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# One-Electron Reduction of Molybdenum $\eta^2$(4e)-Alkyne Complexes as a Pathway to the $\eta^2$(3e) Vinyl Ligand

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*Summary: Reaction of the molybdenum alkyne complex* $[\mathrm{Mo(P\{OMe\}_3)_2(\eta^2\{4e\}\text{-}PhC_2Ph)(\eta^5\text{-}C_5H_5)][BF_4]}$ *with* $\mathrm{K[Fe(CO)_2(\eta^5\text{-}C_5H_5)]}$ *results in the formation of the* $\eta^2$*(3e)-vinyl complex* $[\overline{\mathrm{Mo(P\{OMe\}_3)_2(\eta^2\{3e\}{=}CPh{-}C}}\mathrm{HPh)(\eta^5\text{-}C_5H_5)}]$ *and* $\mathrm{[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2}$*. A study of the reaction by EPR spectroscopy implies that the reaction proceeds via* $\mathrm{[Mo(P\{OMe\}_3)_2(\eta^2\{4e\}\text{-}PhC_2Ph)(\eta^5\text{-}C_5H_5)]}$*, which is then thought to undergo a hydrogen-abstraction reaction to give the observed product. The same radical was observed in the reaction of* $\mathrm{[Mo(P\{OMe\}_3)_2(\eta^2\{4e\}\text{-}PhC_2Ph)(\eta^5\text{-}C_5H_5)][BF_4]}$ *with* $\mathrm{LiBEt_3H}$*, implying the presence of an alternative mechanistic pathway to the direct addition of hydride to the molybdenum alkyne complex.*

## Introduction

Organometallic complexes containing a single unpaired electron frequently show markedly different reactivity patterns compared to their diamagnetic analogues.[1−3] For example, it has long been known that the rate of CO substitution in $\mathrm{V(CO)_6}$ (an associative process) is more than 10 orders of magnitude faster than that of $\mathrm{Cr(CO)_6}$ (a dissociative pathway),[4] and one-electron electrocatalysis can promote ligand substitution reactions via odd-electron species.[5] Furthermore, one-electron reduction or oxidation of diamagnetic substrates can induce some remarkable ligand-coupling reactions both within the coordination sphere of a single metal and between ligands on different metal centers.[6−8]

Insight into the structure and bonding of metal alkyne complexes has also been gained by systematic study of their redox properties. In particular, the ramifications of changes in both formal d-electron count and the number of electrons donated by the alkyne ligands across a series of complexes have been elegantly probed.[9−13] These studies demonstrate that alkyne ligands are extremely flexible in the bonding modes that they can adopt within the coordination sphere of metals: a property that may enhance their reactivity.[14] As well as providing insight into the electronic structure of metal alkyne complexes, one-electron-transfer reactions may also initiate some interesting intramolecular ligand couplings. For example, one-electron reduction of the Mo(II) alkyne complex $\mathrm{[Mo(NCMe)(\eta^2\text{-}PhC_2Ph)_2(\eta^5\text{-}C_5H_5)][BF_4]}$ with $\mathrm{[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^-}$ results in a coupling reaction between the alkyne ligands of two molybdenum centers, giving a remarkable flyover complex.[15]

