Synthesis of a Mononuclear η²(4e)-Bonded Phosphaalkyne Complex, Transformation into an η⁴-1,3-Diphosphacyclobutadiene Complex

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The synthesis of the first mononuclear η²(4e)-bonded phosphaalkyne complex 1 is described, the ³¹P and ¹³C NMR spectra showing the expected low field contact resonances; reaction of 1 with a molecule of Bu^{t}C≡P leads to the formation of an η⁴-1,3-diphosphacyclobutadiene complex, thus demonstrating the stepwise nature of the formation of the P₂C₂ ring.

The synthesis of phosphaalkynes[1] and the subsequent development of their organotransition metal chemistry[2-4] has been an important theme in modern organophosphorus chemistry. Although these studies have often demonstrated a relationship between the reactions of phosphaalkynes and alkynes it is interesting that there are no reports† of mononuclear complexes in which the phosphaalkyne ligand adopts an η²(4e)-bonding mode, a type of bonding which is well established[5,6] in alkyne chemistry. We now report the synthesis of the first mononuclear η²(4e)-bonded phosphaalkyne complex, and a study of its reactivity.

Our initial attempt to access complexes of this type had focused on the reaction of Bu^{t}C≡P with cis-[Mo(NCMe)₂(CO)₂(η⁵-C₉H₇)][BF₄] in the expectation of obtaining the cation [Mo(η²-Bu^{t}CP)₂(CO)(η⁵-C₉H₇)][BF₄]; however, as previously reported[7] a facile cyclodimerisation reaction occurs leading to the formation of [Mo{η³-(Bu^{t}CPC(Bu^t)PFBF₃)}-(CO)₂(η⁵-C₉H₇)]. An alternative, and in the event successful, approach to the problem was suggested by the observations[8] summarised in Scheme 1, where it was found that reaction (THF, −78 → 25 °C, 12 h, room temp.) of [Mo(η²-PhC₂Ph)-{P(OMe)₃}₂(η-C₅H₅)][BF₄][9] with the di-Grignard reagent CH₂(MgI)₂ led (78% yield) to the formation of the X-ray crystallographically characterised zwitterionic blue crystalline η²(4e)-bonded diphenylacetylene complex A containing an anionic chair-shaped bidentate ligand. Treatment (THF, −78 → 25 °C) of this complex with K[BHBu^{s}₃] afforded the green anionic η²(3e)-vinyl complex B, which on protonation with HBF₄·Et₂O in the presence of PhC₂Ph, resulted in the regeneration of A and the formation of trans-stilbene. This suggested that the phosphaalkyne Bu^{t}C≡P might also displace trans-stilbene from the presumed intermediate [Mo(η²-trans-stilbene){η²-(MeO)₂POBF₂OP(OMe)₂}(η-C₅H₅)] C, thus providing access to a η²(4e)-bonded phosphaalkyne complex structurally related to A.
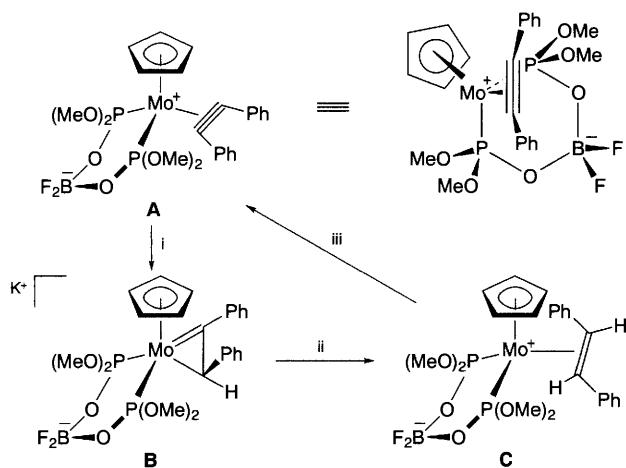
Protonation (THF, −78 → 25 °C) of K[Mo=C(Ph)CHPh{η²-(MeO)₂POBF₂OP(OMe)₂}(η-C₅H₅)] with HBF₄·Et₂O led to a change from green to yellow. When the yellow reaction mixture was recooled to −78 °C, and Bu^{t}C≡P (1 equiv.) was added, there was an immediate change to deep green. Workup by removal of the solvent in vacuo, extraction with toluene followed by addition of hexane and cooling (−20 °C), afforded a low melting green complex 1 (65% yield from B) (Scheme 2).

