjunction with a metal–metal bond. Examples of such binuclear complexes are provided by compounds I where E is Sr, $PR_2$ or $AsR_2$, and L is CO, NO or $\eta^5\text{-}C_5H_5$ [8]. Reduction, oxidation or metal–metal bond homolysis of I are



I

expected (and known in a number of cases [9]) to afford the chemical species analogous to those obtained from $Mn_2(CO)_{10}$, except for their binuclear nature. These species would then be employed, similarly to their manganese counterparts, in the synthesis of a variety of new binuclear complexes such as metal hydrides, alkyls, allyls, acyls and methylenes, as well as trinuclear and tetranuclear metal clusters. Binuclear metal complexes are the subject of intense current research activity [10]; they find important and extensive use in studies related to catalysis by adjacent metal sites [11] and in the designed synthesis of metal clusters [12].

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When we commenced our studies in this area approximately three years ago, we decided to focus on homobinuclear complexes I with phosphido bridging ligands ($E = PR_2$). At that time, it was generally thought that such ligands were chemically inert and that they strongly held together the binuclear framework of the complex [13]. In addition, $PR_2$-containing complexes can be conveniently studied by $^{31}P$ NMR spectroscopy [14]. Terminal ligands L in the complexes selected for our investigation have been either carbonyls or nitrosyls.

The synthesis of complexes I with the aforementioned combination of ligands E and L was first investigated by Chatt [15] and by Hayter [9c, 16]. However, apart from preparative studies, little chemistry has been done on these systems. Oxidation with halogens has been reported for some complexes I ($E = PR_2$) to give $XL_nM(\mu\text{-}PR_2)_2ML_nX$ [9c, d]. Electrochemical reduction of I ($E = PR_2$) was found by Dessy [9a] to proceed to the dianions $L_nM(\mu\text{-}PR_2)_2ML_n^{2-}$ without metal–metal bond.

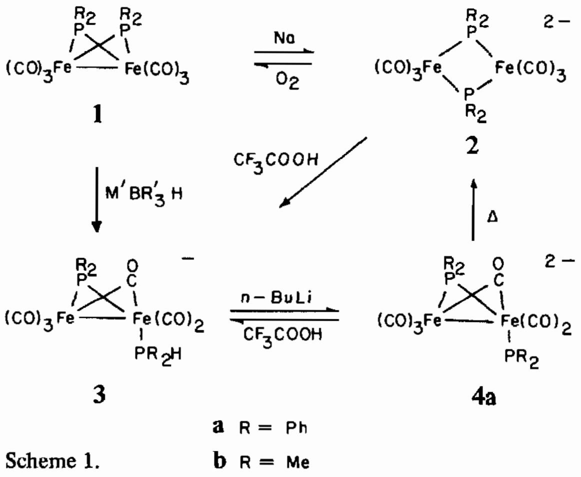
Presented in this paper are developments in our research involving reduction of several phosphido-bridged complexes I and the chemistry of reduced binuclear species. The paper focuses on studies in our laboratory and mentions excellent work in metal–phosphido chemistry conducted elsewhere [17] only to the extent that it bears on our results and conclusions.

## Complexes $(CO)_3\overline{Fe(\mu\text{-}PR_2)_2Fe}(CO)_3$ (R = Ph or Me)

The title complexes were first prepared by Thompson (R = Ph, **1a**) [18] and by Hayter (R = Me, **1b**) [16] and their structures were determined by X-ray crystallography [19]. The $Fe_2P_2$ core of each molecule is symmetrically folded about the Fe–Fe bond, which measures 2.62 and 2.66 Å, respectively.

Before the start of our studies, Dessy reported [9a, 20] that **1b** undergoes a two-electron electrochemical reduction to **2b**, which was assigned a structure with a planar $Fe_2P_2$ core from spectroscopic evidence. More recently, Collman *et al.* [21] reduced **1a** to **2a** by electrochemical techniques and by using Na dispersion in THF, and the isolated $[Na(2,2,2\text{-crypt})]_2^+$**2a** was examined by X-ray crystallography to reveal a planar $Fe_2P_2$ core without metal–metal bond [22]. We found [23] that **2** are also obtained by reduction of **1** with $LiAlH_4$. The anions **2** are very sensitive to oxidation and on exposure to air rapidly and quantitatively regenerate the parent complexes **1**.

