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Synthesis, Reactivity, and Theoretical Studies of the η^2(4e)-Bonded Phosphaalkyne Complex $[CpMo\{P(OMe)_3\}_2\{\eta^2(4e)\text{-}P\equiv CBu^t\}][B(C_6F_5)_4]$ and the Molybdenum-Mediated Cyclocotrimerization of Alkyne and Phosphaalkyne Ligands

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Summary: Whereas the cations $[CpMo\{P(OMe)_3\}_2\{\eta^2(4e)\text{-}alkyne\}]^+$ *do not react with alkynes or* $P\equiv CBu^t$*, the newly synthesized isostructural phosphaalkyne complex* $[CpMo\{P(OMe)_3\}_2\{\eta^2(4e)\text{-}P\equiv CBu^t\}][B(C_6F_5)_4]$*, which is unreactive towards* PhC_2Ph*, readily reacts via an associative stepwise process with* $P\equiv CBu^t$ *to give* $[CpMo\{P(OMe)_3\}_2\{\eta^4\text{-}1,3\text{-}P_2C_2Bu^t{}_2\}][B(C_6F_5)_4]$*. A further interesting difference in alkyne and phosphaalkyne chemistry was observed when it was found that* $CpMoCl(CO)\{\eta^2(4e)\text{-}PhC_2Ph\}$ *reacts with* $TlPF_6$ *and* $P\equiv CBu^t$ *to give the unusual 16-electron cyclocotrimerization product* $[CpMo\{=C(Bu^t)\overline{PC(Bu^t)=PC(Ph)=C}(Ph)\}(CO)][PF_6]$*, identified by single-crystal X-ray crystallography.*

While the isolobal ($P \leftrightarrow CR$) and diagonal (P/C) relationships have been used[1] to relate the structural chemistries of alkyne and phosphaalkyne transition-metal complexes, these simple ideas are of less value in predicting and rationalizing relative reactivity patterns. During investigations[2−4] to develop the chemistry of η^2(4e)-bonded phosphaalkyne complexes, we have extended our studies to molybdenum complexes and, on comparing these compounds with the corresponding alkyne derivatives, we have observed interesting differences in reaction chemistry.

Our initial objective was to synthesize complexes containing the cation $[CpMo\{P(OMe)_3\}_2\{\eta^2(4e)\text{-}P\equiv CBu^t\}]^+$ (**1**), to compare the chemistry of these species with that of the alkyne-substituted[5] cations $[CpMo\{P(OMe)_3\}_2\{\eta^2(4e)\text{-}alkyne\}]^+$. Since it has been shown that both the cation[6] $[(\eta^5\text{-}C_9H_7)Mo(NCMe)_2(CO)_2]^+$ and the neutral complex[7] $CpMoCl(CO)_3$ react (room temperature and 40 °C, respectively) with $P\equiv CBu^t$ to give only η^4-1,3-diphosphacyclobutadiene complexes, we reasoned that in order to avoid the coupling of two coordinated phosphaalkyne ligands it was important to devise a product-forming step which occurred at room temperature or below. Such a synthetic pathway was suggested by our recent observation[8] that the η^2(3e)-vinyl complex $Cp\overline{Mo\{=C(Ph)C}HPh\}\{P(OMe)_3\}_2$ (**2**) (Scheme 1) reacts (CH_2Cl_2, −50 °C → +25 °C) with $[PhNHMe_2][X]$ ($X = B(C_6F_5)_4{}^-$, $BF_4{}^-$) to give the labile cationic complexes $[CpMo\{P(OMe)_3\}_2\{\eta^2(2e)\text{-}\textit{trans}\text{-}stilbene\}][X]$, which in turn react (−78 °C → +25 °C) with $PhC\equiv CPh$ to afford $[CpMo\{P(OMe)_3\}_2\{\eta^2(4e)\text{-}PhC_2Ph\}][X]$ (**3**). Thus, we reacted (CH_2Cl_2, −78 °C) $[PhNHMe_2][X]$ with **2** and warmed the reaction mixture to room temperature before recooling to −78 °C and adding 1 mol equiv of $P\equiv CBu^t$. On subsequent warming of the resulting reaction mixture to room temperature, the color changed (2 h) from red to green and, on addition of hexane, the sought-for cationic complexes $[CpMo\{P(OMe)_3\}_2\{\eta^2(4e)\text{-}P\equiv CBu^t\}][X]$ (**1a**, $X^- = B(C_6F_5)_4{}^-$; **1b**, $X = BF_4{}^-$; 86% yield) precipitated as green microcrystalline powders.

