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Communications

η^2 (3e)-Vinyl Complexes and One-Electron-Transfer **Reactions:** Tris(pentafluorophenyl)borane as a **One-Electron Oxidant**

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Summary: The $\eta^2(3e)$ -vinyl complex [Mo{=C(Ph)CHPh}- $\{P(OMe)_3\}_2Cp\}$ is oxidized by $[FeCp_2]^+$, $[CPh_3]^+$, or

 $B(C_6F_5)_3$ to form the 17-electron cation |Mo| = C(Ph)C-HPh { $P(OMe)_3$ } $_2Cp$]⁺, which on warming loses H to form the cationic $\eta^2(4e)$ -alkyne complex [$Mo(\eta^2-PhC \equiv$ CPh { $P(OMe)_3$ } $_2Cp$]⁺. In the case of the borane there is evidence for a competing reaction between the η^2 -vinyl complex and the acid $(H_2O)B(C_6F_5)_3$, resulting in the formation of a labile trans-stilbene complex.

The last two decades have seen the development of the transition-metal chemistry of coordinated CHCH2fragments where both carbons are bonded to the metal center.¹⁻⁴ Computational studies^{1d,3d} led to the description of these species as $\eta^2(3e)$ -vinyls or metallacyclopropenes and show a relationship between the bonding capabilities of $\eta^2(4e)$ -alkyne and $\eta^2(3e)$ -vinyl ligands. Given that the metal-alkyne moiety can act as an electron sink in the d^4-d^5 redox-related pair [Mo(CO)₂- $(\eta^2 - PhC \equiv CPh)Tp' | [PF_6] (Tp' = HB(3,5-dimethylpyra$ zolyl)) and $[Mo(CO)_2(\eta^2 - PhC \equiv CPh)Tp']$,⁵ and a previous indication of a one-electron-transfer reaction involving

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⁽¹⁾ Mo: (a) Green, M.; Norman, N. C.; Orpen, A. G. J. Am. Chem. Soc. **1981**, 103, 1267. (b) Davidson, J. L.; Murray, I. E. P.; Preston, P. N.; Russo, M. V.; Manojlovic-Muir, L.; Muir, K. W. J. Chem. Soc., Chem. Commun. **1981**, 1059. (c) Davidson, J. L.; Murray, I. E. P.; Preston, P. N.; Russo, M. V. J. Chem. Soc., Dalton Trans. **1983**, 1783. (d) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, S. K., Beevor, K. G., Green, M., Norman, N. C., Orperi, A. G., Willams, I. D. J. Chem. Soc., Dalton Trans. 1985, 435. (e) Feher, F. J.; Green, M.; Rodrigues, R. A. J. Chem. Soc., Chem. Commun. 1987, 1206. (f) Allen, S. R.; Beevor, R. G.; Green, M.; Orpen, A. G.; Paddick, K. E.; Williams, I. D. J. Chem. Soc., Dalton Trans. 1987, 591. (g) Gamble, A. S.; White P. S.; Tompleton, I. L. Orgenematellice 1901, 10, 693. (b) Winanis, F. D. J. Chem. Soc., Dation Trans. 1967, 531. (g) Camble, A. S.; White, P. S.; Templeton, J. L. Organometallics 1991, 10, 693. (h) Agh-Atabay, N. M.; Canoira, L. J.; Carlton, L.; Davidson, J. L. J. Chem. Soc., Dalton Trans. 1991, 1175. (i) Kiplinger, J. L.; Richmond, T. G Polyhedron 1997, 16, 409.

