Synthesis, Reactivity, and Theoretical Studies of the η^2 (4e)-Bonded Phosphaalkyne Complex $[CpMo{P(OMe)_{3}}_{2}{\eta^{2}(4e)} \rightarrow ECBu^{t}][B(C_{6}F_{5})_{4}]$ and the **Molybdenum-Mediated Cyclocotrimerization of Alkyne** and Phosphaalkyne Ligands

Andrew D. Burrows,[†] Nicholas Carr,[†] Michael Green,^{*,†,‡} Jason M. Lynam,^{†,‡} Mary F. Mahon,[†] Martin Murray,[‡] Boggavarapu Kiran,[§] Minh T. Nguyen,^{§,||} and Cameron Jones⊥

Department of Chemistry, University of Bath, Claverton Down, Bath, U.K. BA2 7AY, Śchool of Chemistry, University of Bristol, Cantock's Close, Bristol, U.K. BS8 1TS, Department of Chemistry, University of Leuven, Celestijueleua 200F, B-3001 Leuven, Belgium, and Department of Chemistry, University of Wales, Cardiff, P.O. Box 912, Park Place, Cardiff, U.K. CF1 3TB

Received February 26, 2002

Summary: Whereas the cations $[CpMo\{P(OMe)_3\}_2\{\eta^2(4e)\}$ alkyne}]⁺ do not react with alkynes or $P = CBu^t$, the newly synthesized isostructural phosphaalkyne complex $[CpMo\{P(OMe)_3\}_{2}\{\eta^2(4e)-P=CBu^t\}][B(C_6F_5)_4], which is$ unreactive towards PhC₂Ph, readily reacts via an associative stepwise process with $P = CBu^t$ to give [CpMo- $\{P(OMe)_3\}_2[\eta^4-1, 3-P_2C_2Bu^t_2\}][B(C_6F_5)_4]$. A further interesting difference in alkyne and phosphaalkyne chemistry was observed when it was found that CpMoCl(CO)- $\{\eta^2(4e)-PhC_2Ph\}$ reacts with $TlPF_6$ and $P \equiv CBu^t$ to give the unusual 16-electron cyclocotrimerization product

 $[CpMo] = C(Bu^t)PC(Bu^t) = PC(Ph) = C(Ph) \} (CO)][PF_6], iden$ tified by single-crystal X-ray crystallography.

While the isolobal $(P \leftrightarrow CR)$ and diagonal (P/C)relationships have been used¹ to relate the structural chemistries of alkyne and phosphaalkyne transitionmetal complexes, these simple ideas are of less value in predicting and rationalizing relative reactivity patterns. During investigations^{2–4} to develop the chemistry of $\eta^2(4e)$ -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 $[CpMo{P(OMe)_3}_2{\eta^2(4e)}-P=C Bu^{t}$]⁺ (1), to compare the chemistry of these species with that of the alkyne-substituted⁵ cations [CpMo- $\{P(OMe)_3\}_2 \{\eta^2(4e)\text{-alkyne}\}\}^+$. Since it has been shown that both the cation⁶ $[(\eta^5-C_9H_7)Mo(NCMe)_2(CO)_2]^+$ and

- (3) Carr, N.; Green, M.; Mahon, M. F.; Jones, C.; Nixon, J. F. J. Chem. Soc., Chem. Commun. **1995**, 2191.

the neutral complex⁷ CpMoCl(CO)₃ react (room temperature and 40 °C, respectively) with P≡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 observation⁸ that the $\eta^2(3e)$ -vinyl complex