The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra (CD_2Cl_2) of **1a** showed resonances consistent[4] with the presence of an η^2(4e)-bonded $P\equiv CBu^t$ ligand. The contact carbon appeared as a doublet ($^1J_{PC} = 122.7$ Hz) at δ 334.8 and the contact phosphorus as a triplet ($^2J_{PP} = 33.4$ Hz) at very low field, δ 491.6. Interestingly the appearance of the contact phosphaalkyne ^{31}P signal as a triplet and the presence of only one $P(OMe)_3$ resonance at δ 174.1 suggests the occurrence at room temperature of a "windscreen wiper" motion by the phosphaalkyne, analogous to that observed[5a] with alkyne complexes such as

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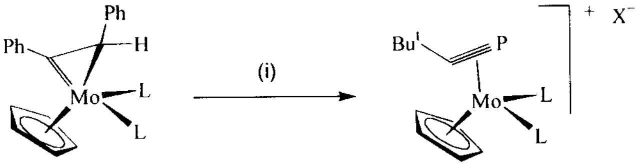
Scheme 1[a]



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1a X = B(C$_6$F$_5$)$_4$
1b X = BF$_4$

[a] L = P(OMe)$_3$. Legend: (i) +[PhNHMe$_2$][X], +P≡CBu^t, −*trans*-stilbene, −PhNMe$_2$, CH$_2$Cl$_2$.

3. This latter NMR spectrum was essentially invariant on cooling to −78 °C, indicating that the fluxional process was still rapid at this temperature.

In the absence of an X-ray structure the optimum geometry of [CpMo{P(OH)$_3$}$_2${η^2(4e)-P≡CMe}]$^+$ (**A**) was calculated at the B3LYP/TZVP level using the Turbomole program,[9] and for purposes of comparison the geometry of the related cation [CpMo{P(OH)$_3$}$_2${η^2(4e)-HC≡CMe}]$^+$ (**B**) was also calculated. The computed topologies of **A** and **B** are essentially identical with that observed[5b] for the solid-state structure of the cation [CpMo{P(OMe)$_3$}$_2${η^2(4e)-HC$_2$Bu^t}]$^+$, where the alkyne is orientated parallel to one of the Mo−P vectors. The calculated Mo−C(Me) distance in the phosphaalkyne complex **A** is short, and since this structural feature is also found[10] within a range of transition-metal η^2(4e)-bonded alkynes, it is reasonable to infer that **1a** and **1b** can be depicted as η^2(4e)-P≡CBu^t complexes. Moreover, this thesis is consistent with our recent[4] findings that a short tantalum to carbon contact distance, Ta−CBu^t (2.079(9) Å), occurs in the complex Cp*TaCl$_2${η^2-(4e)-P≡CBu^t}.

EHMO calculations[11] based on the DFT-calculated bond parameters for **A** and **B** of the $\pi_{\|}$, $\pi_{\perp}$, $\pi_{\|}$*, and $\pi_{\perp}$* orbital occupancies gave further structural insight. The phosphaalkyne complex **A** has the orbital occupancies $\pi_{\|}$ (1.866), $\pi_{\perp}$ (1.898), $\pi_{\|}$* (1.064), and $\pi_{\perp}$* (0.312) and the alkyne complex **B** occupancies $\pi_{\|}$ (1.724), $\pi_{\perp}$ (1.796), $\pi_{\|}$* (0.894), and $\pi_{\perp}$* (0.081). This indicates that the phosphaalkyne ligand in **A** is a poorer donor and better acceptor than the alkyne ligand in **B**. Of particular interest is the relative occupancy of the $\pi_{\perp}$* orbital in each complex. The alkyne ligands in the cations [CpMo{P(OMe)$_3$}$_2${η^2(4e)-alkyne}]$^+$ align themselves parallel to one of the Mo−P vectors to maximize π-back-bonding from a metal d orbital into the $\pi_{\perp}$* orbital; clearly in the case of the **A** this back-bonding is more efficient than in **B**, possibly due to 3p−4d and to 2p−4d overlap, respectively.