We have shown (Scheme 1) that one-electron oxidation ($\mathrm{[Ph_3C]^+}$ or $\mathrm{[Fe\{\eta^5\text{-}C_5H_5\}_2]^+}$) of the electron-rich $\eta^2$-(3e)-vinyl complex $[\overline{\mathrm{Mo(P\{OMe\}_3)_2(\eta^2\{3e\}{=}CPh{-}C}}\mathrm{HPh)(\eta^5\text{-}C_5H_5)}]$ results in the initial formation of 17-electron $[\overline{\mathrm{Mo(P\{OMe\}_3)_2(\eta^2\{3e\}{=}CPh{-}C}}\mathrm{HPh)(\eta^5\text{-}C_5H_5)}]^+$, which, on warming to room temperature, undergoes formal loss of a hydrogen atom to give the alkyne complex $\mathrm{[Mo(P\{OMe\}_3)_2(\eta^2\{4e\}\text{-}RC_2R)(\eta^5\text{-}C_5H_5)]^+}$.[16] It therefore appears to be a logical extension of these studies that one-electron reduction of $\mathrm{[Mo(P\{OMe\}_3)_2(\eta^2\{4e\}\text{-}RC_2R)(\eta^5\text{-}C_5H_5)]^+}$ might, in the presence of a suitable hydrogen atom donor, provide a route to the $\eta^2$-(3e)-vinyl complexes $[\overline{\mathrm{Mo(P\{OMe\}_3)_2(\eta^2\{3e\}{=}CPh{-}C}}\mathrm{HPh)(\eta^5\text{-}C_5H_5)}]$ and thus complete this circle of reactivity involving one-electron-transfer processes. This idea was further reinforced by the elegant study of Adams, Connelly, and Rieger, who demonstrated that one-electron reduction of complexes $\mathrm{[Mo(P\{OMe\}_3)_2(\eta^2\{4e\}\text{-}RC_2R)(\eta^5\text{-}C_5H_5)][BF_4]}$ with $\mathrm{Co(\eta^5\text{-}C_5Me_5)_2}$ gives 19-electron $\mathrm{[Mo(P\{OMe\}_3)_2(\eta^2\{4e\}\text{-}RC_2R)(\eta^5\text{-}C_5H_5)]}$: in this species a significant amount of unpaired electron density is based on the alkyne ligand.[13] In both the 18- and 19-electron species the alkyne ligands align themselves parallel to the Mo−P vector and exhibit “windscreen wiper” rotation: in the case of the odd-electron species the rate of this motion is of a comparable rate to the EPR time scale.

As part of our continuing studies on the reaction of the molybdenum alkyne complexes[17]with nucleophilic reagents, we decided to explore the reaction of $\mathrm{[Mo(P\{OMe\}_3)_2(\eta^2\{4e\}}$-

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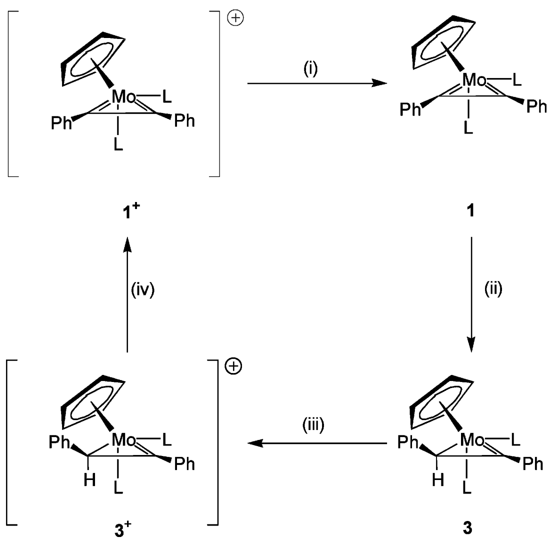
**Scheme 1** [a]



[a] L = P(OMe)$_3$. (i) + K[Fe(CO)$_2$($\eta^5$-C$_5$H$_5$)], − [Fe(CO)$_2$($\eta^5$-C$_5$H$_5$)]$_2$, − KBF$_4$; (ii) + "H"; (iii) [CPh$_3$][BF$_4$] or [Fe($\eta^5$-C$_5$H$_5$)$_2$][PF$_6$]; (iv) − "H".

PhC$_2$Ph)($\eta^5$-C$_5$H$_5$)][BF$_4$], **1[BF$_4$]**, with K[Fe(CO)$_2$($\eta^5$-C$_5$H$_5$)], **2**. Two possible reaction outcomes were predicted: either nucleophilic attack by the iron center to give a mixed-metal alkyne complex or, mindful of the results described above, one-electron reduction of **1[BF$_4$]**.