 $CpMo{=C(Ph)CHPh}{P(OMe)_3}_2$ (2) (Scheme 1) reacts $(CH_2Cl_2, -50 \ ^\circ C \rightarrow +25 \ ^\circ C)$ with $[PhNHMe_2][X]$ (X = $B(C_6F_5)_4^-$, BF_4^-) to give the labile cationic complexes $[CpMo{P(OMe)_3}_2{\eta^2(2e)-trans-stilbene}][X], which in$ turn react ($-78 \degree C \rightarrow +25 \degree C$) with PhC=CPh to afford $[CpMo{P(OMe)_3}_2{\eta^2(4e)-PhC_2Ph}][X]$ (3). Thus, we reacted (CH₂Cl₂, -78 °C) [PhNHMe₂][X] with 2 and warmed the reaction mixture to room temperature before recooling to -78 °C and adding 1 mol equiv of P≡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 $[CpMo{P(OMe)_3}_2{\eta^2(4e)}$ - $P = CBu^{t}$][X] (**1a**, X⁻ = B(C₆F₅)₄⁻; **1b**, X = BF₄⁻; 86% yield) precipitated as green microcrystalline powders.

The ${}^{13}C{}^{1}H$ and ${}^{31}P{}^{1}H$ NMR spectra (CD₂Cl₂) of 1a showed resonances consistent⁴ with the presence of an $\eta^2(4e)$ -bonded P=CBu^t ligand. The contact carbon appeared as a doublet (${}^{1}J_{PC} = 122.7$ Hz) at δ 334.8 and the contact phosphorus as a triplet (${}^{2}J_{PP} = 33.4 \text{ Hz}$) at very low field, δ 491.6. Interestingly the appearance of the contact phosphaalkyne ³¹P 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

^{*} To whom correspondence should be addressed at the University of Bristol. E-mail: michael.green@bris.ac.uk.

University of Bath.

[‡] University of Bristol.

[§] University of Leuven.

[&]quot;E-mail: minh.nguyen@chem.kuleuven.ac.be.

[⊥] University of Wales.

Conversity of wates.
 Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*, Wiley: New York, 1998.
 Brauers, G.; Green, M.; Jones, C.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* 1995, 1125.

⁽⁴⁾ Burrows, A. D.; Dransfeld, A.; Green, M.; Jeffrey, J. C.; Jones, C.; Lynam, J. M.; Nguyen, M. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 3221.

^{(5) (}a) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen,

⁽a) Anien, S. K.; Beevor, K. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435. (b) Allen, S. R.; Beevor, R. G.; Green, M.; Orpen, A. G.; Paddick, K. E.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 591.
(6) Hitchcock, P. B.; Maah, M. J.; Nixon, J. F.; Green, M. *J. Organomet. Chem.* **1994**, 466, 153.

⁽⁷⁾ Weller, A. S.; Andrews, C. D.; Burrows, A. D.; Green, M.; Lynam,
J. M.; Mahon, M. F.; Jones, C. *Chem. Commun.* **1999**, 2147.
(8) Beddows, C. J.; Burrows, A. D.; Connelly, N. G.; Green, M.; Lynam, J. M.; Paget, T. J. *Organometallics* **2001**, *20*, 231.



^{*a*} L = P(OMe)₃. Legend: (i) +[PhNHMe₂][X], +P=CBu^t, *–trans*-stilbene, –PhŇMe₂, CH₂Cl₂.

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 $[CpMo{P(OH)_3}_2{\eta^2(4e)-P=CMe}]^+$ (A) was calculated at the B3LYP/TZVP level using the Turbomole program,⁹ and for purposes of comparison the geometry of the related cation $[CpMo{P(OH)_3}_2{\eta^2(4e)}$ - $HC \equiv CMe\}]^+$ (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 $[CpMo{P(OMe)_3}_2{\eta^2(4e)-HC_2Bu^t}]^+$, 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 found¹⁰ within a range of transition-metal $\eta^2(4e)$ 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 recent⁴ findings that a short tantalum to carbon contact distance, Ta-CBu^t (2.079(9) Å), occurs in the complex Cp*TaCl₂{ η^2 -(4e)-P=CBu^t}.

