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Ligand exchange reactions within the coordination sphere of a molybdenum η^2(4e)-alkyne complex: the formation of an indole in a cascade reaction involving an alkyne and isonitrile ligands

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The exchange of phosphorus-containing ligands within the coordination sphere of molybdenum alkyne complexes is shown to be facile, a similar reaction with CNxyl (xyl = $C_6H_3Me_2$-2,5) results in a remarkable coupling between the alkyne and three isonitrile ligands and C–H bond activation.

Although our earlier studies of the reactions of nucleophilic reagents with mononuclear η^2(4e)-bonded alkyne complexes [Mo{η^2(4e)-alkyne}{P(OMe)$_3$}$_2$(η^5-C_5H_5)][BF_4] led to the discovery of interesting new chemistry including the formation of η^2(3e)-vinyl complexes,[1] there was little evidence to suggest that the trimethylphosphite ligands in these complexes were labile. Recently, however, ^{31}P NMR magnetisation transfer experiments have shown that facile exchange occurs between free P(OMe)$_3$ and the coordinated P(OMe)$_3$ in the complex [Mo{η^2(4e)-PhC$_2$Ph}{P(OMe)$_3$}$_2$(η^5-C_5H_5)][BF_4] **1**.[2] This led us to explore the reaction of these complexes with other ligands and, in expanding our investigation to isonitriles, we have observed the surprising formation of a coordinated substituted indole.

Our preliminary studies with phosphorus ligands indicated that, as expected, ligand exchange at molybdenum was facile, but reversible. Therefore, in order to drive the equilibrium process to completion, an excess of reacting ligand was used. For example, treatment of a CH_2Cl_2 solution (room temperature) of **1** with 10 equivalents of PMe$_2$Ph resulted in an instantaneous colour change from deep purple to blue. Slow diffusion of an Et$_2$O layer into this solution afforded blue crystals of the product **2** in 86% yield. The NMR spectra‡ of a CD_2Cl_2 solution of the crystals indicated that a selective reaction had occurred and that only one P(OMe)$_3$ ligand had been exchanged by a PMe$_2$Ph. Therefore the product was assigned the formula [Mo{η^2(4e)-PhC$_2$Ph}{P(OMe)$_3$}(PMe$_2$Ph)(η^5-C_5H_5)][BF_4].

The structure of **2** was confirmed by a single crystal X-ray diffraction study,§ (Fig. 1), and showed that the alkyne ligand was lying parallel to the Mo–P(OMe)$_3$ vector, consistent with more effective interaction with the $\pi_{\parallel}^{*}$-orbital of the coordinated alkyne.[3] The short Mo–C(alkyne) bond lengths [2.0006(26) and 2.0309(25) Å] and the appearance of a low field resonance (δ 222.5) for the contact-carbons of the alkyne ligand in the ^{13}C NMR spectrum of **2** are consistent with the proposed four-electron bonding mode of the alkyne.[4] In a similar experiment, treatment of a CH_2Cl_2 solution of **1** with dppe {dppe = 1,2-bis(diphenylphosphinoethane)} afforded the known complex [Mo{η^2(4e)-PhC$_2$Ph}(dppe)(η^5-C_5H_5)][BF_4], **3**, in 85% yield. In this case, however, only one equivalent of dppe was required to drive the reaction to completion: presumably the chelate effect prevents any appreciable reaction between **3** and P(OMe)$_3$ to yield **1**. Previously this complex had been obtained in 60% yield by reaction of PhC$_2$Ph with [Mo(dppe)$_2$(η^5-C_5H_5)][BF_4].[5]

In seeking to extend our studies to the preparation of the compound [Mo{η^2(4e)-PhC$_2$Ph}(CNxyl)$_2$(η^5-C_5H_5)][BF_4], we were surprised to observe the molybdenum-mediated formation of a substituted indole. Treatment of a CH_2Cl_2 solution of **1** with 10 equivalents of CNxyl resulted in an instantaneous colour change to deep red. Slow diffusion of Et$_2$O into this solution afforded crystals of **4** in 62% yield. Although the NMR spectra¶ of a CD_2Cl_2 solution of **4** confirmed the presence of a η^5-C_5H_5 ligand the nature of the remaining ligands could not be deduced and therefore the structure of **4** was unambiguously determined by a single crystal X-ray diffraction study.§ The unit cell of **4** contained two crystallographically-independent cations, one of which is shown in Fig. 2.[6] The resulting structure demonstrated that as well as being coordinated to a η^5-C_5H_5 ligand the molybdenum was also bonded to two terminally-bound CNxyl ligands. The remaining coordination sites at the metal were