In contrast to the foregoing reduction, treatment of **1** with 1 or 2 equiv. of $M'BR'_3H$ ($M'$ = Li, Na, or K; $R'$ = Et or sec-Bu) results in the cleavage of one of the Fe–P bonds and the formation of the new monoanions **3**, which were characterized spectroscopically [23]. Use of $LiBEt_3{}^2H$ in conjunction with **1a** yields **3a** containing $PPh_2{}^2H$ to demonstrate that the source of the phosphine hydrogen is the reducing agent. These air-sensitive species are stable in solution under $N_2$ at ambient temperatures. The monoanion **3a** has been deprotonated with n-BuLi at −78 °C to afford the corresponding dianion **4a** [24]. On warming to *ca.* −40 °C in THF solution, **4a** rearranges irreversibly to **2a**. The anions **2** also result when complexes **1** are treated with 2 equiv. of $M'BR'_3H$ above room temperature*, or with 3 equiv. of $M'BR'_3H$ at *ca.* 25 °C [23]. These transformations undoubtedly proceed via the intermediacy of **4** and are accompanied by evolution of $H_2$. Notwithstanding its low thermal stability, **4a** has proved to be a very useful reagent for the synthesis of a number of new diiron complexes owing to its unusually high reactivity even at −78 °C. These reactions will be given later in the present section. The transformations described so far are set out in Scheme 1.



Scheme 1.

The mechanism of conversion of **1** to **3** by the action of $M'BEt_3H$ in THF was investigated by variable temperature $^2H$ and $^{31}P$ NMR spectroscopy [26]. Reaction between **1** and $M'BEt_3H$ does not commence until temperatures of *ca.* 0 °C have been reached, and at these temperatures affords no detectable intermediates. However, if the reaction is allowed to start at *ca.* 0 °C and then the mixture is rapidly cooled to −78 °C, intermediate species can be observed and their chemistry followed by $^{31}P$ NMR spectroscopy. By employing this procedure, we were able to detect metal formyl complexes, formulated as **5** in part on the basis of their $^{31}P$ NMR spectroscopic similarities to the corresponding acetyl compounds **8**, which arise by reaction of **1**

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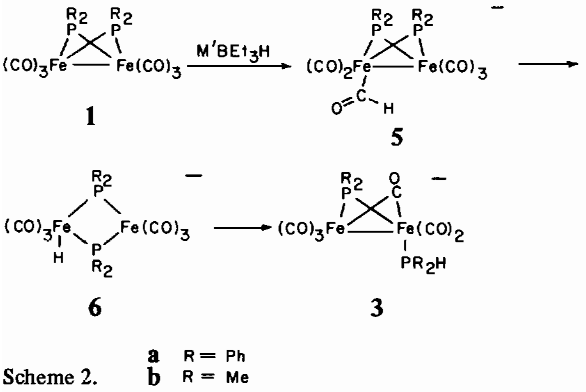
*It has been reported [25] that a second equivalent of $M'BR'_3H$ reacts with released $BR'_3$ at ambient temperatures to give $M'[R'_3BHBR'_3]$, which should be a much poorer hydride donor.

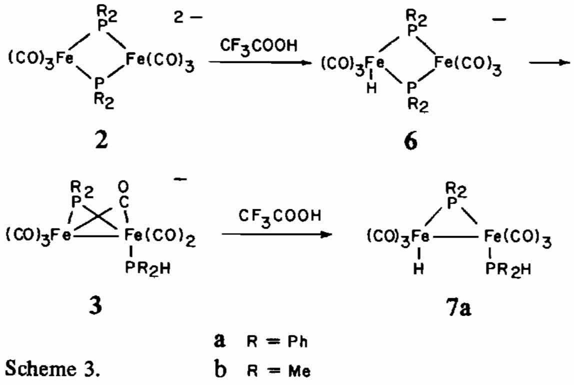
with LiMe (*vide infra*). The formation of formyl complexes by reaction of metal carbonyls with $LiBEt_3H$ or $KB(O\text{-}i\text{-}Pr)_3H$ has been investigated by Gladysz [27] and by Casey [28]; moreover, Geoffroy recently reported [29] the synthesis of stable complexes $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_2(COH)L]$ ($L = PMe_3$ and $PPh_2Me$) from the appropriate binuclear bis(μ-phosphido) species and $LiBEt_3H$. The formyls **5** rearrange on warming to *ca.* −20 °C by hydride shift from C(O)H to the metal with cleavage of the Fe–Fe bond to yield **6**, which at −10 to 0 °C undergo reductive elimination of $\mu$-$PR_2$ and H as Fe-bound $PR_2H$ to give **3**. Decomposition of metal formyl complexes to metal hydrides represents a known reaction in organometallic chemistry [30]. The observed sequence of steps leading to the conversion of **1** to **3** is given in Scheme 2. It is worthy of note that this multistep pathway contrasts with the behavior of a related, linked bis(μ-phosphido) complex, $(CO)_3Fe(\mu,\mu'\text{-}(1\text{-}PPh\text{-}2\text{-}PPhC_6H_4))Fe(CO)_3$, toward $LiBEt_3H$. There, evidence suggests direct attack of $H^-$ at $\mu$-$PPhC_6H_4$ to yield $Li[(CO)_3Fe(1\text{-}\mu\text{-}PPh\text{-}2\text{-}PPhHC_6H_4)(\mu\text{-}CO)Fe(CO)_2]$ [31].