EHMO calculations¹¹ based on the DFT-calculated bond parameters for **A** and **B** of the π_{\parallel} , π_{\perp} , π_{\parallel}^* , and π_{\perp}^* orbital occupancies gave further structural insight. The phosphaalkyne complex A has the orbital occupancies π_{\parallel} (1.866), π_{\perp} (1.898), π_{\parallel}^{*} (1.064), and π_{\perp}^{*} (0.312) and the alkyne complex **B** occupancies π_{\parallel} (1.724), π_{\perp} (1.796), π_{\parallel}^* (0.894), and π_{\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 π_{\perp}^* orbital in each complex. The alkyne ligands in the cations [CpMo- $\{P(OMe)_3\}_2 \{\eta^2(4e)\text{-alkyne}\}^+$ align themselves parallel to one of the Mo–P vectors to maximize π -back-bonding from a metal d orbital into the π_{\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 $[CpMo{P(OMe)_3}_2{\eta^2(4e)}$ alkyne}]⁺. However, whereas the alkyne cations are unreactive toward excess alkyne, 1a was found to react (1d) at room temperature with $P \equiv CBu^t$ in CH_2Cl_2 to give a high yield of the complex $[CpMo{P(OMe)_3}_2{\eta^4}$ -

 $1,3-P_2C_2Bu_2^{t}$ [B(C₆F₅)₄] (**4**). The room-temperature ³¹P- $\{^{1}H\}$ NMR (CH₂Cl₂) 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-P₂C₂Bu^t₂ ligand. When the temperature is lowered to -60 °C, this broad signal⁷ collapsed to give two sharp resonances at δ 59.7 and 49.2, implying that the η^4 -1,3-P₂C₂Bu^t₂ 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, $\Delta v = 1691$ Hz, $\Delta G^{\ddagger} =$ 48.0 kJ mol⁻¹).12

In a previous study² we had obtained evidence for the stepwise formation of the η^4 -1,3-P₂C₂Bu^t₂ ligand; however, our observation of the reaction $1a \rightarrow 4$ 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-P₂C₂Bu^t₂) 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 $P \equiv CBu^t$ in CD_2Cl_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 secondorder kinetics ($k = (6.79 \pm 0.05) \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Further mechanistic insight was gained from a series of ³¹P magnetization transfer experiments. When a solution (CD_2Cl_2) containing approximately equimolar amounts of **1a** and P(OMe)₃ was prepared and a ³¹P-^{{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 \times 10⁻³ dm³ mol⁻¹ s⁻¹. The same result was obtained with the alkyne complex $[CpMo{P(OMe)_3}_2$ - $\{\eta^2(4e)-PhC_2Ph\}|[BF_4]^{5a}$ (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 ($\omega_{1/2}(P{OMe}_3) = 77.7 \text{ Hz})$, 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 $\eta^2(4e)$ to $\eta^2(2e)$ to allow coordination of a third phosphite.

⁽⁹⁾ Ahlrichs, R.; Bar, M.; Huser, M.; Horn, H.; Kolmel, C. Chem. (b) Hill (19) (12) (162, 165.
 (10) Templeton, J. L. Adv. Organomet. Chem. 1989, 29, 1.

⁽¹¹⁾ EHMO calculations were performed with the CACAO 98 program: Mealli, C.; Prosierpio, D. M. *J. Chem. Educ.* **1990**, *67*, 399.

⁽¹²⁾ The low-temperature (-50 °C) ³¹P NMR spectrum (CH₂Cl₂) did not show any evidence for an interaction between the η^4 -1,3-P₂C₂But₂ ligand and $B(C_6F_5)_4^-$; this makes an interesting comparison with the findings⁶ that, in the solid-state structure of the complex $[(\eta^5-C_9H_7) Mo(CO)_{2}\{\eta^{4}-1, 3-P_{2}C_{2}Bu^{t}_{2}\}][BF_{4}]$, the BF_{4}^{-} anion is interacting with one of the phosphorus centers, this species undergoing reversible dissociation in solution.

