New coordination modes at molybdenum for 2-diphenylphosphinoaniline derived ligands

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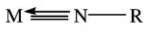
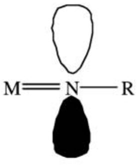
The complexes [$MoCl_3$(1-*N*,2-Ph_2P-C_6H_4)$_2$] (1) and {MoCl(N*t*-Bu)[1-μ(*N*),2-(Ph_2P)C_6H_4]}$_2$ (2) have been obtained from the reaction of 2-diphenylphosphinoaniline [1,2-(NH_2)(Ph_2P)C_6H_4] with either sodium molybdate [Na_2MoO_4] (in the presence of Et_3N and Me_3SiCl) or [$MoCl_2$(N*t*-Bu)$_2$(DME)]; the crystal structure of 1 reveals a novel $MoNC_2PN$ six-membered conjugated ring system derived from a P–N coupling reaction between two ligands, whilst that of 2 reveals bridging imido/terminal phosphine ligation.

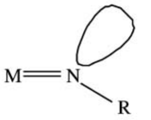
Over the last decade, there has been a great deal of interest in the chemistry of transition metal imido species.[1] In particular, bis(imido) complexes of group VI continue to be of interest as precursors to useful catalytic systems.[2] An important issue in metal imido chemistry is the nature of the metal–nitrogen bond, and three binding modes have been identified, *viz* **I–III**.



I



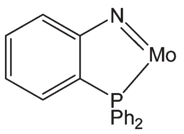
II



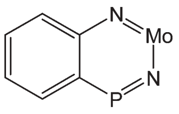
III

We have described five-coordinate bis(imido) molybdenum complexes, in which one of the imido ligands shows marked bending at the metal-bound nitrogen,[3] derivatives that contain functionalised substituents[4] and the first chelating bis(imido) complexes.[5] In such bis(imido) complexes, the large chelate ring size means that both imido linkages are effectively linear 4e$^-$ donors. We decided to attempt the synthesis of a smaller chelate ring derived from the ligand 2-diphenylphosphinoaniline, [1,2-(NH_2)(Ph_2P)-C_6H_4], and either sodium molybdate [Na_2MoO_4] or [$MoCl_2$(N*t*-Bu)$_2$(DME)] under standard reaction conditions in the expectation that a chelating imido-phosphine ligand might be generated (**IV**), in which the imido nitrogen would necessarily be bent. Here we present our unexpected findings.

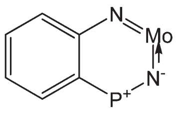
The only previous studies of the ligand 2-diphenylphosphinoaniline have resulted in chelating amido complexes (M = Tc, Re, Pt or Ni),[6] a chelating imido complex (M = Re)[7] and the organotungsten(VI) imido complex [Cp*WCl($NC_6H_4PPh_2$)$_2$], containing *ortho* pendant PPh_2 groups,[8] and more recently the parent ligand has been utilised to produce new Schiff base/imine-type ligands.[9] Interestingly, anilido-phosphinimine ligands have recently been prepared *via* lithiation of bromo-2-fluorobenzene, quenching with chlorodiphenylphosphine and subsequent treatment with lithium amide LiNHAr (Ar = 2,6-*i*-Pr_2-C_6H_3N).[10] Bidentate *P*,*N* ligands are of interest for use in asymmetric catalysis.[11]