Scheme 2.

Protonation of **2** with 1 equiv. of $CF_3COOH$ readily proceeds at room temperature to the respective monoanions **3** [26] (see Scheme 1). Monitoring this reaction by variable temperature $^2H$ and $^{31}P$ NMR spectroscopy revealed that **2** have already been converted to the iron hydrido complexes **6** at *ca.* −35 °C. These metal hydrides then rearrange to **3** at −10 to 0 °C, as in the reaction of **1** with $M'BEt_3H$ (*vide supra*). Treatment of **3a** with 1 equiv. of $CF_3COOH$, or of **4a** with 2 equiv. of $CF_3COOH$, affords the iron hydride **7a**, which has been isolated [23]. Scheme 3 depicts these successive transformations.

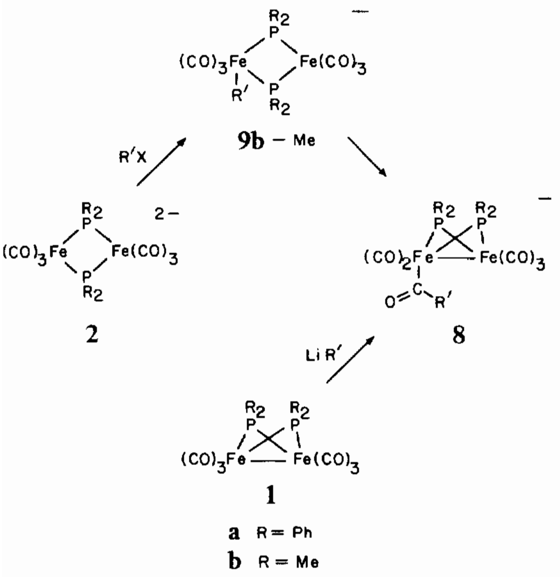
The dianions **2** are readily alkylated to the iron acyl monoanions **8** [21, 34]. The acetyl and benzoyl complexes $[(Ph_3P)_2N]^+$**8a**-Me and $[Li(THF)_3]^+$**8a**-Ph, respectively, were examined by X-ray crystallography; the structures of the anions are similar to that of **1a**, with a negatively charged acyl ligand replacing a CO group cis to the Fe–Fe bond [32]. The alkylation reactions of **2a** proceed much more rapidly with alkyl iodides than with bromides, and bromides react faster than chlorides. Alkylation with $CH_2CH_2CHCH_2I$ affords an essentially quantitative yield of the acyl complex **8a** in which the cyclopropylmethyl group has not rearranged, thus arguing against a radical mechanism [33].



Scheme 3.

A variable temperature $^2H$ and $^{31}P$ NMR study [26] of the alkylation reactions of **2** with MeI showed that even at −60 °C **2a** was already converted to **8a**-Me. In contrast, reaction between **2b** and MeI at −70 °C affords an intermediate species which is assigned a metal–alkyl structure, **9b**-Me. On warming to *ca.* −35 °C, this alkyl starts to rearrange to the final isolable product containing the iron acetyl anion **8b**-Me. It is likely that this transformation occurs by migration of the Me group to CO accompanied by the formation of an Fe–Fe bond [21]. The anions **8**-Me can also be obtained by reaction of **1** with LiMe at ambient temperatures [21, 34]. These reactions are presented in Scheme 4.

As noted earlier in this section, dianion **4a** is a highly reactive species. Its reactions with alkyl and allyl iodides (R'I) occur rapidly at −78 °C to afford P-alkylated monoanions, **10a**, which are stable in THF solution under $N_2$ at ambient temperatures in the absence of excess R'I [24]. With an excess of alkyl iodide, **10a** undergo further alkylation on warming from −78 °C to room temperature to yield the acyl-bridged complexes **11a**. The structure of **11a**-Me, Me was elucidated by X-ray crystallography [23]; the molecule possesses a folded $Fe_2P$(acetyl CO) core, and the Fe–Fe bond distance is 2.66 Å. Its formation from **10a**-Me and MeI was found [24] by variable temperature $^{31}P$ and $^{13}C$ NMR spectroscopy to proceed via two detectable intermediates. Although available data do not allow complete characterization of these species, they appear to be Fe–Me and Fe–C(O)Me complexes. This suggests that the reaction proceeds by methylation at the $Fe(CO)_3$ iron followed by migratory insertion of CO into the Fe–Me bond and closure of the acetyl bridge.



