ChemComm

Facile, metal promoted, oxidation of η^4-1,3-diphosphacyclobutadiene by water or methanol: synthesis of [MoCl(CO)(η^4-1,3-$P_2C_2Bu^t_2$)(η^5-L)] (L = C_5H_5, C_5Me_5) and [MoCl(CO){$\eta^3,\lambda^3,\lambda^5$-$PC_2Bu^t_2PH(OR)$}($\eta^5$-L)] (L = C_5H_5, R = H, Me)

Andrew S. Weller,[a] **Christopher D. Andrews,**[a] **Andrew D. Burrows,**[a] **Michael Green,***[a] **Jason M. Lynam,**[a] **Mary F. Mahon**[a] **and Cameron Jones**[b]

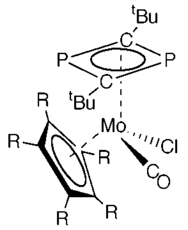
[a] *Department of Chemistry, University of Bath, Claverton Down, Bath, UK BA2 7AY. E-mail: a.s.weller@bath.ac.uk*
[b] *Department of Chemistry, University of Wales Cardiff, PO Box 912, Park Place, Cardiff, UK CF1 3TB*

Received (in Basel, Switzerland) 29th June 1999, Accepted 13th September 1999

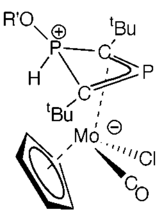
The new complexes [MoCl(CO)(η^4-1,3-$P_2C_2Bu^t_2$)(η^5-L)] (L = C_5H_5 1, C_5Me_5 2) are reported; facile oxidation of 1 with water or methanol affords a rare example of a mixed valence phosphaphosphonietinyl in [MoCl(CO){$\eta^3,\lambda^3,\lambda^5$-$PC_2Bu^t_2$-PH(OR)}($\eta^5$-$C_5H_5$)] (R = H, Me), which has also been structurally characterised for R = H.

We have previously reported on studies directed towards the development of the transition metal chemistry of η^2(4e)-bonded phosphaalkynes.[1,2] Mindful of the relationship between phosphaalkynes and their isoelectronic alkyne counterparts we have examined the reactivity of P≡CBu^t towards the molybdenum complexes [MoCl(CO)$_3$L] (L = η^5-C_5H_5 or η^5-C_5Me_5). It has been shown[3,4] that [MoCl(CO)$_3$(η^5-C_5H_5)] reacts thermally with PhC_2Ph to form the four-electron donor diphenylacetylene complex [MoCl(η^2-PhC_2Ph)(CO)(η^5-C_5H_5)]. In the event, however, this study has revealed for the first time that a coordinated 1,3-diphosphacyclobutadiene ligand can undergo a facile and selective reaction with water or methanol to give a mixed valence $\eta^3,\lambda^3,\lambda^5$-phosphaphosphonietinyl ligand.

Addition of 2.1 equiv. of P≡CBu^t to pentane solutions of [MoCl(CO)$_3$L] (L = η^5-C_5H_5 or η^5-C_5Me_5) and gentle heating (40 °C) for 78 and 24 h respectively, results in the isolation of orange [MoCl(CO)(η^4-1,3-$P_2C_2Bu^t_2$)L] (L = η^5-C_5H_5 **1**, η^5-C_5Me_5 **2**) in moderate and good yield, respectively.



1 R = H
2 R = Me



3 R' = H
4 R' = Me

A single crystal X-ray diffraction study performed on **2** confirmed the structure, and this will be reported in full at a later date.[5] The NMR spectra of **1** and **2** are also fully consistent with this description.† Two different environments are observed for each of the phosphorus and carbon atoms in the 1,3-diphosphacyclobutadiene ring and the appended Bu^t groups, as a consequence of the asymmetry introduced by the carbonyl and chloride ligands. This demonstrates that the 1,3-$P_2C_2Bu^t_2$ ligand does not rotate on the NMR timescale at room temperature, an observation that has been precluded previously by the relatively high symmetry of associated metal fragments in other 1,3-diphosphacyclobutadiene complexes.[6,7] However, the 1,3-diphosphacyclobutadiene ligand in **1** does begin to rotate on the NMR timescale at higher temperatures, the onset of coalescence of the Bu^t signals being observed in the ^{1}H NMR spectrum at +60 °C at 400 MHz.