## Results and Discussion

Dropwise addition of a THF solution of K[Fe(CO)$_2$($\eta^5$-C$_5$H$_5$)], **2**, to a cooled (173 K) THF solution of **1[BF$_4$]** resulted, on warming, in a color change from deep purple to green. A deep green solid could be isolated from the reaction, and a $^{31}$P{$^1$H} NMR spectrum of this residue (in C$_6$D$_6$ solution) showed that the major phosphorus-containing product present was characterized by two doublet resonances at $\delta$ 195.4 and 202.2 ($^2J_{PP}$ = 79 Hz). These resonances were found to be identical to those observed in the $^{31}$P{$^1$H} NMR spectrum of an authentic sample of the known $\eta^2$(3e)-vinyl complex [Mo(P{OMe}$_3$)$_2$($\eta^2${3e}═CPh−CHPh) ($\eta^5$-C$_5$H$_5$)], **3**.[18] Resonances attributable to **3** were also observed in the $^1$H NMR spectrum, as was a further resonance in the region characteristic for a coordinated $\eta^5$-C$_5$H$_5$ group at $\delta$ 4.22. The IR spectrum of the reaction mixture exhibited bands at 1783, 1954, and 1993 cm$^{-1}$: these peaks were found to be identical to an authentic sample of the dimer [Fe(CO)$_2$($\eta^5$-C$_5$H$_5$)]$_2$, **4**, as was the resonance in the $^1$H NMR spectrum at $\delta$ 4.22. A similar set of results was obtained when the reaction was performed using CH$_3$CN as solvent.

It was therefore clear that nucleophilic attack by iron on **1[BF$_4$]** had not occurred. The fact that **4** had been identified as the major iron-containing product from the reaction led us to believe that **2** had undergone a one-electron oxidation to give the highly reactive 17-electron species Fe(CO)$_2$($\eta^5$-C$_5$H$_5$), which is known to dimerize rapidly.[19] Therefore it was logical to infer that **1[BF$_4$]** must have undergone a one-electron reduction to give [Mo(P{OMe}$_3$)$_2$($\eta^2${4e}-PhC$_2$Ph)($\eta^5$-C$_5$H$_5$)], **1**, similar to the observation made for the reduction of alkyne complexes [Mo(P{OMe}$_3$)$_2$($\eta^2${4e}-RC$_2$R)($\eta^5$-C$_5$H$_5$)]$^+$ with Co($\eta^5$-C$_5$Me$_5$)$_2$.[13]

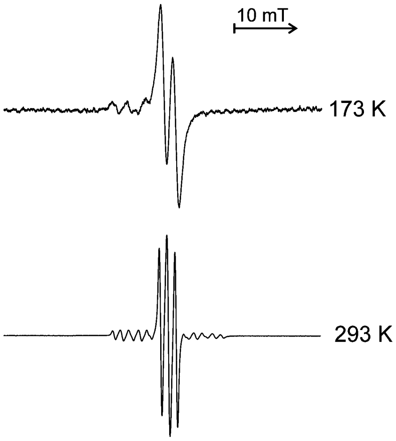


**Figure 1.** EPR spectra of THF solutions containing **1[BF$_4$]** and **2** at 173 and 293 K.

In order to ascertain if this was indeed the case, the reaction was repeated and monitored by EPR spectroscopy. To a thawing THF solution of **1[BF$_4$]** was added a THF solution of **2** and the tube placed in the EPR cavity, which had been cooled to 173 K. The resulting EPR spectrum (Figure 1) exhibited a doublet resonance, with molybdenum satellites centered at 339 mT [$a$($^{31}$P) = 1.9 mT, $a$($^{95,97}$Mo) = 2.82 mT]. When the temperature of the sample was raised (in this case to 293 K), the doublet resonance became a triplet [$a$($^{31}$P) = 1.24 mT, $a$($^{95,97}$Mo) = 2.82 mT] (Figure 1). These signals are very similar to those observed previously for the species [Mo(P{OMe}$_3$)$_2$($\eta^2$(4e)-MeC$_2$Me)($\eta^5$-C$_5$H$_5$)],[13] where values of $a$($^{31}$P) reported are 1.84 mT (doublet) at 160 K and 1.125 mT (triplet) at 280 K. In this case it was proposed that the changes in the EPR spectra were due to alkyne ligand oscillation, which is slow on the EPR time scale at low temperatures, but fast at high temperatures. This would also appear to be the case in **1**.