R′ = Me, Et, i-Pr, $CH_2CMe_3$, $CH_2Ph$, $CH_2CH=CH_2$, $(CH_2)_4CH=CH_2$, or $\overline{CH_2CHCH_2CH_2}$ ; X = I, Br, or Cl

Scheme 4.

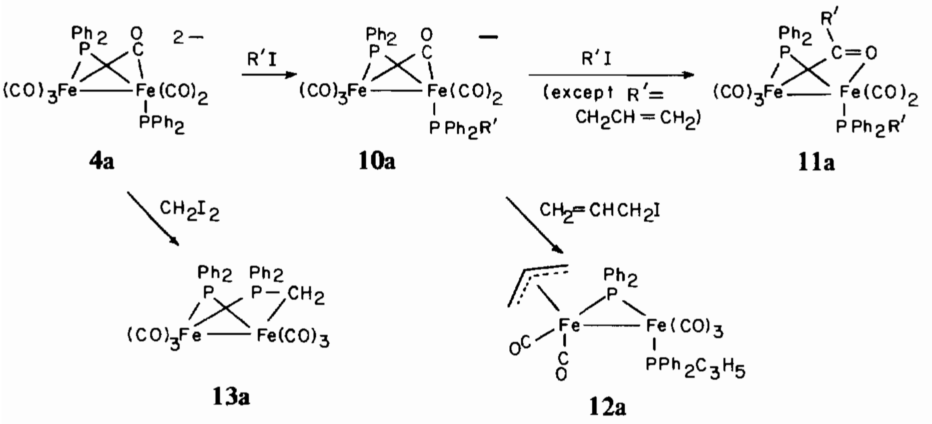
The anion **10a**-$CH_2CH=CH_2$ reacts with allyl iodide on warming from −78 °C to 25 °C to yield the $\eta^3$-allyl complex **12a**-$CH_2CH=CH_2$. The structure of this complex, established by X-ray diffraction [24], shows a single $PPh_2$ bridge and a relatively long Fe–Fe bond of 2.80 Å. Since allylation almost certainly occurs at iron, rearrangement of $\eta^1$-allyl to $\eta^3$-allyl with loss of a CO ligand represents a more facile process than migratory insertion of CO into the Fe–$CH_2CH=CH_2$ bond for this binuclear system.

The aforementioned reactions illustrate the propensity of **4a** to react with electrophilic reagents at the terminal phosphido phosphorus and at the $Fe(CO)_3$ iron. Another example of such behavior is provided by the reaction of **4a** with $CH_2I_2$, which at *ca.* −78 °C affords the $CH_2PPh_2$-bridged complex **13a**, the structure of which was inferred from spectroscopic data [24]. Studies are underway to extend this reaction to the synthesis of trimetallic clusters by using $ML_nI_2$ in place of $CH_2I_2$. Scheme 5 summarizes reactions of **4a** with iodohydrocarbons.

## Complex $(NO)_2\overline{Fe(\mu\text{-}PPh_2)_2Fe}(NO)_2$

This complex (**14**), which is isoelectronic with **1a**, was originally prepared by Hayter [16] and its structure was determined by Vahrenkamp [34]. Unlike **1a**, **14** contains a planar $Fe_2P_2$ core, the metal–metal bond distance being 2.70 Å. Apart from an electrochemical study [9a], which revealed two successive one-electron reduction steps in the conversion of **14** to the symmetrical dianion **15**, the chemistry of **14** had not been explored prior to the start of this investigation.

