

Bis(η -cyclopentadienyl)-molybdenum and -tungsten Imido Complexes: X-Ray Structures of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}^t)]$ and $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Me})_2(\text{NBu}^t)\text{Me}]$

Jennifer C. Green, Malcolm L. H. Green, J. Thomas James, Peter C. Konidaris, Graham H. Maunder and Philip Mountford

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK

The pseudo-trigonal bis(η -cyclopentadienyl)-molybdenum and -tungsten imido complexes $[\text{M}(\eta\text{-C}_5\text{H}_4\text{R})(\eta\text{-C}_5\text{H}_4\text{R}')(\text{NBu}^t)]$ ($\text{M} = \text{Mo}$ or W ; $\text{R} = \text{R}' = \text{Me}$ or H , $\text{R}' = \text{Pr}^i$, $\text{R} = \text{H}$) are reported together with the ring-slipped indenyl analogue $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Pr}^i)(\eta^3\text{-C}_9\text{H}_7)(\text{NBu}^t)]$ and the metal-methylated salts $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Me})_2(\text{NBu}^t)\text{Me}]\text{X}$ ($\text{X} = \text{I}$ or BF_4); the X-ray structures of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}^t)]$ and $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Me})_2(\text{NBu}^t)\text{Me}]\text{BF}_4$ suggest that the NBu^t ligand acts as a strong π -donor to the metal centre; photoelectron studies identify an unusually low ionization-energy band largely localized on the ligands.

Bis(η -cyclopentadienyl) derivatives of the transition metals occupy a prominent position in organometallic chemistry and have been a focus of considerable synthetic and theoretical interest for many years.¹ In particular, many derivatives of this class are known for molybdenum and tungsten. The metal-ligand doubly bonded species $[\text{M}(\eta\text{-C}_5\text{R}_5)_2(=\text{E})]$ ($\text{M} = \text{Mo}$ or W) have been described for $\text{E} = \text{Pr}$,² O^3 and CHR .⁴ However, the corresponding imido ($\text{E} = \text{NR}$) analogues have remained elusive.⁵ Following our recent studies of mono(η -cyclopenta-

dienyl) imido complexes of molybdenum⁶ we now report the synthesis for the first time of the bis(η -cyclopentadienyl) imido derivatives $[\text{M}(\eta\text{-C}_5\text{H}_4\text{R})(\eta\text{-C}_5\text{H}_4\text{R}')(\text{NBu}^t)]$, where $\text{M} = \text{Mo}$ or W .

Photolysis of solutions of the readily available mono(η -cyclopentadienyl) imido species $[\text{M}(\eta\text{-C}_5\text{H}_4\text{R})(\text{NBu}^t)(\eta\text{-C}_2\text{H}_4)\text{Cl}]$ ($\text{M} = \text{Mo}$ or W)^{6b,7} in the presence of one equivalent of $\text{Na}[\text{C}_5\text{H}_4\text{R}']$ afforded red, air-sensitive compounds $[\text{M}(\eta\text{-C}_5\text{H}_4\text{R})(\eta\text{-C}_5\text{H}_4\text{R}')(\text{NBu}^t)]$ ($\text{M} = \text{Mo}$, $\text{R} = \text{R}' = \text{Me}$ **1a**; $\text{M} =$

Mo, R = Pri, R' = H **1b**; M = W, R = R' = Me **2**) in good yields (see Scheme 1).[†] In a typical reaction, 4.07 g of [Mo(η -C₅H₄Me)(NBu')(η -C₂H₄)Cl] afforded 2.0 g of **1a**.