⁽²⁾ W: (a) Davidson, J. L.; Shiralian, M.; Manojlovic-Muir, L.; Muir, (c) W. (a) Davidson, J. L., Shi anan, W., Manglovie-Main, E., Main, K. W. J. Chem. Soc., Chem. Commun. 1979, 30. (b) Carlton, L.; Davidson, J. L.; Miller, J. C.; Muir, K. W. J. Chem. Soc., Chem. Commun. 1984, 11. (c) Carlton, L.; Davidson, J. L. J. Chem. Soc., Dalton Trans. 1987, 895. (d) Gamble, A. S.; Birdwhistell, K. R.; Templeton, J. L. J. Am. Chem. Soc. 1990, 112, 1818. (e) Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 2951. (f) Kiplinger, J. L.; Richmond, T. G.; Arif, A. M.; Dücker-Benfer, C.; van Eldik, R. Organometallics **1996**, *15*, 1545. (g) Kiplinger, J. L.; King, M. A.; Fechtenkötter, A.; Arif, A. M.; Richmond, T. G. Organometallics 1996, 15, 5292. (h) Cairns, G. A.; Carr, N.; Green, M.; Mahon, M. F.; Chem. Commun. 1996, 2431.

⁽a) Re: (a) Pombeiro, A. J. L.; Hughes, D. L.; Richards, R. L.;
Silvestre, J.; Hoffmann, R. J. Chem. Soc., Chem. Commun. 1986, 1125.
(b) Carfagna, C.; Carr, N.; Deeth, R. J.; Dossett, S. J.; Green, M.;
Mahon, M. F.; Vaughan, C. J. Chem. Soc., Dalton Trans. 1996, 415.
(c) Casey, C. P.; Brady, J. T. Organometallics 1998, 17, 4620. (d) Casey,
C. P.; Brady, J. T.; Boller, T. M.; Weinhold, F.; Hayashi, R. K. J. Am. Chem. Soc. 1008, 120, 12500. Chem. Soc. 1998, 120, 12500.

⁽⁴⁾ Os: (a) LaPointe, A. M.; Schrock, R. R.; Davis, W. M. J. Am. Chem. Soc. **1995**, *117*, 4802. (b) Chen, H.; Harman, W. D. J. Am. Chem. Soc. **1996**, *118*, 5672. (c) Buil, M. L.; Eisenstein, O.; Esteruelas, M. A.; Garcia-Yebra, C.; Gutierrez-Puebla, E.; Olivan, M.; O.; Esteruetas, M. A.;
Garcia-Yebra, C.; Gutierrez-Puebla, E.; Olivan, M.; Onate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* 1999, *18*, 4949.
(5) Bartlett, I. M.; Connelly, N. G.; Orpen, A. G.; Quayle, M. J.;
Rankin, J. C. *Chem. Commun.* 1996, 2583.



Figure 1. ESR spectrum of the cation $[Mo{=C(Ph)CHPh}{P(OMe)_3}_2Cp]^+$ (1⁺).

an $\eta^2(3e)$ -vinyl,⁶ we have explored the possibility of a related d^3-d^4 redox chemistry for the $\eta^2(3e)$ -vinyl complex [Mo{=C(Ph)CHPh}{P(OMe)_3}_2Cp] (1).^{1a,1d} In this investigation we have also discovered that the Lewis acid $B(C_6F_5)_3^7$ can act as a one-electron oxidant toward an $\eta^2(3e)$ -vinyl complex.

Addition (195 K) of 1 equiv of [FeCp₂][PF₆] to a solution of 1 in CH₂Cl₂ led to a rapid change in color and, on warming to room temperature, the formation in quantitative yield of the $[PF_6]^-$ salt of the fourelectron-donor alkyne cation $[Mo(\eta^2-PhC \equiv CPh) \{P(OMe)_3\}_2Cp]^+$ (2⁺). An insight into the processes involved in this reaction was obtained by electrochemical and ESR spectroscopic studies. The cyclic voltammogram of $\mathbf{1}$, in CH₂Cl₂ at a platinum electrode, shows a reversible oxidation wave at -0.11 V, implying the ready formation of 1^+ , followed by a second wave at ca. 0.1 V. When a mixture of **1** and [FeCp₂][PF₆] at 195 K in CH₂Cl₂/thf (1:2) was warmed to 260 K, the wellresolved isotropic ESR spectrum observed, a doublet of doublets of doublets with Mo satellites ($A(^{1}H) = 8.0$ G, $A(^{31}P^1) = 23.7 \text{ G}, A(^{31}P^2) = 37.8 \text{ G}; A(^{95,97}Mo) = 17.0 \text{ G};$ $g_{\rm iso} = 2.011$), was consistent with the formation of 1^+ (Figure 1). When the reaction mixture was warmed further, to room temperature, this signal disappeared. These results suggest that the formation of 2^+ involves initial one-electron oxidation of 1 to form the 17-electron cation 1⁺, stabilized by delocalization of unpaired spin density onto the η^2 -vinyl fragment. Cation **1**⁺ then loses a hydrogen atom⁸ from the β -carbon of the η^2 -vinyl to form $\mathbf{2}^+$ (Scheme 1). When the reaction was repeated (260 K, CH₂Cl₂) with the deuterated η^2 (3e)-vinyl com-