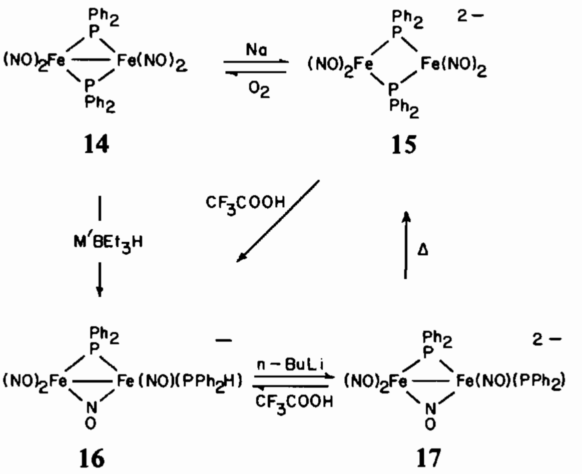
Our initial studies [35] on reduction of **14** showed that this complex undergoes conversion to **15** also by the action of Na dispersion or $LiAlH_4$ in THF. The anion **15**, which was characterized spectroscopically, rapidly reverts to **14** on contact with air. In contrast to the aforementioned reduction and similarly to the behavior of **1**, **14** reacts with 1 or 2 equiv. of $M'BEt_3H$ (M′ = Li, Na, or K) at ambient temperatures to yield the monoanion **16**, which was characterized in solution by IR, $^1H$ and $^{31}P$ NMR spectroscopy. Use of $LiBEt_3{}^2H$ affords the corresponding species containing $PPh_2{}^2H$. However, at higher temperatures, reaction between **14** and 2 equiv. of $M'BEt_3H$ gives the dianion **15** via deprotonation of **16** with a second equivalent of $M'BEt_3H$. Limited solubility of **14** in THF has so far precluded a variable temperature mechanistic study of the formation of **16** with a



R′ = Me, Et, n-Pr, i-Pr, or $CH_2CH=CH_2$

Scheme 5.

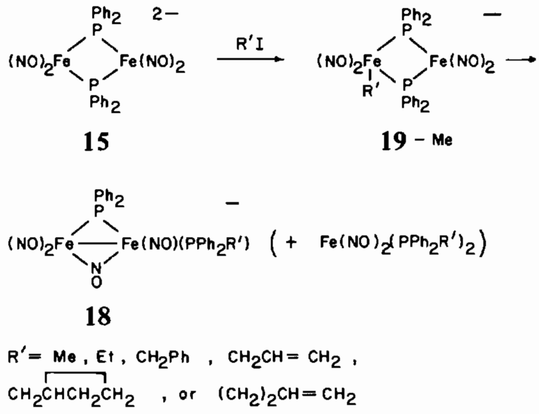
view to establishing whether $H^-$ first interacts with a nitrosyl ligand or attacks $\mu$-$PPh_2$ directly. The anion **16**, like its **3a** analogue, can be deprotonated with n-BuLi at −78 °C; however, the resulting species of proposed structure **17** is appreciably less stable thermally than **4a**. At *ca.* −70 °C, it begins to isomerize to the symmetric dianion **15**. Protonation of **17** with 1 equiv. of $CF_3COOH$ at −78 °C regenerates **16** [36]. These reactions are set out in Scheme 6.



Scheme 6.

The anion **15** is converted to **16** by treatment with 1 equiv. of $CF_3COOH$ [36] (see Scheme 6). This reaction occurs at *ca.* −25 °C and, unlike the corresponding transformation of **2** to **3**, does not produce an observable iron hydrido intermediate in the variable temperature $^{31}P$ NMR spectra. Further protonation with another equivalent of $CF_3COOH$ leads to the formation of **14** and $Fe(NO)_2(PPh_2H)_2$ as a major and a minor product, respectively. This apparent decomposition may proceed by addition of $H^+$ to the $Fe(NO)_2$ iron of **16** to give a metal hydride complex analogous to **7a** (*cf.* Scheme 3), followed by fragmentation of such a binuclear species.

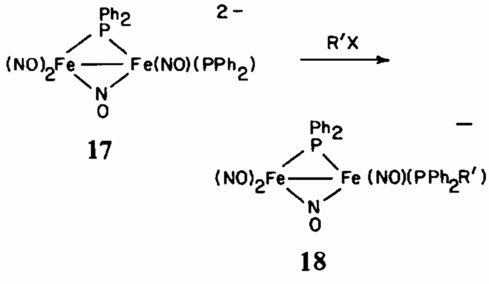
Alkylation reactions of **15** proceed to the monoanions **18** if 1 equiv. of the alkylating reagent is employed [36]. When methylation of **15** with MeI or $MeOS(O)_2CF_3$ is followed by variable temperature $^2H$ and $^{31}P$ NMR spectroscopy, an intermediate which is assigned structure **19**-Me with an Fe–Me bond can be observed at −60 °C. On warming to *ca.* −15 °C, it furnishes **18**-Me and some $Fe(NO)_2(PPh_2Me)_2$. The corresponding reaction of **15** with EtI affords **18**-Et and $Fe(NO)_2(PPh_2Et)_2$ at similar temperatures, but an intermediate analogous to **19**-Me could not be detected. The iodides $PhCH_2I$ and $CH_2{=}CHCH_2I$ convert **15** to **18**-$CH_2Ph$ and **18**-$CH_2CH{=}CH_2$, respectively, even at −70 °C.