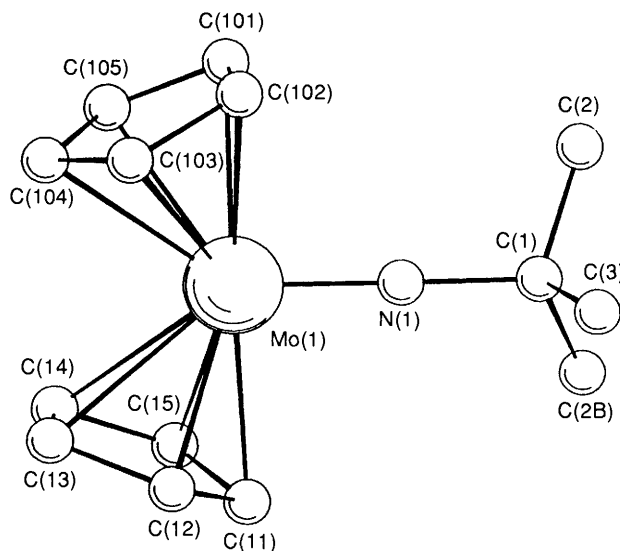


Fig. 1 Molecular structure of [Mo(η -C₅H₅)₂(NBu')] **1c**.[‡] Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) as follows: Mo(1)–N(1) 1.738(2), Mo(1)–C(11) 2.37(1), Mo(1)–C(12) 2.34(3), Mo(1)–C(13) 2.53(2), Mo(1)–C(14) 2.50(1), Mo(1)–C(15) 2.39(1), Mo(1)–C(101) 2.35(1), Mo(1)–C(102) 2.34(1), Mo(1)–C(103) 2.35(1), Mo(1)–C(104) 2.41(1), Mo(1)–C(105) 2.35, Mo(1)–C₅H₅scnt(1) 2.12, Mo(1)–C₅H₅scnt(2) 2.04, Mo(1)–N(1)–C(1) 177.7(2), N(1)–Mo(1)–C₅H₅scnt(1) 117.6, N(1)–Mo(1)–C₅H₅scnt(2) 114.5, C₅H₅scnt(1)–Mo(1)–C₅H₅scnt(2) 127.9 where C₅H₅scnt(1) and C₅H₅scnt(2) refer to the computed ring centroids for atoms C(11)–C(15) and C(101)–C(105), respectively.

[†] Satisfactory analyses have been obtained for all the new compounds described, except **1b** and **4-BF₄**, which have been spectroscopically characterised.

Selected spectroscopic data: NMR data recorded at 300 MHz (¹H) or at 75 MHz (¹³C-¹H)) and given as δ relative to SiMe₄, relative intensity, multiplicity, coupling constant, (in Hz) and assignment; *J* refers to the ¹H-¹H coupling constant unless otherwise stated (for virtually coupled multiplets *J* is the apparent coupling constant). DEPT = distortionless enhancement by polarisation transfer. Mass spectra (MS) measured using electron-impact techniques. ^a in [²H₈]-toluene, ^b in [²H₆]-benzene, ^c in [²H₂]-dichloromethane.

1a: ¹H:^a 5.17, 4.77 [2 × 4 H, 2 × virtual t (*J* 2.3), C₅H₄Me], 1.90 (6 H, s, C₅H₄Me), 1.08 (9 H, s, Bu'). MS: 327 (M⁺), 312 (M⁺ – Me), 254 (M⁺ – NBu').

1b: ¹H:^b 5.30 [2 H, virtual t (*J* 2.3), C₅H₄Pri], 5.14 (5 H, s, η -C₅H₅), 4.23 [2 H, virtual t (*J* 2.3), C₅H₄Pri], 2.65 [1 H, sept (*J* 6.8), CHMe₂], 1.31 [6 H, d (*J* 6.8), CHMe₂], 1.05 (9 H, s, Bu'). ¹³C-DEPT:^b 101.5 (C-Pr), 95.1 (C₅H₅), 91.5 (overlapping 2 × CH of C₅H₄Pri), 30.4 (CHMe₂), 29.0 (CHMe₂), 25.4 (CMe₃).

1c: ¹H:^b 5.12 (10 H, s, 2 × C₅H₅), 1.04 (9 H, s, Bu'). MS: 299 (M⁺), 284 (M⁺ – Me), 228 (M⁺ – NBu').