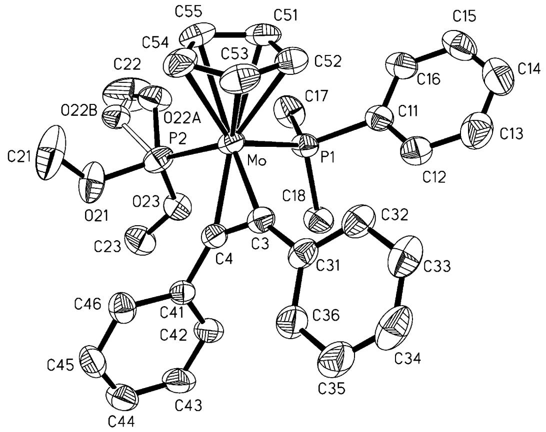

Fig. 1 The molecular structure of the cation of complex **2**. Hydrogen atoms removed for clarity and thermal ellipsoids are shown at the 50% probability level. O(22) is disordered between the two sites O(22A) (80%) and O(22B) (20%).

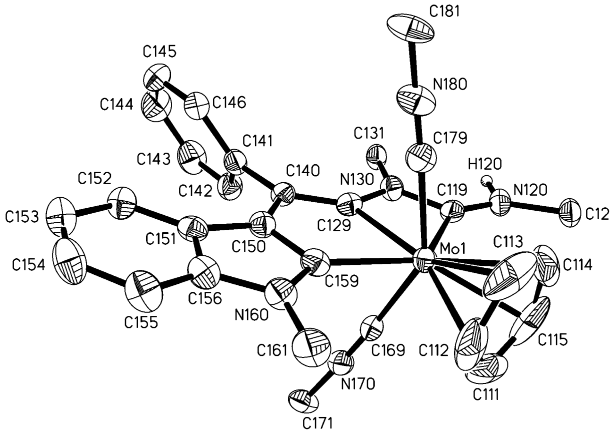

Fig. 2 The molecular structure of one of the independent cations of complex **4**. Only the *ipso* carbons of the xyl rings are shown: hydrogen atoms (except H120) have been removed for clarity. Thermal ellipsoids are shown at the 50% probability level.

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taken up by a single tridentate ligand, formed by the coupling of three isonitrile ligands and the alkyne. Remarkably, one of the phenyl rings which was previously part of the diphenylacetylene ligand had undergone an *ortho*-C–H activation and coupled with an isonitrile to give an indole group. The remainder of the ligand consisted of the carbon and phenyl group of the alkyne and two isonitrile residues forming a C(Ph)–C–N(xyl)–C–NH(xyl) backbone. It is presumed that the proton attached to N(120) was previously attached to the phenyl ring of the alkyne and migrated during the C–H activation process. The three molybdenum–carbon bond lengths [Mo(1)–C(119) 2.209(4), Mo(1)–C(129) 2.189(3), Mo(1)–C(159) 2.254(4), Mo(2)–C(219) 2.203(4), Mo(2)–C(229) 2.195(4), Mo(2)–C(259) 2.271(4) Å] are consistent with metal–carbon single bonds: the lack of low-field resonances in the ^{13}C NMR spectrum of **4** also demonstrates the absence of metal–carbon multiple bonding. This would imply that the molybdenum atom in **4** has undergone a formal oxidation from Mo(II) (in complex **1**) to Mo(IV). On the basis of the bond lengths within the ligand framework, the bonding within the complex is best described by canonical form **A**, (Scheme 1), although a contribution to the bonding from form **B** cannot be excluded. The ligand backbone is planar (maximum torsion angle 7.2°), indicating a significant amount of delocalisation across the skeleton.