The ¹H NMR spectrum‡ of 1 showed the features expected for a complex containing only one phosphaalkyne coordinated to a [Mo{η²-(MeO)₂POBF₂OP(OMe)₂}(η-C₅H₅)] fragment, where in solution on the NMR timescale the phosphaalkyne, in a similar way to alkynes,[6] undergoes a facile windscreen-wiper motion. This was confirmed by the appearance in the ³¹P{¹H} NMR spectrum,‡ which is invariant in the temperature range +25 → −80 °C, of two singlet resonances, one at δ 157.3 owing to the bidentate ligand [(MeO)₂POBF₂OP(OMe)₂]⁻, and the other at δ 467.8. This low-field signal is assigned to the phosphorus of an η²(4e)-bonded Bu^{t}C≡P, and is very deshielded compared with the resonances exhibited by the η²(2e)-bonded Bu^{t}C≡P ligands present in the platinum complexes [Pt(η²-Bu^{t}CP)(PPh₃)₂] (δ 84.1),[10] [Pt(η²-Bu^{t}CP)(diphos)] (δ 87.7)[11] and [Pt(η²-Bu^{t}CP)(η²-Ph₂PCH₂CMe(CH₂PPh₂)CH₂PPh₂)] (δ 82.3).[12] Support for this assignment is, interestingly, provided by the recent[13] report that the ³¹P{¹H} NMR spectrum of the aromatic phosphirenylium cation [PhCC(Bu^t)P][B(OSO₂-CF₃)₄] shows a resonance at δ 309.7 deshielded by 313 ppm from PhC=C(Bu^t)POSO₂CF₃. Thus, because of the isolobal relationship MoL₂(η-C₅H₅) ←→ CR, a similar low-field resonance would be expected (see Scheme 3) in the ³¹P{¹H} NMR spectrum of 1; indeed, it is proposed that the signature of a η²(4e)-bonded phosphaalkyne is a ³¹P resonance in the region of δ 450.

The ¹³C NMR spectrum of 1 also provides an insight into the bonding mode adopted by the coordinated phosphaalkyne. It is well known[5] that with mononuclear transition metal alkyne
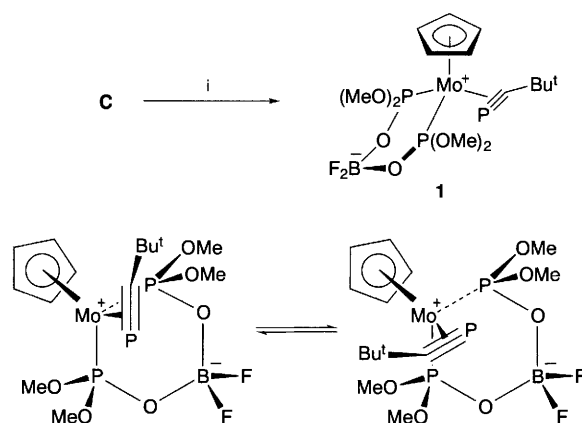

Scheme 1 Reagents and conditions: i, K[BHBu^{s}₃], THF, −78 → 25 °C; ii, HBF₄·Et₂O, THF, −78 → 25 °C; iii, PhC₂Ph, CH₂Cl₂, −trans-stilbene

Scheme 2 Reagents and conditions: i, Bu^{t}C≡P, −trans-stilbene, THF, −78 → 25 °C

complexes there is a correlation between the contact ^{13}C chemical shifts and the effective number of electrons donated to the metal, and it was clearly important to consider whether a similar correlation exists for phosphaalkyne complexes. The ^{13}C{^{1}H} spectrum‡ of **1** shows a low field doublet [*J*(PC) 114.4 Hz] of triplet [*J*(PC) 6.6 Hz] at δ 328.5, which on comparison with the ^{13}C shift observed for uncoordinated Bu^{t}C≡P [δ 184.3 (C₆D₆), d, *J*(PC) 38.6 Hz], and for the presumed η²(2e)-bonded phosphaalkyne complex [Pt(η²-Bu^{t}CP)(PPh₃)₂] [δ 242.0–239.5 (C₆D₆), m] suggests that such a correlation does indeed exist. However, it has been reported[15] that the complex [Ti(η²-Bu^{t}CP)(PMe₃)(η-C₅H₅)₂] shows phosphaalkyne contact carbon and phosphorus resonances at δ 298.6 and 122.7, respectively, suggesting that although the ^{13}C shift observed for **1** is consistent with an η²(4e)-bonding mode, the distinction between η²(4e)- and η²(2e)-bonding for a phosphaalkyne as observed by contact carbon shifts, is less pronounced than with alkynes.§ Thus, in summarising the NMR data it is the ^{31}P chemical shift which clearly suggests that the phosphaalkyne ligand present in **1** is able to act simultaneously as a single-faced π-acid (through π∥) and as a single-faced π-base (through π⊥).