2: ¹H:^b 5.39, 4.97 [2 × 4 H, 2 × virtual t (*J* 2.3), C₅H₄Me], 1.97 (6 H, s, C₅H₄Me), 1.08 (9 H, s, Bu'). MS: 413 (M⁺), 398 (M⁺ – Me), 342 (M⁺ – NBu').

3: ¹H:^b 6.9 (2 H, m, H₄ or H₅ of indene), 6.7 (4 H, m, H₂ and H₅ or H₄ of indene), 5.02 [2 H, virtual t (*J* 2.3), C₅H₄Pri], 4.71 [1 H, t (*J* 2.6), H₁ of indene], 3.15 [2 H, virtual t (*J* 2.3), C₅H₄Pri], 2.62 [1 H, sept (*J* 6.8), CHMe₂], 1.35 [6 H, d (*J* 6.8), CHMe₂], 0.98 (9 H, s, Bu'). ¹³C-¹H (assignments confirmed by ¹³C-¹H correlation spectrum):^b 135.8 (C₃ of indene), 123.9, 119.6 (H₄ and H₅ of indene), 118.9 (C-Pr), 109.6 (C₁ of indene), 98.8, 93.5 (2 × CH of C₅H₄Pri), 70.0 (NCMe₃), 65.6 (C₂ of indene), 30.4 (CMe₃), 28.1 (CHMe₂), 25.6 (CHMe₂). MS: 389 (M⁺), 374 (M⁺ – Me), 318 (M⁺ – NBu').

4-I: ¹H:^c 6.78, 6.41, 5.67, 5.59 [4 × 2 H, 4 × virtual q (*J* 2.3), C₅H₄Me], 2.20 (6 H, s, C₅H₄Me), 1.68 (3 H, s, Mo-Me), 1.20 (9 H, s, Bu'). ¹³C-DEPT:^c 115.8, 110.0, 108.3, 107.6 (4 × CH of C₅H₄Me), 28.5 (CMe₃), 14.8 (C₅H₄Me), 10.4 (Mo-Me).

4-BF₄: ¹H:^c 6.61, 6.35, 5.60, 5.44 [4 × 2 H, 4 × virtual q (*J* 2.3), C₅H₄Me], 2.18 (6 H, s, C₅H₄Me), 1.67 (3 H, s, Mo-Me), 1.19 (9 H, s, Bu').

Surprisingly, treatment of [Mo(η -C₅H₄Pri)(NBu')(η -C₂H₄)Cl] with an excess of Na(C₅H₅) under similar conditions gave the compound [Mo(η -C₅H₅)₂(NBu')] **1c** in which the η -C₅H₄Pri has been replaced by η -C₅H₅.

The X-ray structure of **1c** has been determined[‡] and the molecular structure is shown in Fig. 1. The compound **1c** is a monomer in the solid state consistent with the spectroscopic data.[†] The solution ¹H and ¹³C NMR, IR and mass spectral data for the compounds **1a–b** and **2** are consistent with structures analogous to that found for **1c**.

The bent Mo(η -C₅H₅)₂ moiety of **1c** has mutually staggered cyclopentadienyl rings[‡] and the Mo–N–C linkage is nearly

[‡] *Crystal data for 1c:* C₁₄H₁₉NMo, *M* = 297.25, crystal size = ca. 0.50 × 0.50 × 0.65, orthorhombic, space group *Pnma*, *a* = 11.290(2), *b* = 12.758(4), *c* = 9.247(2) Å, *V* = 1331.9 Å³, *Z* = 8, *D_c* = 1.48 g cm⁻³, μ (Mo–K α) 9.36 cm⁻¹, *F*(000) = 608, scan type ω -2 θ , *T* = 293 K, 2 < 2 θ < 50°, total unique data 1222, no. of observations [(*I* > 3 σ (*I*)] 1069, observations/variables 8.5, *R*_{merge} = 0.021, *R* = 0.024, *R_w* = 0.025 (Chebyshev parameters 9.22, –3.81, 7.33, 0.247), maximum peak in final Fourier difference synthesis 0.41 eÅ⁻³.