plex [$Mo{=}C(Ph)CDPh{P(OMe)_3}_2Cp$] (**3**), the corresponding ESR signal of **3**⁺ appeared (Figure 2) as a doublet of doublets with Mo satellites ($A(P^1) = 23.8$ G, $A(P^2) = 37.9$ G, A(Mo) = 16.9 G; $g_{iso} = 2.011$). An EHMO calculation, based on the established bond parameters for **1**,^{1d} is consistent with removal of the electron from a metal-centered HOMO (32% d_z², 42\% d_{xy}).





^{*a*} L = P(OMe)₃. Legend: (i) +[FeCp₂][PF₆] or +[CPh₃][BF₄]; (ii) -H or -D.



Figure 2. ESR spectrum of the cation $[Mo{=C(Ph)CDPh}-{P(OMe)_3}_2Cp]$ (**3**⁺).

As noted earlier, $\eta^2(3e)$ -vinyl complexes can be viewed as metallacyclopropenes and, because of the isolobal relationship CH \leftrightarrow MoL₂Cp, **1** might be expected to show reactivity patterns similar to those of cyclopropenes. Indeed, addition (190 K, CH₂Cl₂) of [CPh₃][BF₄] to a solution of **1** followed by warming the mixture to room temperature led to the formation in high yield of CHPh₃ and the η^2 (4e)-alkyne cation **2**⁺, a complex isoelectronic with a cyclopropenium cation (Scheme 1). However, ESR spectroscopy showed that one-electron oxidation by CPh₃⁺ rather than simple hydride abstraction was involved. Thus, warming a mixture of 1 and [CPh₃][BF₄] in CH₂Cl₂ from 195 to 260 K led to the same ESR spectrum as observed when $[FeCp_2]^+$ was used as oxidant: i.e., the spectrum of 1^+ . In addition there was the characteristic signal of the CPh₃ radical.⁹ These signals disappear when the mixture is warmed to room temperature.

The facility with which the d⁴ η^2 (3e)-vinyl complex **1** undergoes one-electron oxidation suggested the pos-

⁽⁶⁾ Clegg, W.; Green, M.; Hall, C. A.; Hockless, D. C. R.; Norman, N. C.; Woolhouse, C. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1330.
(7) Review: Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345.

⁽⁷⁾ Review: Piers, W. E.; Chivers, T. Chem. Soc. Rev. 1997, 26, 345.
(8) For recent examples of hydrogen atom loss from a 17-electron cation see: (a) Bleeke, J. R.; Hinkle, P. V.; Rath, N. P. J. Am. Chem. Soc. 1999, 121, 595. (b) Burrows, A. D.; Green, M.; Jeffery, J. C.; Lynam, J. M.; Mahon, M. F. Angew. Chem., Int. Ed. 1999, 38, 3043.

 ⁽⁹⁾ Connelly, N. G.; Geiger, W. E. Chem. Rev. 1996, 96, 877.
 (10) Galakhov, M. V.; Heinz, G.; Royo, P. Chem. Commun. 1998,

sibility that it might also undergo electron transfer with $B(C_6F_5)_3$, which is isoelectronic with $[CPh_3]^+$. This prediction proved to be correct. When solid 1 was added to a frozen solution of $B(C_6F_5)_3$ in $CH_2Cl_2/1, 2$ -dichloroethane (1:1) at 77 K and the reaction mixture warmed to 260 K, a strong, well-resolved signal of 1⁺ appeared in the ESR spectrum (together with a signal due to a minor unidentified molybdenum-centered radical species); there was no evidence for the formation of a boroncentered radical. Similarly, when $B(C_6F_5)_3$ was reacted with the deuterated complex **3** the ESR signal for 3^+ was observed. In the context of the known^{7,10,11} reactions of $B(C_6F_5)_3$ with organometallic complexes, this is an especially interesting observation, since it has recently been reported¹² that $B(C_6F_5)_3$ acts as a one-electron oxidant toward an azazirconacyclobutene.