Although the transition metal centred coupling of an alkyne and one or two isonitriles has previously been observed[7–9] the formation of compounds like **4** is without precedent. This cascade process apparently involves *ortho*-C–H activation and the selective linking of three isonitriles with an alkyne. There is currently interest in the metal-mediated formation of indoles[10] and we are exploring the scope of this reaction and also methods for the removal of the indole from the molybdenum centre.

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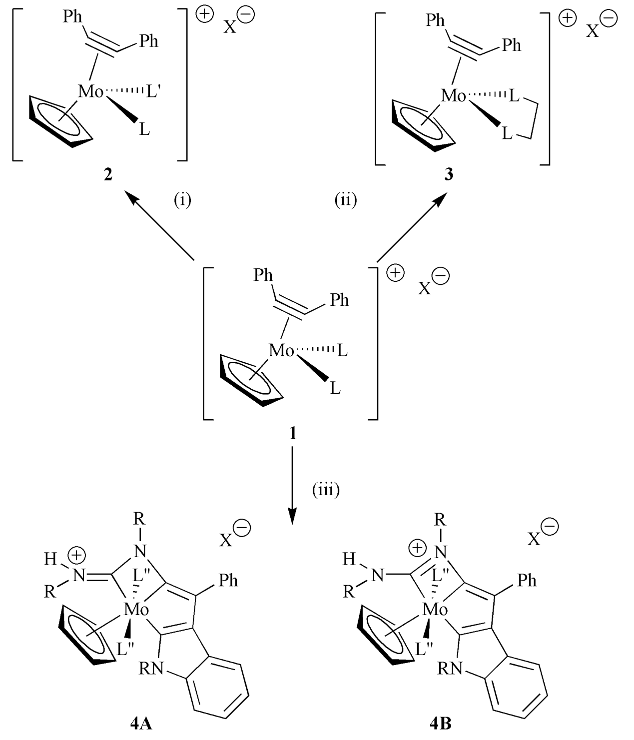

Scheme 1 R = xyl, X$^-$ = BF$_4$, L = P(OMe)$_3$, L′ = PMe$_2$Ph, $\overline{\mathrm{LL}}$ = dppe, L″ = CNxyl. (i) +PMe$_2$Ph, −P(OMe)$_3$; (ii) +dppe, −P(OMe)$_3$; (iii) +CNxyl, −P(OMe)$_3$.

Notes and references

‡ *Selected NMR data* for complex **2**: ^{1}H (CD$_2$Cl$_2$) δ 5.37 (dd, 5 H, $^3J_{PH}$ 1.8, $^3J_{PH}$ 0.7 Hz, C$_5$H$_5$), 3.60 (d, 9 H, $^3J_{PH}$ 11.1 Hz, P{OMe}$_3$), 1.80 (d, 3 H, $^2J_{PH}$ 10.2 Hz, P*Me*$_2$Ph), 1.48 (d, 3 H, $^2J_{PH}$ 10.1 Hz, P*Me*$_2$Ph); ^{31}P (CD$_2$Cl$_2$) δ 175.8 (d, $^2J_{PP}$ 53.0 Hz, P{OMe}$_3$), 30.2 (d, $^2J_{PP}$ 53.0 Hz, PMe$_2$Ph); ^{13}C (CD$_2$Cl$_2$) δ 221.5 (br, Ph*C*$_2$Ph), 139.6 (br, *Ph*C$_2$Ph), 138.9 (dd, $^1J_{PC}$ 48.1, $^3J_{PC}$ 2.0 Hz, PMe$_2$*Ph* C$_1$), 130.2 (d, $^4J_{PC}$ 2.9 Hz, PMe$_2$Ph C$_4$), 129.3 (br, *Ph*C$_2$Ph), 129.0 (d, $^3J_{PC}$ 9.2 Hz PMe$_2$*Ph* C$_3$), 128.5 (d, $^2J_{PC}$ 9.8 Hz PMe$_2$*Ph* C$_2$), 128.5 (s, *Ph*C$_2$Ph), 127.3 (br, *Ph*C$_2$Ph), 95.1 (s, C$_5$H$_5$), 53.6 (d, $^2J_{PC}$ 8.1 Hz, P{OMe}$_3$), 20.4 (d, $^1J_{PC}$ 30.5 Hz, P*Me*$_2$Ph), 18.5 (dd, $^1J_{PC}$ 33.4, $^3J_{PC}$ 1.7 Hz, P*Me*$_2$Ph). All the resonances in the ^{13}C NMR spectrum due to the alkyne ligand in this complex show significant broadening which, coupled with appearance of only one contact-carbon resonance, is consistent with restricted rotation of the alkyne ligand. We are currently investigating this behaviour using variable temperature NMR studies. Elemental analysis: calc.: C, 52.35; H, 5.13; found: C, 52.31; H, 5.34%.