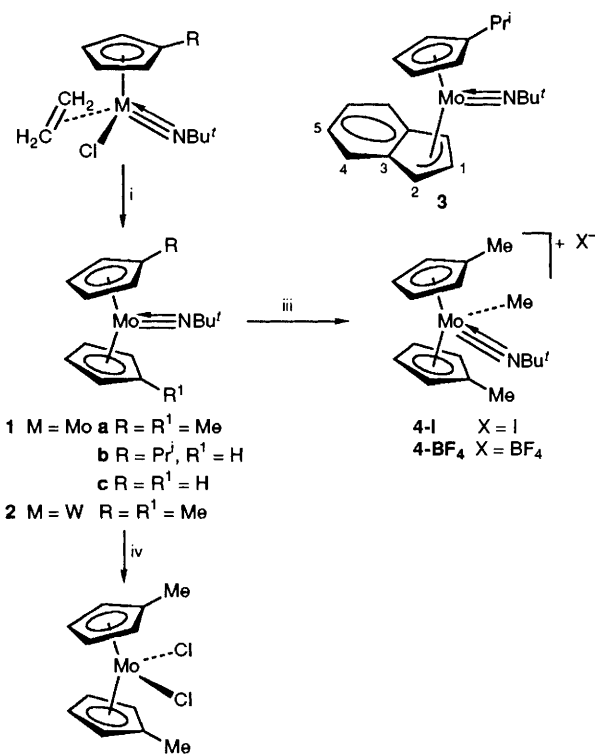
4-I: C₁₇H₂₆IMoN, *M* = 467.24, crystal size = ca. 0.20 × 0.20 × 0.30, orthorhombic, space group *Pc2₁b* (non-standard setting of no. 29), *a* = 7.254(3), *b* = 15.775(4), *c* = 15.962(2) Å, *V* = 1826.0 Å³, *Z* = 4, *D_c* = 1.704 g cm⁻³, μ (Mo–K α) 23.74 cm⁻¹, *F*(000) = 920, scan type ω -2 θ , *T* = 293 K, 2 < 2 θ < 52°, total unique data 1854, no. of observations [(*I* > 3 σ (*I*)] 1346, observations/variables 7.5, *R*_{merge} = 0.016, *R* = 0.029, *R_w* = 0.035 (Chebyshev parameters 3.593, –1.660, 2.233, –0.3710), maximum peak in final Fourier difference synthesis 0.50 eÅ⁻³.

Data were collected on an Enraf-Nonius CAD4-F diffractometer. An empirical absorption correction based on azimuthal scan data was applied and the data were corrected for Lp effects. Systematically absent reflections were rejected and equivalent reflections were merged. The heavy-atom positions were determined from a Patterson synthesis (for **1c**) or by direct methods using the SIR88 program.¹⁵ Subsequent difference syntheses revealed the positions of all other non-hydrogen atoms. Hydrogen atoms were placed in estimated positions (C–H 0.96 Å) with isotropic thermal parameters 1.3 times that of the *U*_{equiv} of the attached carbon atom. The non-hydrogen atoms were refined using full-matrix least-squares procedures with the hydrogen atoms 'riding' on their supporting carbon atoms. A weighting scheme was applied and the data were corrected for the effects of anomalous dispersion and isotropic extinction in the final stages of refinement.

The molecules of **1c** lie across a crystallographic mirror plane and two sets of η -C₅H₅ ring carbons could be located from a Fourier difference synthesis during the structure determination. The X-ray data may be interpreted as indicating that the two η -C₅H₅ rings of **1c** are eclipsed in the solid state with a 50% contribution from two different eclipsed orientations. An alternative interpretation is that the two rings in any individual molecule are mutually staggered, but that the crystallographic mirror plane forces the projection of the two rings onto each other giving the apparent site disorder. We have chosen the latter interpretation since the majority of bis(η -cyclopentadienyl) metal complexes have a staggered ring conformation (possibly due to steric factors). No evidence for site disorder in the methyl groups of the Bu'^t ligand was apparent from inspection of the carbon atom thermal ellipsoids or a Fourier difference synthesis. The carbon atoms in each of the two η -C₅H₅ ring sites were well-behaved in refinement and were satisfactorily modelled with 50% chemical occupancies and anisotropic temperature factors.