Complexes containing η²(4e)-bonded phosphaalkyne ligands are also interesting in the context of reactivity. Indeed, treatment of a toluene solution of **1** with Bu^{t}C≡P (1 equiv.) resulted in a colour change over a period of three days from green to yellow. Column chromatography of the reaction mixture on alumina and elution with dichloromethane afforded a single yellow band, which on recrystallisation from CH₂Cl₂–hexane afforded (48% yield) yellow crystals of **2**, characterised by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy‡ as a 1,3-diphosphacyclobutadiene complex with the structure illustrated in Scheme 4. Although there is an example in the literature of an alkyne complex reacting with a phosphaalkyne to give a
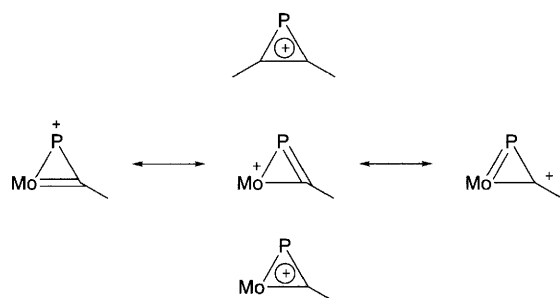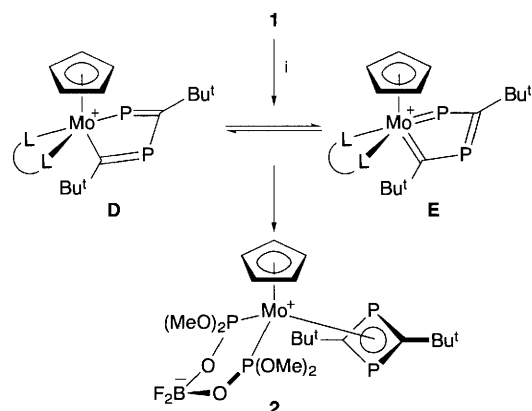
η⁴-phosphacyclobutadiene ligand,[14] the stepwise nature of the formation of η⁴-1,3-diphosphacyclobutadienes has prior to this work not been demonstrated, despite frequent reports of the formation of this ligand on reaction of metal complexes with phosphaalkynes.[2,4] It is suggested that the transformation **1** → **2** involves a switch [η²(4e) → η²(2e)] in the bonding mode of the coordinated Bu^{t}C≡P ligand, which is present in **1**, so as to accommodate a second η²(2e)-bonded phosphaalkyne prior to its head-to-tail coupling to form the possible precursors **D** and **E** (Scheme 4) of the 1,3-diphosphacyclobutadiene ring.

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Footnotes

† It is interesting to note, however, that it has been reported[15] that treatment of the complex [Ti(η²-Bu^{t}CP)(PMe₃)(η-C₅H₅)₂] with BEt₃ leads to loss of PMe₃ as the adduct Me₃PBEt₃ and formation of an equilibrium mixture, which is thought to contain [Ti(η²-Bu^{t}CP)(η-C₅H₅)₂] and the corresponding phosphorus bridging dimer. Interestingly, the ^{31}P{^{1}H} NMR spectrum ([²H₈]THF, −40 °C) of the mixture shows a low-field signal at δ 431.6; however, the signal was very broad (*h*½ ca. 970 Hz), and from this mixture only the aforementioned dimer was isolated.

‡ *Selected spectroscopic data* for **1**: NMR ^{1}H(C₆D₆) δ 5.43 [t, 5 H, C₅H₅, *J*(PH) 1.4 Hz], 3.52 (vt, 6 H, POMe, *N* 11.2 Hz), 3.31 (vt, 6 H, POMe, *N* 11.5 Hz), 1.52 (s, 9 H, Bu^t); ^{13}C{^{1}H}(C₆D₆) δ 328.5 [dt, P≡C, ^{1}*J*(PC) 114 Hz, ^{2}*J*(PC) 6.6 Hz], 93.8 (s, C₅H₅), 52.0 (vt, POMe, *N* 8.5 Hz), 51.5 (vt, POMe, *N* 6.1 Hz), 34.0 (s, C*Me*₃), 30.1 (s, C*Me*₃); ^{31}P{^{1}H}(C₆D₆) δ 467.8 (s, P≡C), 157.3 (s, POMe). For **2**: NMR ^{1}H(CDCl₃) δ 5.56–5.54 (m, 5 H, C₅H₅), 3.68 (vt, 6 H, POMe, *N* 11.5 Hz), 3.62 (vt, 6 H, POMe, *N* 10.9 Hz), 0.90 (s, 18 H, Bu^t); ^{13}C{^{1}H}(CDCl₃), 128.6–128.2 (m, Bu^{t}C=P), 93.8 (s, C₅H₅), 52.7 (vt, POMe, *N* 10.8 Hz), 34.8–34.6 (m, C*Me*₃), 33.7–33.6 (m, C*Me*₃); ^{31}P{^{1}H}(CDCl₃) δ 151.7 (s, POMe), 56.5 (s, Bu^{t}CP), 51.1 (s, Bu^{t}CP).

§ It is interesting that the complex [WCl(η²-MeCN)(PMe₃)₂(bipy)][PF₆], which contains an η²(4e)-bonded nitrile, shows a low-field contact ^{13}C resonance at δ 135 to low field of uncoordinated methylcyanide.[16]

Scheme 3

Scheme 4 *Reagents and conditions*: i, Bu^{t}C≡P, toluene, 25 °C, 3 d. L L = [(MeO)₂POBF₂OP(OMe)₂]⁻.

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