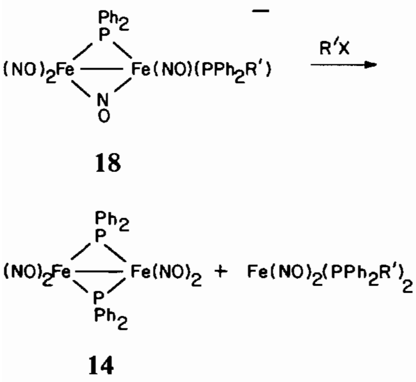


Scheme 7.

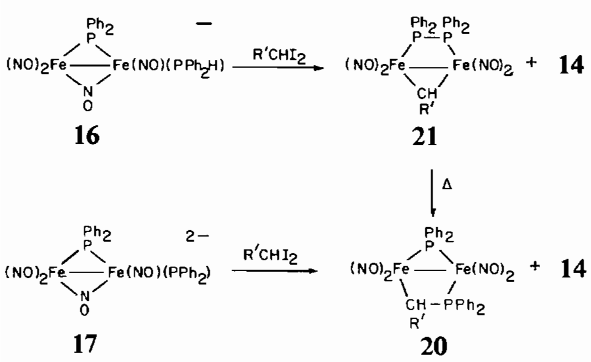
The foregoing alkylation reactions of **15** (see Scheme 7) differ from those of the corresponding carbonyl dianions **2**, where migratory insertion of CO follows the initial formation of an Fe–R′ bond (*cf.* Scheme 4). The observed difference may be ascribed to the generally more facile migratory insertion of CO than of NO into a metal–carbon σ bond [37]. It is worthy of note that reaction of **15** with $\overline{CH_2CH_2CH}CH_2I$, which commences at *ca.* −5 °C, affords approximately a 1:1 mixture of **18**-$CH_2\overline{CHCH_2CH_2}$ and **18**-$(CH_2)_2CH{=}CH_2$ [36] to indicate a significant contribution of a free radical mechanism to the overall transformation. Contrasting with this mechanistic result is the facile formation of **19**-Me from **15** and $MeOS(O)_2CF_3$ which supports a nucleophilic displacement (ionic) pathway to generate the Fe–Me bond. Thus, both radical and ionic mechanisms may be operative in the conversion of **15** to **18**, depending on the alkylating reagent.

The anions **18** also arise when **17** is treated with 1 equiv. of alkyl halide, R′X (R′ = Me, Et, $CH_2Ph$, $(CH_2)_2CH{=}CH_2$, $C_6H_{11}$, and $CH_2\overline{CHCH_2CH_2}$; X = I or Br), at −78 °C [36]. The reaction of **17** with $\overline{CH_2CH_2CH}CH_2I$ affords *ca.* 9:1 **18**-$CH_2\overline{CHCH_2CH_2}$ and **18**-$(CH_2)_2CH{=}CH_2$ to show that an ionic pathway dominates in this conversion. Further treatment of **18** with R′I (R′ = Me or Et) furnishes (*ca.* 30%) appropriate $Fe(NO)_2(PPh_2R')_2$ and trace amounts of **14**. This reaction probably proceeds by alkylation at the $Fe(NO)_2$ iron.



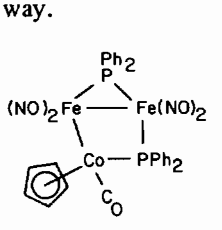


The foregoing reactions demonstrate that neutral binuclear iron nitrosyl complexes are much more susceptible to fragmentation than the corresponding carbonyl complexes. Exceptions to this generalization are provided by the complexes derived from **16** or **17** and $R'CHI_2$ ($R' = H$ or Me) [35, 36]. Accordingly, **17** reacts with $R'CHI_2$ at −78 °C to produce the ($PPh_2$, $R'CHPPh_2$)-bridged complexes **20**, as well as **14**. In contrast, reaction between **16** and $R'CHI_2$ commences around −63 °C to yield the isomeric ($R'CH$, $Ph_2PPPh_2$)-bridged species **21** in addition to **14**. These reactions are presented in Scheme 8. The structures of **20**-H and **21**-H were determined by X-ray crystallography [35]. Whereas the formation of **20** from **17** is analogous to that of **13a** from **4a** (*cf.* Scheme 5) and conforms to the expected pattern of behavior, the synthesis of **21** is unusual. It is possible that the latter arises by the formation of an $(NO)_2Fe\text{-}CH(R')I$ bond and oxidative addition of $FeCH(R')I$ to the other iron atom. On warming at 40–60 °C, **21** isomerize to the respective **20** (see Scheme 8). The mechanism of this transformation is presently under investigation. It is relevant that **16** does not react with $CH_2(OS(O)_2C_6H_4Me\text{-}p)_2$, even at room temperature, and **17** and $CH_2(OS(O)_2\text{-}C_6H_4Me\text{-}p)_2$ give what appears to be a product of alkylation at phosphorus, **18** [36].