For **4-I**, a SIR88¹⁵ analysis of the normalised structure factors confirmed the choice of the non-centrosymmetric space group *Pc2₁b* rather than the alternative centrosymmetric *Pcmb* (non-standard setting of No. 57), which was equally likely from inspection of the systematic absences alone. For **1c** the centrosymmetric choice (*Pnma*) was favoured over the alternative *Pn2₁a* (non-standard setting of No. 33) and attempted refinement of a staggered model in the lower symmetry was unsatisfactory.

Crystallographic calculations were carried out using the CRYSTALS¹⁶ program on a Micro VAX 3800 computer in the Chemical Crystallography Laboratory, Oxford. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1 Reagents and conditions: i Na[C₅H₄R'] [1 equiv. (for **1a-b** or **2**) or an excess of (for **1c**)], thf, hv, 30 min, 30–50%; ii Li[C₉H₇] (1 equiv.), thf, hv, 30 min, 32%; iii (for **4-I**) MeI (excess), thf, 20 min, 61% (**4-BF₄** is obtained by adding NaBF₄ to an aqueous solution of **4-I**); iv HCl(g), thf, –70 °C, 2 min, 50%

linear [Mo(1)–N(1)–C(1) = 177.7(2)°]. This is in contrast with the corresponding phosphinidene analogue [(η-C₅H₅)₂Mo(P-2,4,6-C₆H₂Bu₃)₃] which has a Mo–P–C angle of 115.8(2)°. The metal–nitrogen bond length [Mo(1)–N(1) = 1.738 (Å)] in **1c** is comparable with the values found for other Mo=NR groups where NR is a linear four-electron donor,⁸ and, in particular, with the closely related Mo^{IV} species [Mo(η-C₅H₄R)(NBU^t)(η-C₂H₄)Cl] [Mo–N = 1.704(6) Å] or {[Mo(η-C₅H₅)(NBU^t)(η-C₂H₄)₂(μ-Hg)] [Mo–N = 1.75(2) and 1.72(3) Å].^{5b}

The Mo(η-C₅H₅)₂ moiety in **1c** exhibits some unusual features. Thus, the molybdenum to ring centroid (Mo–C₅H₅cent) distances (2.04 and 2.12 Å) are substantially longer than most other d² bis(η-cyclopentadienyl)-molybdenum or -tungsten complexes. Typically metal–ring centroid distances for bent Mo or W d² metallocene derivatives are in the range 1.95–1.99 Å. Moreover, in the closely related pseudo-trigonal analogues [Mo(η-C₅H₅)₂(P-2,4,6-C₆H₂Bu₃)₃],² [W(η-C₅H₅)₂-C(H)Ph]^{4a} and [W(η-C₅H₅)₂C(H)OZr(H)(η-C₅Me₅)₂]^{4b} the average metal–ring centroid distances are 1.96, 1.96 and 1.94 Å, respectively. The oxo compound [Mo(η-C₅H₅)₂(O)]^{3b} which is valence isoelectronic with **1c**, also shows a molybdenum–ring centroid distance (average 2.04 Å) approaching that of **1c**.

The lengthening of the Mo–C₅H₅cent distance in **1c** can be traced to specific Mo–C bond lengths in each ring. Thus, the metal to carbon bond lengths to the ring carbons *trans* to the NBU^t moiety [C(104), C(13) and C(14)] are significantly

§ For congeneric pairs of bis(η-cyclopentadienyl) compounds the metal to ring centroid distance remains almost constant from the 2nd to the 3rd transition series.¹⁷ Thus, we may compare data both from bis(η-cyclopentadienyl)-molybdenum and bis(η-cyclopentadienyl)-tungsten structures.