§ *Crystal data*: for complex **2**: C$_{30}$H$_{35}$BO$_3$F$_4$P$_2$Mo, *M* = 688.3, monoclinic, space group $P2_1/c$, a = 12.0856(13), b = 21.494(2), c = 11.8962(13) Å, β = 97.473(2)°, V = 3064.1(6) Å^3, T = 173 K, Z = 4, μ = 0.59 mm^{-1}, λ(Mo-Kα) = 0.71073 Å. 19836 reflections measured, 6992 unique (R_{int} = 0.0228) which were used in all calculations. The final $wR(F^2)$ was 0.1006 (all data).

For complex **4**: C$_{64}$H$_{60}$BF$_4$MoN$_5$, *M* = 1081.95, monoclinic, space group $P2_1/c$, a = 18.992(2), b = 36.245(4), c = 16.5204(18) Å, β = 93.070(2)°, V = 11356(2) Å^3, T = 173 K, Z = 8, μ = 0.290 mm^{-1}, λ(Mo-Kα) = 0.71073 Å.74235 reflections measured, 26054 unique (R_{int} = 0.0574) which were used in all calculations. The final $wR(F^2)$ was 0.1904 (all data). The crystal structure determination of **4** indicated the presence of some disordered solvent molecules which could not be succesfully modelled, this probably accounts for the discrepancy in analytical data.

CCDC reference numbers 193466 (**2**) and 193467 (**4**). See http://www.rsc.org/suppdata/cc/b2/b208867c/ for crystallographic data in CIF or other electronic format.

¶ *Selected NMR data* for complex **4**: ^{1}H (CD$_2$Cl$_2$) δ 7.48 (s, NH), 4.79 (s, 5 H, C$_5$H$_5$), 2.44 (s, 6 H, CNC$_6$H$_3$*Me*$_2$), 2.20 (s, 6 H, CNC$_6$H$_3$*Me*$_2$), 2.18 (s, 12 H, terminal CNC$_6$H$_3$*Me*$_2$), 1.81 (s, 6 H, CNC$_6$H$_3$*Me*$_2$); ^{13}C (CD$_2$Cl$_2$), all resonances are singlets; δ 201.9, 171.7, 167.6, 145.6, 142.0, 140.4, 137.3, 136.6, 135.8, 135.5, 135.3, 134.8 (terminal C$_6$H$_3$*Me*$_2$), 134.2, 130.2, 129.9, 129.3, 129.1, 129.0, 128.8, 128.5 (terminal C$_6$H$_3$*Me*$_2$), 128.4, 127.3, 126.7, 126.1 (terminal C$_6$H$_3$*Me*$_2$), 118.7, 118.4, 116.8, 108.5, 90.4 (C$_5$H$_5$), 19.4 (C$_6$H$_3$*Me*$_2$), 18.5 (terminal C$_6$H$_3$*Me*$_2$), 18.1 (C$_6$H$_3$*Me*$_2$), 17.4 (C$_6$H$_3$*Me*$_2$). The NH proton was assigned on the basis of a D$_2$O shake coupled with ^{1}H–^{1}H COSY, ^{1}H–^{13}C HETCOR and ^{1}H–^{13}C COLOC experiments. IR (CH$_2$Cl$_2$): 2129 (terminal CNxyl), 1605 and 1507 cm^{-1} (ligand backbone). Elemental analysis: calc.: C, 71.04; H, 5.56; N, 6.47; found: C, 69.66; H, 6.35; N, 6.63%.

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