Scheme 8.

The reaction of **17** with $R'CHI_2$ has been extended to metal diiodo complexes with a view to synthesizing heterotrinuclear clusters. Thus, treatment of **17** with $\eta^5\text{-}C_5H_5Co(CO)I_2$ at −78 °C furnished an $Fe_2Co$ complex of proposed structure **22** [36]. Synthetic studies on other, related trinuclear systems are underway.



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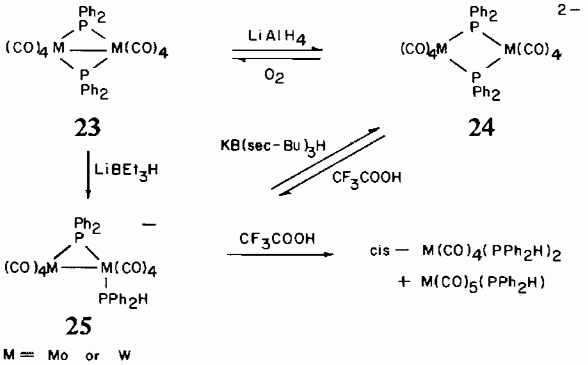
### Complexes $(CO)_4\overline{M(\mu\text{-}PPh_2)_2M}(CO)_4$ (M = Mo or W)

The molybdenum and tungsten analogues of **1a**, **23**-Mo and **23**-W, respectively, were first prepared in 1964 by reaction of $M(CO)_6$ with $Ph_2PPPh_2$ [15a]. Since then, more convenient and higher-yield syntheses have been developed that utilize $M(CO)_5$-$(PPh_2H)$ [38–40]. The structure of **23**-W was recently determined and found to consist of two essentiallly octahedral tungsten atoms symmetrically joined by $PPh_2$ bridges and a W–W bond of 3.03 Å [41]. This distance is comparable to that reported [42] for the analogous molybdenum and tungsten $(\mu\text{-}PEt_2)_2$ complexes (3.06 and 3.05 Å, respectively).

Reduction chemistry of **23** shows many similarities to that of **1** and **14**, and is presented in Scheme 9 [40]. Thus, treatment of **23** with 2 equiv. of $LiAlH_4$ or $KB(sec\text{-}Bu)_3H$ at 25 °C affords the symmetric dianions **24**.* The structure of $[Li(THF)_3]_2^+$**24**-W, elucidated by X-ray diffraction [41], reveals a W···W separation of 4.10 Å. This is 1.07 Å longer than the separation in **23**-W and corresponds to the absence of a metal–metal bond. The anions **24** are oxidized in air back to **23**.



Scheme 9.

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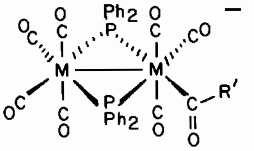
*The anion **24**-W was reported earlier by Keiter; see ref. [39].

Reaction of **23** with 1 equiv. of $LiBEt_3H$ or another $M'BR_3'H$ ($M = Li$, Na or K; $R' = Et$ or sec-Bu) yields the air-sensitive monoanions **25**, which were characterized in solution. Use of another equivalent of $M'BR_3'H$ leads to the formation of **24** at the rate that depends on both M′ and R′. The monoanions **25** also arise when **24** is treated with 1 equiv. of $CF_3COOH$. However, when 2 equiv. of $CF_3COOH$ are employed, or when **25** reacts with $CF_3COOH$, *cis*-$M(CO)_4(PPh_2H)_2$ and $M(CO)_5(PPh_2H)$ become major and minor products, respectively, presumably via protonation of the $M(CO)_4$ metal and reductive elimination of H and μ-$PPh_2$ as $MPPh_2H$. Hence this tendency toward reductive elimination of the molybdenum and tungsten systems appears to be comparable to that of the iron nitrosyl system and is substantially greater than that of the iron carbonyl system derived from **1a**.