Complex **2** is remarkably stable to the ambient environment, C_6D_6 solutions remaining unchanged (by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy) on exposure to air or water for 2 weeks. In sharp contrast, **1** undergoes reaction with water (slowly with atmospheric, *ca.* 2 days on addition of 10 equiv.) or methanol (7 days) to afford complexes in which one of the coordinated phosphorus atoms has undergone formal oxidative addition of HOR (R = H, Me). The resulting complexes [MoCl(CO){$\eta^3,\lambda^3,\lambda^5$-$PC_2$-$Bu^t_2PH(OR)$}L] (L = η^5-C_5H_5, R = H **3**, or Me **4**), are formed in essentially quantitative yield for **3** and in *ca.* 90% yield for **4** (impurities present are compound **3** and at least two other unidentified compounds). The solid state structure of **3** is shown in Fig. 1.‡

It is apparent that one of the phosphorus atoms is no longer coordinated to the metal [Mo(1)···P(1) 2.8745(13) Å]. Moreover, P(1) is bent away from the plane of the η^3-phosphaallyl group [C(12)–P(2)–C(7)] by 25.12° and also bears a hydroxy group [P(1)–O(1) 1.581(3) Å] and a direct P–H bond. Both the hydroxy and phosphorus bound hydrogens were located in the difference map and refined without constraints. The remaining bond lengths and angles are consistent with the description of **3** as a $\eta^3,\lambda^3,\lambda^5$-phosphaphosphonietinyl complex, and as such are unremarkable.

From a bonding perspective, **3** can be viewed in terms of the two canonical forms **A** and **B**; one in which there is a formal bond between Mo and P(1) (**A**) or a zwitterionic alternative in which there is no bond between these two atoms (**B**). On the basis of the long Mo–P(1) distance coupled with the fact that in the IR spectrum the carbonyl group stretch is observed at > 60 cm^{-1} to lower frequency compared with **1,** which is consistent with a negative charge on Mo, we suggest that **B** represents the

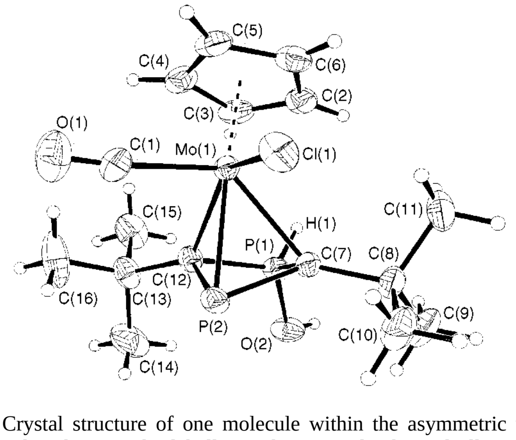
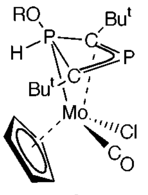
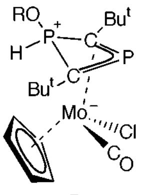


Fig. 1 Crystal structure of one molecule within the asymmetric unit of compound **3** showing the labelling scheme used. Thermal ellipsoids are represented at the 30% probability level. Selected bonds distances (Å): Mo(1)–Cl(1) 2.5468(11), Mo(1)–C(1) 2.036(4), Mo(1)–P(1) 2.8745(13), Mo(1)–P(2) 2.4179(10), P(2)–C(12) 1.848(3), P(2)–C(7) 1.839(3), P(1)–C(12) 1.742(3), P(1)–C(7) 1.742(3), P(1)–O(2) 1.581(3).



A

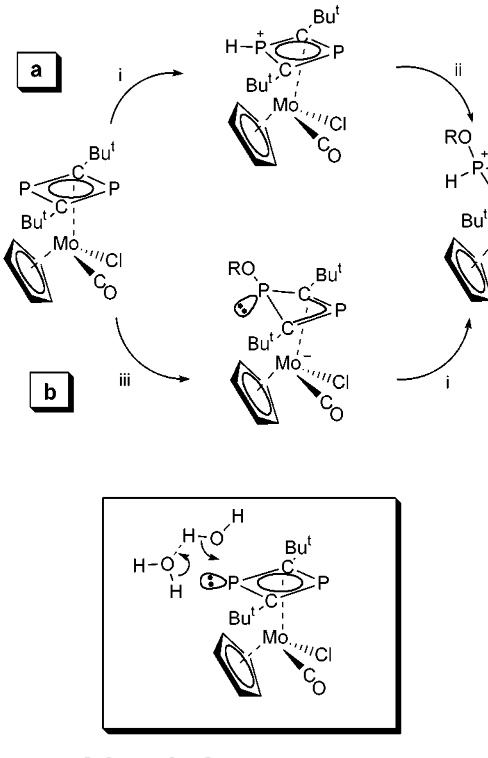


B

mode of bonding in **3**. In either canonical form P(1) may be considered formally as being phosphorus(v).