⁽¹³⁾ Creve, S.; Nguyen, M. T.; Vanquickenborne, L. G. Eur. J. Inorg. Chem. 1999, 1281.

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 ($\eta^2(4e) \rightarrow \eta^2(2e)$) so as to facilitate coordination of a second $P \equiv CBu^t$. Significantly, when ³¹P 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 $[CpMo\{P(OMe)_3\}_2 - \{\eta^2(2e)-P \equiv CBu^t\}_2][B(C_6F_5)_4]$ 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 $[CpMo(CO)(\eta^2 - PhC_2Ph)(\eta^2 - P \equiv CBu^t)]^+$. However, the subtle nature of this chemistry was revealed when we examined the reaction of $P \equiv CBu^t$ with $CpMoCl\{\eta^2(4e)-PhC_2Ph\}(CO)$ (**6**) in CH_2Cl_2 solution in the presence of $TlPF_6$.

Addition at room temperature of P=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 TICI and a change in color of the reaction mixture. Filtration (Celite) gave a red solution which on addition of Et₂O 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 ³¹P{¹H} NMR spectra (CDCl₃) revealed resonances corresponding to the linking of two phosphaalkynes and one PhC₂Ph ligand to form a P₂C₄Bu^t₂Ph₂ fragment coordinated onto a [Mo- $(CO)(\eta^5-C_5H_5)]^+$ center. Although the presence of two doublet resonances in the ³¹P{¹H} NMR spectrum at δ 47.7 ($J_{PP} = 20$ Hz) and $\delta - 86.8$ ($J_{PP} = 20$ Hz) implied that a novel coupling reaction had occurred, attempts to obtain further structural insight by recording a ¹³C-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 $[CpMo={C(Bu^t)PC(Bu^t)=PC(Ph)=C(Ph)}(CO)]-[PF_6]$ was established by a single-crystal X-ray diffraction study.¹⁴ This revealed (see Figure 1) that a [Mo- $(CO)(\eta^5-C_5H_5)$]⁺ 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 puck-



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

ered 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 1,3diphosphacyclopentadiene 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.

This remarkable reaction is without precedent and serves to emphasize not only the versatility of the P= 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{ η^4 (4e)-1,3-P₂C₂Bu^t₂} η^6 -2,4-di-*tert*-butyl-1,3-diphosphabenzene)] on reaction of [Fe(η^2 -C₂H₄)₂(η^6 -toluene)] with P=CBu^t and HC=CH and the stepwise rhodium-mediated formation of (η^5 -C₉H₇)Rh(η^4 -2,4-di-*tert*-butyl-5,6-diphenyl-1,3-diphosphabenzene) from RhCl(η^2 -PhC₂-Ph)(PCy₃)₂ and P=CBu^t.^{15,16}

Acknowledgment. We thank the EPSRC (N.C., J.M.L.), the Ramsay Memorial Fellowship Trust and the University of Bristol (for a fellowship to J.M.L.), and the Leverhulme Trust for an Emeritus Professorship (M.G.); the Leuven group is indebted to the KULeuven Research Council (GOA program) for financial support. We also thank Dr. C. J. Beddows for preliminary experiments.

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.

OM020169G

⁽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, $\alpha = 90^\circ$, $\beta = 104.41(2)^\circ$, $\gamma = 90^\circ$, V = 3453.6(14) Å³, Z = 4, R indices $(I > 2\sigma(J))$ R1 = 0.0511 and wR2 = 0.1251.

⁽¹⁵⁾ Böhm, D.; Knoch, S.; Kummer, U.; Schmidt, U.; Zenneck, U. Angew. Chem., Int. Ed. Engl. **1995**, *34*, 198.

⁽¹⁶⁾ Binger, P.; Haas, J.; Betz, P.; Krüger, C. *Chem. Ber.* **1995**, *128*, 737.