These results illustrate that the reaction between **1[BF$_4$]** and **2** does result in the formation of some **1**. An EPR spectrum recorded on the sample after standing for 16 h at room temperature revealed that no signals due to **1** remained, and an examination of the resulting green solution by NMR spectroscopy illustrated that **3** was once again the major diamagnetic phosphorus-containing product from the reaction. In a complementary series of experiments, the reaction of **1[BF$_4$]** with **2** was monitored by NMR spectroscopy. Immediately after the addition, the $^{31}$P{$^1$H} NMR spectrum of the reaction mixture did not show any resonances apart from a weak peak due to uncoordinated P(OMe)$_3$. This is consistent with the formation of a paramagnetic compound, such as **1**. Over the course of several hours, resonances due to **3** were observed to grow into the $^{31}$P{$^1$H} NMR spectrum, **3**, again, ultimately becoming the major phosphorus-containing product from the reaction.

Connelly and co-workers have shown that the unpaired electron in systems such as **1** has significant electron density on the alkyne ligand, and *C*-centered-radical-like behavior was anticipated. In the reactions that we now report we believe that this is indeed the case and that after initial one-electron reduction of **1**$^+$ to **1** (Scheme 1) the formation of **3** occurs via the abstraction of a hydrogen atom by **1**, presumably from the

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[19] See, for example, Dixon, A. J.; George, M. W.; Hughes, C.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1991**, *102*, 1719.

solvent.[20,21] This is, as predicted by Connelly and co-workers,[13] a classic example of carbon-centered radical behavior.[22]

Although we were able to prove conclusively by $^{31}P$ NMR spectroscopy that **3** was the major product of the reaction between **1[BF$_4$]** and **2**, isolation of **3** from the reaction mixture proved to be extremely troublesome, even when employing identical conditions to those used routinely to isolate **3** from the reaction of **1[BF$_4$]** with $LiBEt_3H$.[18] Solutions obtained from this reaction proved to be very sensitive to air—much more so than those containing **3** alone—and extensive decomposition was observed during attempts to purify the reaction mixtures by column chromatography. Deliberate introduction of the ambient atmosphere into solutions of **3** prepared from the reaction of **1[BF$_4$]** with **2** led to the immediate formation of free $P(OMe)_3$, as demonstrated by $^{31}P\{^1H\}$ NMR spectroscopy. Consistent with this observation, exposure of the reaction mixtures to trace quantities of air resulted in a second iron-containing product, $[Fe_2(CO)_3(P\{OMe_3\})(\eta^5\text{-}C_5H_5)_2]$,[23] **5**, being isolated from the reaction: stilbene was also observed in these cases. In contrast, a solution of **3** (prepared from **1[BF$_4$]** and $LiBEt_3H$) deliberately contaminated with **4** (0.5 equiv) proved to be far more robust. Column chromatography of this solution did not result in any appreciable decomposition, and exposure to the ambient atmosphere did not result in the liberation of $P(OMe)_3$. These results indicate that the liberation of $P(OMe)_3$ from **1**, which may be oxygen-promoted, is facile and may explain the difficulty we have encountered in isolating **3** from these reactions.

One further intriguing ramification of these results was also explored. The reaction of **1[BF$_4$]** with hydride reagents is thought to proceed via one of two competing mechanisms, either attack at the metal or attack onto the coordinated ligand.[18] Our results offered a further possibility; the reaction could proceed via a one-electron-transfer process followed by hydrogen atom transfer. Similar electron transfer/hydrogen atom abstraction pathways have been observed in the case of the reaction of, for example, $[Mo(CO)_3(PMe_3)(\eta^5\text{-}C_5Me_5)]PF_6$[24] and $[Fe(CO)(dppe)(\eta^5\text{-}C_5Me_5)]PF_6$[25]with hydride sources. Also, the electroreduction of $Cr(CO)_6$ and $Fe(CO)_5$ followed by treatment with the hydride atom source $HSnBu^n{}_3$ results in the formation of the formyl anions $[Cr(CO)_5(CHO)]^-$ and $[Fe(CO)_4(CHO)]^-$, respectively.[26] These reactions are thought to proceed via 19-electron carbonyl radicals, which then abstract a hydrogen atom from the stannane: the net result of this reaction is the formal addition of hydride. In order to test if this was a viable hypothesis, a THF solution of **1[BF$_4$]** was frozen and treated with $LiBEt_3H$. On warming to room temperature in the cavity of the EPR spectrometer, the radical **1** was again observed and a $^{31}P$ NMR spectrum of the resulting reaction mixture illustrated that, as expected, **3** was the major product from the reaction.