IV



V



VI

A convenient route to bis(imido) molybdenum compounds is provided by the treatment of sodium molybdate with an appropriate primary amine or aniline.[12] The reaction of 2-diphenylphosphinoaniline with [Na_2MoO_4] in the presence of Me_3SiCl and Et_3N affords, after work-up, golden yellow prisms in *ca.* 35% yield.† The ^1H NMR (DMSO-d_6, 298 K) showed only broad unresolved multiplets in the aromatic region, and there was no observable ^{31}P NMR signal. However, an EPR spectrum of the crystalline solid (298 K) was sharp with g_{iso} = 1.958, consistent with molybdenum(V); the limited solubility of the compound precluded any further analysis. The reduction of molybdenum(VI) in the presence of phosphines is well established.[13] In order to elucidate the nature of this product, single crystals suitable for X-ray determination were obtained by prolonged standing of a saturated acetonitrile solution at ambient temperature. The structure is shown in Fig. 1; selected bond lengths and angles are given in the caption.‡ The molecule has an approximately octahedral geometry at molybdenum with a *fac* arrangement of the chlorines and a facially-coordinated tridentate ligand, resulting from the attack of the soft, formally phosphorus(III) atom P(1) at the hard N(2) atom of the adjacent anilino group. There is some evidence for delocalisation within this six-membered ring system (see **V**): the N(2)–P(1) distance of 1.636(2) Å lies midway between that expected for phosphorus–nitrogen single and double bonds, the Mo(1)–N(1) bond [1.740(2) Å] is acting as a 4e$^-$ donor, whilst the geometry at N(2) is trigonal-planar [angles ranging from 118.03(8) to 119.63(12)°], and Mo(1)–N(2) [2.209(2) Å] distance is consistent with that of an amine (there is no ν_{N-H} stretch in the IR spectrum). An alternative description for this ligand is that of an internal zwitterion, with P(1) acting as a phosphonium centre (see **VI**).

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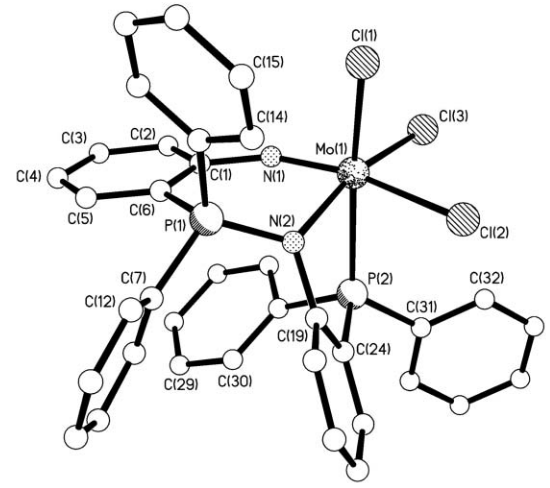

Fig. 1 Molecular structure of **1**, showing the atom labelling scheme. Hydrogen atoms and the half molecule of CH_3CN solvent are omitted. Selected geometric parameters (Å and °): Mo(1)–Cl(1) 2.3984(5), Mo(1)–Cl(2) 2.4589(5), Mo(1)–Cl(3) 2.3768(5), Mo(1)–N(1) 1.7397(16), Mo(1)–N(2) 2.2085(15), Mo(1)–P(2) 2.5406(5), N(2)–P(1) 1.6362(15); Mo–N(1)–C(1) 154.61(14), Mo(1)–N(2)–P(1) 118.03(8), Mo(1)–N(2)–C(19) 118.42(11), P(1)–N(2)–C(19) 119.63(12).