Overall, our findings suggest that both in terms of bonding and structure there is a close relationship between the phosphaalkyne-substituted cation **1** and the alkyne-substituted cations [CpMo{P(OMe)$_3$}$_2${η^2(4e)-alkyne}]$^+$. However, whereas the alkyne cations are unreactive toward excess alkyne, **1a** was found to react (1d) at room temperature with P≡CBu^t in CH$_2$Cl$_2$ to give a high yield of the complex [CpMo{P(OMe)$_3$}$_2${η^4-1,3-P$_2$C$_2$Bu$^t_2$}][B(C$_6$F$_5$)$_4$] (**4**). The room-temperature ^{31}P-{^{1}H} NMR (CH$_2$Cl$_2$) spectrum of **4** showed a triplet resonance at δ 162.2 (P(OMe)$_3$, $^2J_{PP}$ = 2.8 Hz) and a broad signal at δ 58.5 due to the η^4-1,3-P$_2$C$_2$Bu$^t_2$ ligand. When the temperature is lowered to −60 °C, this broad signal[7] collapsed to give two sharp resonances at δ 59.7 and 49.2, implying that the η^4-1,3-P$_2$C$_2$Bu$^t_2$ ligand is undergoing restricted rotation on the NMR timescale and allowing us to measure, for the first time, the barrier to rotation (T_c = 273 K, $\Delta\nu$ = 1691 Hz, $\Delta G^{\ddagger}$ = 48.0 kJ mol^{-1}).[12]

In a previous study[2] we had obtained evidence for the stepwise formation of the η^4-1,3-P$_2$C$_2$Bu$^t_2$ ligand; however, our observation of the reaction **1a** → **4** provided an opportunity to examine more closely this type of reaction as a prelude to a more detailed study of the mechanism using DFT techniques. This was important, because in our earlier theoretical study (DFT) of the formation of CpCo(η^4-1,3-P$_2$C$_2$Bu$^t_2$) it was concluded that cobaltadiphosphacyclopentadienes were unlikely to be intermediates in these reactions, although there was an interesting possibility that a tilted 1,3-diphosphabicyclo[1.1.0]butanediyl ligand was involved.[13]

When the reaction of **1a** with P≡CBu^t in CD$_2$Cl$_2$ was studied by NMR, no evidence for the formation on the NMR time scale of any intermediates was obtained. In addition, the reaction was observed to follow second-order kinetics (k = (6.79 ± 0.05) × 10^{-3} dm^3 mol^{-1} s^{-1}). Further mechanistic insight was gained from a series of ^{31}P magnetization transfer experiments. When a solution (CD$_2$Cl$_2$) containing approximately equimolar amounts of **1a** and P(OMe)$_3$ was prepared and a ^{31}P-{^{1}H} spectrum of the solution acquired with preirradiation (2 s) of the resonance due to uncomplexed P(OMe)$_3$, the spectrum did *not* exhibit the characteristic doublet resonance for **1a** at δ 174.1. Similarly, preirradiation of this latter resonance resulted in the bleaching of the signal for the uncomplexed P(OMe)$_3$. These analyses imply that exchange of free and coordinated P(OMe)$_3$ was occurring, and since the signals for the free and complexed P(OMe)$_3$ did not show any significant broadening, the rate of exchange (k_{ex}) must be less than 9.0 × 10^{-3} dm^3 mol^{-1} s^{-1}. The same result was obtained with the alkyne complex [CpMo{P(OMe)$_3$}$_2$-{η^2(4e)-PhC$_2$Ph}][BF$_4$][5a] (**5**) and P(OMe)$_3$; however, in this case the signals for both free and coordinated P(OMe)$_3$ showed significant broadening ($\omega_{1/2}$(P{OMe}$_3$) = 30.4 Hz). Addition of a further 5 equiv of P(OMe)$_3$ caused increased broadening ($\omega_{1/2}$(P{OMe}$_3$) = 77.7 Hz), implying that exchange between free and coordinated P(OMe)$_3$ is more rapid in the case of **5** and the reaction occurs via an ***associative*** mechanism. These results suggest that in the exchange of phosphite ligands within the coordination sphere of molybdenum the phosphaalkyne or alkyne switches its bonding mode from η^2(4e) to η^2(2e) to allow coordination of a third phosphite.