The NMR data for **3** and **4** are very similar; for both compounds H(1) is observed as a doublet of doublets in the ^{1}H NMR spectrum, the very large value of one of the couples [J(PH) ≈ 500 Hz] confirming the presence of a direct P–H bond. Although the hydroxy proton in **3** is not observed in the ^{1}H NMR spectrum, presumably owing to fast exchange in solution, in **4** the methoxy group is clearly seen as an integral 3H doublet. In the ^{31}P{^{1}H} NMR spectra of **3** and **4** two different phosphorus environments are observed [**3**: δ(^{31}P) 8.9, −15.8, **4**: δ(^{31}P) 10.6, −16.7], shifted significantly to higher field from those in **1**, with the broader, low field resonance, split on retention of coupling to ^{1}H.

As previously stated, the formulation of compounds **3** and **4** corresponds to the unprecedented selective oxidative [P(iii)→P(v)] addition of water or methanol respectively to one of the phosphorus centres present in the 1,3-diphosphacyclobutadiene complex, **1**. Although it has been previously shown that one of the phosphorus lone pairs of a coordinated 1,3-diphosphacyclobutadiene can coordinate onto transition metal Lewis acid fragments,[8] it seems unlikely that the formation of **3** or **4** involves an initial deprotonation of H_2O or MeOH (Scheme 1, pathway **a**,) followed by nucleophilic attack by HO$^-$ or MeO$^-$ on the resulting [1,3-PP(H)C$_2$]$^+$ ring. More likely is pathway **b** of Scheme 1 since it has been previously reported [9] that in the solid state structure of [Mo(η^5-C$_9$H$_7$)(CO)$_2$(η^4-1,3-P$_2$C$_2$Bu$^t{}_2$)][BF$_4$] the [BF$_4$]$^-$ anion is bonded to one of the phosphorus centres resulting in the formation of the zwitterionic species [Mo(η^5-C$_9$H$_7$)(CO)$_2$(η^3-1,3-PC$_2$Bu$^t{}_2$PFBF$_3$)] **5**. Whereas, in solution, [BF$_4$]$^-$ rapidly dissociates from **5**, in the case of the formation of **3** and **4**, *trans*-nucleophilic attack by H_2O or MeOH is consummated by addition of H$^+$ to the phosphorus centre. Additional support for this mechanism comes from the zwitterionic complex [Ru(η^5-C$_5$H$_5$)(η^3-1,3-PC$_2$Bu$^t{}_2$PFCBu^{t}P)] **6**, generated from a putative intermediate resulting from [PF$_6$]$^-$ attack at a coordinated 1,3-diphosphacyclobutadiene ring.[10] There is, of course, a more subtle variation on these two pathways, which depends on hydrogen bonding (Scheme 1) and involves simultaneous protonation and nucleophilic attack. In agreement with these suggestions, involving rate determining breaking of an OH bond, is the observation of a large positive kinetic isotope effect $k_D/k_H \approx 3.6$ [$t_{1/2}$(H$_2$O) 5.5 h, $t_{1/2}$ (D$_2$O) 20 h].



Scheme 1 *i* + [H]$^+$; *ii* + [OR]$^-$ (R = H or Me); *iii* + HOR (R = H or Me), −[H]$^+$.

We have reported here the synthesis of two new readily accessible 1,3-diphosphacyclobutadiene complexes, and for one, facile oxidative addition of water or methanol, a reaction without precedent. The robust nature of **2** combined with the reactivity of **1** presages a wealth of chemistry associated with this system which is currently under investigation.

We thank the EPSRC (J. M. L.) and the University of Bath (C. D. A.) for support.