Interestingly, when **1** was reacted (CD₂Cl₂, 190 K \rightarrow room temperature) on a preparative scale (0.1 mmol), the yield of species containing the **2**⁺ cation was observed (¹H, ³¹P, ¹¹B NMR) to vary (80 \rightarrow 50%). These findings were rationalized when it was found that bubbling CO through the reaction mixture (warmed to room temperature) gave the complex **2**⁺ together with *trans*-stilbene (MS, NMR) and the dicarbonyl species [Mo(CO)₂{P(OMe)₃₃₂Cp]⁺ (**4**⁺) (MS, NMR, ν (CO) (1998 and 1927 cm⁻¹)). This suggested that competing reactions were occurring in which the η^2 (3e)-vinyl complex **1** underwent either a one-electron-oxidation reaction (**1** \rightarrow **2**⁺) with B(C₆F₅)₃ or proton transfer (**1** \rightarrow *trans*-stilbene complex) with the acid (H₂O)B(C₆F₅)₃^{-1b} formed in varying amounts by the reaction of traces of H₂O with B(C₆F₅)₃.

Strong support for this rationale was obtained when it was observed that **1** reacted (CD_2Cl_2 , 190 K \rightarrow room temperature) with [PhNHMe₂]BF₄ or HBF₄·OEt₂, i.e. [HOEt₂]BF₄, to form in quantitative yield the cationic *trans*-stilbene complex $\mathbf{5}^+$ (X⁻ = BF₄⁻) (Scheme 2), which was fully characterized by NMR spectroscopy¹⁶ $({}^{1}H, {}^{3}P{}^{1}H{}, and {}^{1}C{}^{1}H{}).{}^{17}$ When **1** was treated with $(H_2O)B(C_6F_5)_3$, the cation 5⁺ with the counteranion $[B(OH)(C_6F_5)_3]^-$ (¹¹B NMR (CD₂Cl₂) δ -3.8 (lit.^{13,14} δ -3.8, CDCl₃)) was formed. Moreover, when the cationic species $\mathbf{5}^+$ (X⁻ = [BF₄]⁻ or [B(OH)(C₆F₅)₃]⁻) was reacted (room temperature) with either carbon monoxide or diphenylacetylene, the *cis*-dicarbonyl species 4⁺ (Scheme 2) or the $\eta^2(4e)$ -alkyne cation $\mathbf{2}^+$ was formed, respectively, in quantitative yield. It is important to note that $(H_2O)B(C_6F_5)_3$ has recently^{11b} been shown to act as a one-electron oxidant toward $[MCp_2]$ (M = Cr, Fe, Co). However, in the reaction of 1 with [PhNHMe₂]BF₄ and [HOEt₂]BF₄ only the *trans*-stilbene complex 4^+ is formed.



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 $^{a}L = P(OMe)_{3}.$ Legend: (i) $+(H_{2}O)B(C_{6}F_{5})_{3},$ $X^{-} = [B(OH)-(C_{6}F_{5})_{3}]^{-};$ (ii) $+[PhNHMe_{2}]BF_{4},$ $-C_{6}H_{5}NMe_{2},$ $X^{-} = [BF_{4}]^{-};$ (iii) $+HBF_{4}\cdot OEt_{2},$ $X^{-} = [BF_{4}]^{-};$ (iv) +CO; (v) $+Ph_{2}C_{2},$ -transstilbene, $X^{-} = [B(OH)(C_{6}F_{5})_{3}]^{-}$ or $[BF_{4}]^{-}.$

Therefore, in the reaction of **1** with a mixture of $B(C_6F_5)_3$ and $(H_2O)B(C_6F_5)_3$ any **2**⁺, i.e. $\eta^2(4e)$ -alkyne substituted cation, which is formed must arise as a result of $B(C_6F_5)_3$ acting as a one-electron oxidant.