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[12] The low-temperature (−50 °C) ^{31}P NMR spectrum (CH$_2$Cl$_2$) did not show any evidence for an interaction between the η^4-1,3-P$_2$C$_2$Bu$^t_2$ ligand and B(C$_6$F$_5$)$_4^-$; this makes an interesting comparison with the findings[6] that, in the solid-state structure of the complex [(η^5-C$_9$H$_7$)-Mo(CO)$_2${η^4-1,3-P$_2$C$_2$Bu$^t_2$}][BF$_4$], the BF$_4^-$ anion is interacting with one of the phosphorus centers, this species undergoing reversible dissociation in solution.

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Intramolecular exchange of the phosphite environments then occurs, followed by dissociation of phosphite.

It is, therefore, reasonable to postulate that in the formation of **4** by reaction of **1a** with $P{\equiv}CBu^t$, the coordinated phosphaalkyne already present in **1a** switches its bonding mode (η^2(4e) → η^2(2e)) so as to facilitate coordination of a second $P{\equiv}CBu^t$. Significantly, when ^{31}P magnetization transfer experiments with a solution of **1a** and $P{\equiv}CBu^t$ in CH_2Cl_2 were attempted, no exchange was observed, which suggests that, once formed, the presumed intermediate $[CpMo\{P(OMe)_3\}_2\{\eta^2(2e)\text{-}P{\equiv}CBu^t\}_2][B(C_6F_5)_4]$ rapidly reacts further to give **4** by a process which remains to be elucidated.

When we found that $P{\equiv}CBu^t$ did not react with **5** and that **1a** did not react with PhC_2Ph, we speculated that it might be possible to synthesize interesting mixed alkyne/phosphaalkyne complexes such as the cation $[CpMo(CO)(\eta^2\text{-}PhC_2Ph)(\eta^2\text{-}P{\equiv}CBu^t)]^+$. However, the subtle nature of this chemistry was revealed when we examined the reaction of $P{\equiv}CBu^t$ with $CpMoCl\{\eta^2(4e)\text{-}PhC_2Ph\}(CO)$ (**6**) in CH_2Cl_2 solution in the presence of $TlPF_6$.