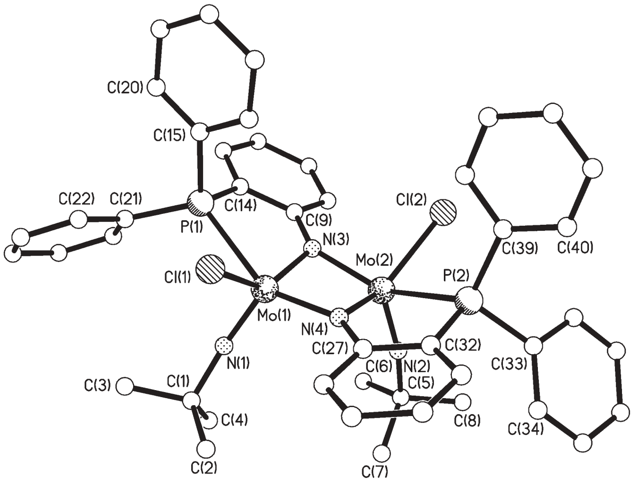

Fig. 2 Molecular structure of **2**, showing the atom labelling scheme. Hydrogen atoms and the CH_3CN solvent molecules are omitted. Selected geometric parameters (Å and °): Mo(1)–N(1) 1.719(2), Mo(2)–N(2) 1.716(2), Mo(1)–N(3) 1.995(2), Mo(2)–N(3) 1.975(2), Mo(1)–N(4) 1.978(2), Mo(2)–N(4) 1.990(2), Mo(1)–P(1) 2.5525(7), Mo(2)–P(2) 2.5502(7), Mo(1)–Cl(1) 2.4345(6), Mo(2)–Cl(2) 2.4274(7); Mo(1)–N(3)–Mo(2) 85.25(8), Mo(1)–N(4)–Mo(2) 85.31(8), Mo(1)–N(1)–C(1) 164.29(18), Mo(2)–N(2)–C(5) 168.89(18).

The formation of this six-membered ring system is thought to arise *via* a hemilabile phosphine group, which is free to attack an adjacent imido group. For the imido group, any bending associated with the Mo–N–C linkage results in a decreased metal–nitrogen interaction, thereby enhancing the reactivity at nitrogen. In the IR spectrum, a strong band at $v = 1109$ cm^{-1} is tentatively assigned to the Mo–N stretch. The Mo(1)–P(2) distance [2.5406(5) Å] is consistent with a molybdenum(V)–phosphine linkage.

Given the failure to form the chelating imido-phosphine **IV** by the 'molybdate' route, we turned our attention to the now well-established imido exchange methodology.[14] Our starting material, $[MoCl_2(Nt\text{-}Bu)_2(DME)]$, has previously been shown to be a convenient synthetic entry point into arylimido molybdenum(VI) chemistry. Reaction of the aniline $[1,2\text{-}(NH_2)(Ph_2P)C_6H_4]$ with $[MoCl_2(Nt\text{-}Bu)_2(DME)]$ in refluxing toluene (or DME) afforded, after work-up, orange blocks of **2**·$2CH_3CN$ in *ca.* 37% yield.† The molecular structure of **2** is shown in Fig. 2, with selected bond lengths and angles given in the caption.‡ The two molybdenum centres in this dimeric complex possess distorted square-based pyramidal geometries (with the *tert*-butyl imido groups apical) and are linked together *via* two approximately symmetric imido bridges. The latter are derived from the aniline ligand, the phosphorus centres of which each coordinate to one molybdenum centre. The bridging imido Mo–N distances [1.975(2)–1.995(2) Å] are at the high end of those observed for terminal imido groups at molybdenum,[1a] and are comparable to previously reported bridging imido groups in molybdenum complexes [1.953(6)–1.991(15) Å].[1,15] Interestingly, the Mo–N–Mo bridging angles at both N(3) and N(4) [*ca.* 85°] are inconsistent with a sp^2 nitrogen centre, doubtless a reflection of the geometric constraints imposed by the phenylene backbone of the ligand. The apical *tert*-butyl groups show slight bending [Mo–N–C *ca.* 164° and 169°], however, this is still well within the range observed for linear imido ligation [150–180°]. The Mo–P distances in **2** are similar to those observed in **1**. One of the solvent molecules of crystallisation (CH_3CN) is partially encapsulated by the aryl rings C(9)–C(14) and C(15)–C(20), as well as Cl(2), whilst the other solvent molecule lies *exo* to the complex. Despite the formal oxidation state of Mo(V), the complex is diamagnetic, as observed for other d^1–d^1 complexes, with a short Mo–Mo distance of 2.6887(3) Å.[16]

In conclusion, we have identified new coordination modes at molybdenum, *viz* the first example of a tridentate ligand derived solely from 2-diphenylphosphinoaniline (in **1**) and the first observation of bridging imido ligation involving a ligand derived from 2-diphenylphosphinoaniline (in **2**).

The EPSRC and the University of East Anglia are thanked for financial support.