Compared to **4a** (*cf.* Scheme 1) and **17** (*cf.* Scheme 6), the analogous unsymmetric dianions of molybdenum and tungsten seem to be much less stable with respect to rearrangement to the symmetric isomers. Accordingly, deprotonation of **25** with n-BuLi at −78 °C afforded only isomerized products, **24** [40].



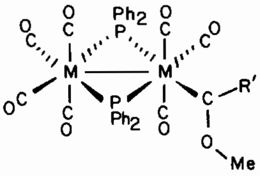
**26**

M = Mo or W

R′= Me , n − Bu , or Ph

In contrast to the behavior of **2** (*cf.* Scheme 4) and **15** (*cf.* Scheme 7), the anions **24** do not react with alkyl iodides in THF at ambient temperatures [40]. In DMF, **24**-Mo and MeI afford the anionic acetyl complex **26**-Mo,Me; however, this reaction is not clean, yielding other products that have not yet been characterized. Complexes **26** are better prepared by treatment of **23** with LiR′ [40, 43]. It is worthy of note that these reactions are regiospecific, proceeding by attack of LiR′ at the carbon atom of an equatorial CO. The observed regiospecificity is best ascribed to steric factors associated with the presence of bulky μ-$PPh_2$ groups.

The anionic acyl complexes **26** ($R' = Me$ or Ph) are converted by the action of $Me_3OBF_4$ to the Fischer carbene complexes **27**. Some of these carbene complexes are directly accessible from **24** and 2 equiv. of $Me_3OBF_4$ in $MeNO_2$, in a reaction that also yields **23** [43].



**27**

M = Mo or W

R′= Me or Ph

## Summary and Conclusion

The bis(μ-phosphido) complexes **1**, **14** and **23** exhibit striking similarities in their reduction chemistry. For each, two pathways resulting in two-electron reduction have been observed. One involves a transfer of two electrons from Na or $LiAlH_4$ to yield the symmetric dianions **2**, **15**, and **24**, respectively, in which the metal–metal bond is absent. The other entails a transfer of $H^-$ from $M'BR_3'H$; this $H^-$ converts a bridging $PR_2$ to a secondary phosphine $PR_2H$ in the product monoanions **3**, **16**, and **25**, respectively. The latter reaction was shown for **1** to proceed via a metal formyl intermediate; however, studies on a related system elsewhere [31] indicate that the hydride can also attack a different site.

The symmetric dianions are protonated by 1 equiv. of $CF_3COOH$ to the monoanions **3**, **16**, and **25**. It was shown for **2** that this reaction proceeds by addition of $H^+$ to the metal. With 2 equiv. of $CF_3COOH$, only **2a** affords a sufficiently stable binuclear metal hydride, **7a**, to be detected and isolated.

Deprotonation of the monoanions at −78 °C leads to the observation of the unsymmetric dianions **4a** and **17** for **3a** and **16**, respectively, and of the symmetric dianions **24** (Mo and W) for **25**. Further studies established that thermal stability of the deprotonated species with respect to isomerization to the symmetric dianions follows the order **4a** (< *ca.* −40 °C) > **17** (< *ca.* −70 °C) > deprotonated **25** (< −78 °C).

Alkylation of the symmetric dianions **2** and **15** proceeds readily with alkyl iodides (R′I), whereas that of **24** generally requires the more reactive oxonium salts. For **2** and **15**, the first step has been shown to consist of the formation of a metal–alkyl bond. The carbonyl complexes react by migratory insertion of CO into the metal–alkyl bond, whereas the nitrosyl complexes reductively eliminate μ-$PPh_2$ and R′ as $MPR_2R'$ in the monoanions **18**.

The unsymmetric dianions **4a** and **17** react with 2 equiv. of R′I first at the $PR_2$ phosphorus and then at the more distant metal. For **4a**, this leads to the formation of stable binuclear μ-acyl (**11a**) and $\eta^3$-allyl (**12a**) complexes. For **17**, no new neutral binuclear complexes are observed; instead fragmentation occurs to mononuclear species. However, by using 1,1-diiodohydrocarbons and metal diiodo complexes, isolable binuclear (**13a** and **20**) and trinuclear (**22**) compounds have been obtained from both **4a** and **17**.

In conclusion, studies to date have shown that anionic species derived by reduction of binuclear bis($\mu$-phosphido) complexes are useful starting materials for the synthesis of binuclear metal hydrides, acyls and allyls, as well as trinuclear clusters. Chemical and possible catalytic properties of these complexes are yet to be investigated.

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