These results do not prove that a radical mechanism is the dominant reaction pathway in the reaction of **1[BF$_4$]** with $LiBEt_3H$, but that it must be considered as a mechanistic alternative. The reaction of **1[BF$_4$]** with $LiBEt_3D$ results in a near total deuterium incorporation into the $\eta^2$(3e)-vinyl product,[27] which suggests that either the dominant reaction pathway proceeds via direct nucleophilic attack or the reaction mechanism involves sequential electron transfer then deuterium atom transfer from $LiBEt_3D$ to **1**.

In summary, we have shown that formal hydride addition to $\eta^2$(4e)-alkyne complexes may be initiated by treatment with **2**, and evidence for the presence of a 19-electron molybdenum complex in this reaction sequence was obtained. We have also observed an identical species in reactions involving hydride transfer to $\eta^2$(4e)-alkyne complexes. These results suggest that a pathway involving one-electron transfer could be considered as a mechanistic alternative to those involving direct nucleophilic addition.

## Experimental Section

All reactions were performed under an atmosphere of nitrogen or argon using standard Schlenk line techniques or an MBraun UniLab drybox. THF and diethyl ether were distilled from sodium/benzophenone, NCMe, and $CH_2Cl_2$ over $CaH_2$ under argon prior to use. $K[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$,[28]$[Fe_2(CO)_3(P\{OMe_3\})(\eta^5\text{-}C_5H_5)_2]$,[23] $[Mo(P\{OMe\}_3)_2(\eta^2\{4e\}\text{-}PhC_2Ph)(\eta^5\text{-}C_5H_5)][BF_4]$,[29]and $\overline{[Mo(P\{OMe\}_3)_2(\eta^2\{3e\}{=}CPh{-}CHPh}(\eta^5\text{-}C_5H_5)]$[18] were all prepared according to literature methods. EPR spectra were acquired on a Bruker ESP 300E X-band EPR spectrometer. NMR spectra were run on either a Bruker AMX500 or AMX 300 with $^1H$ operating frequencies of 500.13 and 300.13 MHz, respectively.

**Reaction of $[Mo(P\{OMe\}_3)_2(\eta^2\{4e\}\text{-}PhC_2Ph)(\eta^5\text{-}C_5H_5)][BF_4]$ with $K[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$.** In a typical reaction, **1[BF$_4$]** (100 mg, 0.15 mmol) was dissolved in THF and cooled to −78 °C. To this solution was added dropwise **2** (27 mg, 0.15 mmol) via a steel cannula with stirring. After the addition was complete the solution was allowed to warm to room temperature, during which time the color changed from purple to deep green. Removal of the solvent and extraction with diethyl ether gave a deep green solution that was shown by NMR spectroscopy to be a mixture of **3** and **4**. Attempts to isolate **3** from **4** by column chromatography on alumina or silica were unsuccessful, even when the purification was attempted in the drybox. In all cases extensive decomposition was observed during the chromatography and, at best, only small quantities of **3** could be obtained, which were contaminated with **4**.

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[21] We are grateful to a reviewer who suggested that if the formation of **3** from **1[BF$_4$]** and **2** does proceed via a one-electron transfer to give **1**, then **3** should also be formed from the reaction of **1[BF$_4$]** with $Co(\eta^5\text{-}C_5Me_5)$. This indeed proved to be the case. The reaction of **1[BF$_4$]** with $Co(\eta^5\text{-}C_5Me_5)$ in thf solution was monitored by $^{31}P\{^1H\}$ NMR spectroscopy: the observations proved to be similar to those obtained in the reaction with **2**. After the initial addition only a small resonance due to free $P(OMe)_3$ could be observed (consistent with the formation of **1**), but over the course of several hours resonances due to **3** grew into the spectra, ultimately becoming the major phosphorus-containing product from the reaction.

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