In summary, the $\eta^2(3e)$ -vinyl complex **1** undergoes one-electron oxidation with $[FeCp_2]^+$ or $[CPh_3]^+$ to form the relatively stable 17-electron species **1**⁺, which can then lose a hydrogen atom to form the cationic $\eta^2(4e)$ alkyne complex **2**⁺. Especially interesting is the observation that **1**⁺ is formed on reaction of B(C₆F₅)₃ with **1** and that (H₂O)B(C₆F₅)₃, present in varying¹⁵ amounts, reacts with **1** by a different reaction pathway involving formal addition of a proton to the α -carbon of the η^2 -(3e)-vinyl ligand to form a *trans*-stilbene complex.

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OM0007668

^{(11) (}a) Danopoulos, A. A.; Galsworthy, J. R.; Green, M. L. H.; Cafferkey, S.; Doerrer, L. H.; Hursthouse, M. B. *Chem. Commun.* **1998**, 2529. (b) Doerrer, L. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1999**, 4325.

⁽¹²⁾ Harlan, C. J.; Hascall, T.; Fujita, E.; Norton, J. R. J. Am. Chem. Soc. **1999**, *121*, 7274. In this important study, evidence was presented for the facile one-electron oxidation of an azazirconacyclobutene and cobaltocene by $B(C_6F_5)_3$. As in the case of the formation of the molybdenum species 1^+ the structural identity of the boron-containing counteranions in the zirconium reaction was not established. As noted by Norton et al., in many reactions with Lewis acids that generate radical cations the structural identity of the counteranion has not been established.

⁽¹⁵⁾ Although all glassware was flame-dried prior to use and CH₂-Cl₂ was distilled under N₂ from CaH₂, traces of water could not be excluded. A similar difficulty was observed by Norton and co-workers.¹² Preparative reactions were carried out on a 0.1 mmol scale in 10 cm³ of solvent. ESR spectra were measured on a 0.01 mmol scale in 0.2 cm³ of solvent.

⁽¹⁶⁾ Selected NMR spectroscopic data for complex **5** recorded in CD₂-Cl₂ at ambient temperature: ¹H, δ 7.6–7.0 (Ar), δ 6.35 (ddd, ³*J*_{PH} = 8.5 Hz, ³*J*_{PH} = 8.5 Hz, ³*J*_{PH} = 4.7 Hz, 1H, PhC*H*=), δ 5.17 (dd, ³*J*_{PH} = 1.4 Hz, ³*J*_{PH} = 0.9 Hz, 5H, C₃*H*₅), δ 3.44 (dd, ³*J*_{PH} = 9.3 Hz, ⁵*J*_{PH} = 1.1 Hz, 9H, P{O*M*e}₃), δ 3.29 (dd, ³*J*_{PH} = 9.5 Hz, ⁵*J*_{PH} = 1.0 Hz, 9H, P{O*M*e}₃), δ 2.51 (dd, ³*J*_{PH} = 7.2 Hz, ³*J*_{HH} = 8.5 Hz, 1H, PhC*H*=); ³¹P-{¹H}, δ 172.1 (d, ²*J*_{PP} = 104.0 Hz, *P*{OMe}₃), δ 170.6 (d, ²*J*_{PP} = 104.0 Hz, *P*{OMe}₃), δ 170.6 (d, ²*J*_{PC} = 6.0 Hz, ²*J*_{PC} = 4.0 Hz, PhCH=), δ 57.1 (dd, ²*J*_{PC} = 5.5 Hz, ²*J*_{PC} = 2.5 Hz, PhCH=).

^{(14) (}a) Hill, G. S.; Manojlovic-Muir, L.; Muir, K. W.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 525. (b) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809. be

⁽¹⁷⁾ An NMR spectroscopic study of the reaction of 1 with [PhNHMe₂]-BF₄ showed smooth conversion to 5^+ and uncoordinated PhNMe₂ between -50 and -25 °C.