Addition at room temperature of $P{\equiv}CBu^t$ (2 molar equiv) to a stirred suspension of $TlPF_6$ and **6** in CH_2Cl_2 led, within 1 h, to the formation of TlCl and a change in color of the reaction mixture. Filtration (Celite) gave a red solution which on addition of Et_2O and cooling gave thermolabile, air- and moisture-sensitive red crystals of **7** (85% yield). The IR (CH_2Cl_2) spectrum of **7** showed one terminal carbonyl band at 2053 cm^{-1}, and examination of the ^1H and $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) revealed resonances corresponding to the linking of two phosphaalkynes and one PhC_2Ph ligand to form a $P_2C_4Bu^t{}_2Ph_2$ fragment coordinated onto a $[Mo(CO)(\eta^5\text{-}C_5H_5)]^+$ center. Although the presence of two doublet resonances in the $^{31}P\{^1H\}$ NMR spectrum at δ 47.7 ($J_{PP} = 20$ Hz) and δ −86.8 ($J_{PP} = 20$ Hz) implied that a novel coupling reaction had occurred, attempts to obtain further structural insight by recording a $^{13}C\{^1H\}$ NMR spectrum were frustrated by the low solubility of the cation in inert solvents and by its thermal sensitivity in solution. However, the structural identity of **7** as $[CpMo{=}\{C(Bu^t)\overline{PC(Bu^t){=}PC(Ph){=}C}(Ph)\}(CO)][PF_6]$ was established by a single-crystal X-ray diffraction study.[14] This revealed (see Figure 1) that a $[Mo(CO)(\eta^5\text{-}C_5H_5)]^+$ fragment is doubly bonded to a Bu^tC group (Mo−C(26) = 1.881(8) Å), which is linked by a single carbon−phosphorus bond (P(1)−C(26) = 1.920(7) Å) to the phosphorus center P(1) of a 1,3-diphosphacyclopentadiene ring system. This ring system is η^2-bonded via the ring phosphaalkene to the molybdenum center (Mo−P(2) = 2.587(2) Å, Mo−C(6) = 2.151(7) Å, P(2)−C(6) = 1.780(7) Å), the ring being slightly puckered and C(6) exhibiting a deviation of 0.384 Å from the plane of the atoms P(1), P(2), C(11), and C(12). Interestingly, the carbon−carbon double bond present in the 1,3-diphosphacyclopentadiene ring is not coordinated to the molybdenum, presumably due to the geometric constraints imposed on the ring by the carbene unit; therefore, the molybdenum is a 16-electron center.

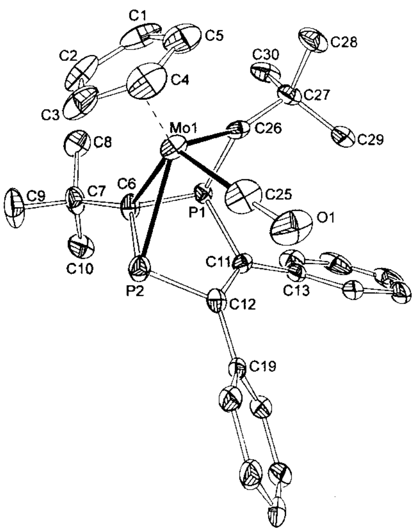

Figure 1. Molecular structure of the cation of complex **7**, with hydrogen atoms removed for clarity.

This remarkable reaction is without precedent and serves to emphasize not only the versatility of the $P{\equiv}CBu^t$ ligand but also how its reaction chemistry differs from that of alkynes. The only previous examples of cyclocotrimerization reactions at a metal center between an alkyne and a phosphaalkyne are the formation of $[Fe\{\eta^4(4e)\text{-}1,3\text{-}P_2C_2Bu^t{}_2\}\{\eta^6$-2,4-di-*tert*-butyl-1,3-diphosphabenzene$\}]$ on reaction of $[Fe(\eta^2\text{-}C_2H_4)_2(\eta^6\text{-toluene})]$ with $P{\equiv}CBu^t$ and $HC{\equiv}CH$ and the stepwise rhodium-mediated formation of $(\eta^5\text{-}C_9H_7)Rh(\eta^4$-2,4-di-*tert*-butyl-5,6-diphenyl-1,3-diphosphabenzene) from $RhCl(\eta^2\text{-}PhC_2Ph)(PCy_3)_2$ and $P{\equiv}CBu^t$.[15,16]

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Supporting Information Available: Experimental and selected characterization details for all of the complexes (including crystallographic data for complex **7**), as well as the coordinates for the optimized geometries of **A**−**C**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] Crystal data for **7**: empirical formula $C_{36.7}H_{33}F_6MoOP_3$, $T = 293(2)$ K, $\lambda = 0.710\,70$ Å, space group $P2_1/c$, $a = 13.526(3)$ Å, $b = 11.326(3)$ Å, $c = 23.276(5)$ Å, $\alpha = 90°$, $\beta = 104.41(2)°$, $\gamma = 90°$, $V = 3453.6(14)$ Å^3, $Z = 4$, R indices ($I > 2\sigma(I)$) R1 = 0.0511 and wR2 = 0.1251.

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