Notes and references

† *Selected NMR data for the new complexes*: **1**: ^{1}H(CD$_2$Cl$_2$) δ 5.66 (s, 5 H, C$_5$*H*$_5$), 0.89 (br, 9 H, Bu^t), 0.69 (br, 9 H, Bu^t). ^{31}P{^{1}H}(CD$_2$Cl$_2$) δ 86.9 (s, 1 P), 71.1 (s, 1 P). IR (pentane) 1988 cm^{-1}. **2**: ^{1}H(CD$_2$Cl$_2$) δ 1.90 (s, 15 H, C$_5$*Me*$_5$), 0.86 (s, 9 H, Bu^t), 0.82 (s, 9 H, Bu^t). ^{31}P{^{1}H}(CD$_2$Cl$_2$) δ 101.7 [d, 1 P, J(PP) 7 Hz], 74.4 (br, 1 P). IR (CH$_2$Cl$_2$) 1961 cm^{-1}. **3** ^{1}H [(CD$_3$)$_2$CO] δ 8.11 [dd, 1 H, P*H*, J(PH) 4, 499 Hz], 5.58 (s, 5 H, C$_5$*H*$_5$), 1.24 (s, 9 H, Bu^t), 1.03 (s, 9 H, Bu^t). ^{31}P [(CD$_3$)$_2$CO] δ 8.9 [d, 1 P, J(HP) 499 Hz], −15.8 (s, 1 P). IR (KBr) 1921 cm^{-1}. **4**: ^{1}H(C$_6$D$_6$) δ 8.00 [dd, 1 H, PH, J(PH) 5, 496 Hz], 5.41 (s, 5 H, *C*$_5$*H*$_5$), 3.90 [d, 3 H, POMe, J(PH) 12 Hz], 1.00 (s, 9 H, Bu^t), 0.80 (s, 9 H, Bu^t). ^{31}P[(CD$_3$)$_2$CO] δ 10.6 [d, 1 P, J(HP) 496 Hz], −16.7 (s, 1 P). IR (KBr) 1889 cm^{-1}.

‡ *Crystal data*: **3**: C$_{16}$H$_{25}$ClMoO$_2$P$_2$·0.25CH$_2$Cl$_2$, M = 463.92, λ = 0.71069 Å, triclinic, space group $P\bar{1}$ (no. 2), a = 10.067(2), b = 13.036(4), c = 17.169(4) Å, α = 67.90(2), β = 87.66(2), γ = 72.60(1)°, U = 1985.5(9) Å^3, Z = 4, T = 293(2) K, D_c = 1.552 g cm^{-3}, μ = 1.028 mm^{-1}, F(000) = 946; 6974 unique reflections, all data; R_1 = 0.0400 wR_2 = 0.0771 (all data). CCDC 182/1420. See http://www.rsc.org/suppdata/cc/1999/2147/ for crystallographic files in .cif format.

1 G. Brauers, M. Green, C. Jones and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1995, 1125.
2 N. Carr, M. Green, M. F. Mahon, C. Jones and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1995, 2191.
3 J. L. Davidson and D. W. A. Sharp, *J. Chem. Soc., Dalton Trans.*, 1975, 2531.
4 J. L. Davidson, M. Green, F. G. A. Stone and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, 1976, 738.
5 A. S. Weller, C. D. Andrews, A. D. Burrows, M. Green, J. M. Lynam and M. F. Mahon, *unpublished work.*
6 (a) P. Binger, R. Milczarek, R. Mynott, M. Regitz and W. Rösch, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 644; (b) F. G. N. Cloke, K. R Flower, P. B. Hitchcock and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1994, 489; (c) P. B. Hitchcock, M. J. Maah and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1986, 737.
7 The complex [Mo(η^4-P$_2$C$_2$Bu$^t{}_2$)$_3$] [ref. 6(*b*)] has static 1,3-diphosphacyclobutadiene rings on the NMR timescale, but is also sterically very crowded.
8 P. B. Hitchcock, M. J. Maah, J. F. Nixon and C. Woodward, *J. Chem. Soc., Chem. Commun.*, 1987, 844; H. F. Dare, J. A. K. Howard, M. U. Pilotti, F. G. A. Stone and J. Szameitat, *J. Chem. Soc., Chem. Commun.*, 1989, 1409.
9 P. B. Hitchcock, M. J. Maah, J. F. Nixon and M. Green, *J. Organomet. Chem.*, 1994, **466**, 153.
10 P. B. Hitchcock, C. Jones, J. F. Nixon, *Angew. Chem. Int. Ed. Engl.* 1994, **33**, 463.

Communication 9/05240B