Notes and references

† *Synthesis of* **1**: Et_3N (2.71 cm^3, 19.44 mmol) and Me_3SiCl (4.97 cm^3, 38.89 mmol) were added to $[Na_2MoO_4]$ (1.00 g, 4.86 mmol) in 1,2-dimethoxyethane (50 cm^3). 2-Diphenylphosphinoaniline (2.72 g, 9.81 mmol) was added, and the reaction mixture was then refluxed for 12 h. Filtration and extraction into hot CH_3CN (3 × 30 cm^3) afforded golden prisms of **1**·½CH_3CN. Yield 1.31 g, 35%. Found: C, 56.9; H, 3.9; N, 4.0. $C_{36}H_{28}N_2P_2Cl_3Mo$·½CH_3CN requires: C, 57.4; H, 3.8; N, 4.5%.

Synthesis of **2**: $[MoCl_2(Nt\text{-}Bu)_2(DME)]$ (0.20 g, 0.50 mmol) and $[1,2\text{-}(NH_2)(Ph_2P)C_6H_4]$ (0.28 g, 1.01 mmol) were refluxed for 12 h in toluene (30 cm^3). Following removal of volatiles *in vacuo*, the residue was extracted into warm CH_3CN (2 × 30 cm^3), affording on prolonged standing at ambient temperature large orange cubes of **2**·$2CH_3CN$. Yield 0.10 g, 37%. Found: C, 55.3; H, 5.0; N, 7.7. $C_{44}H_{46}N_4P_2Cl_2Mo_2$·$2CH_3CN$ requires: C, 55.5; H, 5.1; N, 8.1%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.51–8.24 (overlapping multiplets, 28 H, aryl-*H*), 1.59 (s, 3 H, CH_3CN), 1.21 (s, 18 H, $C(CH_3)_3$)). ^{31}P NMR ($CDCl_3$, 101 MHz): δ 28.3 (s).

‡ *Crystal data for* **1**·½CH_3CN: $C_{36}H_{28}Cl_3MoN_2P_2$·½CH_3CN, M = 773.36, monoclinic, space group $P2_1/c$ (no. 14), a = 12.3107(8), b = 13.0253(8), c = 21.6485(14) Å, β = 101.913(2)°. U = 3396.6(4) Å^3, Z = 4, D_c = 1.512 g cm^{-3}, $F(000)$ = 1568, μ(Mo-K$_\alpha$) = 0.747 mm^{-1}, λ = 0.71073 Å, T = 160 K. 17942 reflections measured, 6718 unique data ($2\theta_{max}$ = 52.7°, R_{int} = 0.0274, semi-empirical absorption correction). A molecule of acetonitrile was modelled as disordered across an inversion centre, to give

w$R2$ = 0.0614 for all data, conventional R = 0.0247 on F values of 6211 reflections having $F_o^2 > 2\sigma(F_o^2)$. CCDC 231263.

Crystal data for **2**·2CH$_3$CN: $C_{44}H_{46}Cl_2Mo_2N_4P_2\cdot 2CH_3CN$, M = 1037.68, triclinic, space group $P\bar{1}$ (no. 2), a = 11.2101(5), b = 12.7462(6), c = 18.1549(9) Å, α = 104.754(2), β = 102.967(2), γ = 92.947°. U = 2428.3(2) Å^3, Z = 2, D_c = 1.419 g cm^{-3}, $F(000)$ = 1060, μ(Mo-K$_\alpha$) = 0.731 mm^{-1}, λ = 0.71073 Å, T = 150 K. 21768 reflections measured, 11278 unique data ($2\theta_{max}$ = 57.9°, R_{int} = 0.0228, semi-empirical absorption correction). w$R2$ = 0.0765 for all data, conventional R = 0.0325 on F values of 8790 reflections having $F_o^2 > 2\sigma(F_o^2)$. CCDC 231264. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b700158d

Programs: Bruker SMART and SAINT[17] control and integration software, Bruker SHELXTL[18] and local programs (for unit cell refinement for **1** and for cif editing).

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