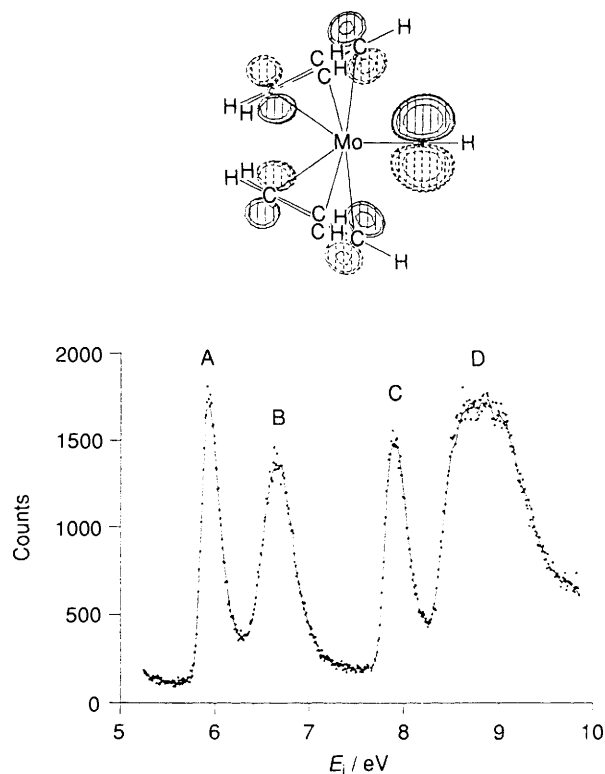


Fig. 2 Low E_1 region of the He I photoelectron spectrum of **1c** together with a representation of the upper occupied b_2 orbital to which band B is assigned

longer than those to the other carbons in each of the respective rings.¶

In addition, the (ring-centroid)–metal–(ring-centroid) angle (θ) for **1c** (127.9°) is unusually small compared with other pseudo-trigonal d² [M(η-C₅R₅)₂(E)] complexes. The corresponding angles in [Mo(η-C₅H₅)₂(P-2,4,6-C₆H₂Bu₃)₃], [W(η-C₅H₅)₂C(H)Ph] and [W(η-C₅H₅)₂C(H)OZr(H)(η-C₅Me₅)₂] are 144.6, 143.2 and 145.6°, respectively. However, we note that value of θ for [Mo(η-C₅H₅)₂(O)] (θ = 133.7°) is closer to that of **1c** than for the other pseudo-trigonal complexes.

The near-linearity of the Mo–N–Bu^t bond in **1c** implies that the nitrogen atom is formally sp hybridised and can, therefore in principle, act as a four-electron donor to the metal centre. However, if we also count each η-C₅H₅ ring as a five-electron donor to the Mo atom then, at first sight **1c** is a twenty-electron complex. Similar electron-counting problems arise in the linear molybdenum nitrosyl complexes [Mo(η-C₅H₅)₂(NO)R] (R = alkyl)⁹ (apparently 20 electrons) and in the linear imido vanadium complex [V(η-C₅Me₅)₂N(2,6-C₆H₃Me₂)] (apparently 19 electrons).¹⁰ The nitrosyl compounds have substantially distorted Mo–C_{ring} interactions akin to those in **1c** and the vanadium imido compound has a relatively small θ value and long vanadium to ring centroid distances. The bonding in the nitrosyl and imido complexes has been investigated using molecular orbital calculations. These suggest that the surplus electrons are located in essentially ligand-based orbitals^{10,11} so

¶ It is not likely that the unusually long metal–ring carbon distances in **1c** are due to inter-ring steric repulsions at small values of θ . For example, in the pseudo-tetrahedral 16–18-electron complexes [M(η-C₅H₅)₂Cl₂] (M = Zr, Nb or Mo) values of θ in the range 126–133° are common but are not accompanied by similar deviations in metal–ring carbon distances.¹⁷

|| It is noteworthy that a similar lengthening of metal–cyclopentadienyl–ring–carbon distances *trans* to an imido ligand has been noted in other cyclopentadienyl–metal–imido complexes.^{6b,18}

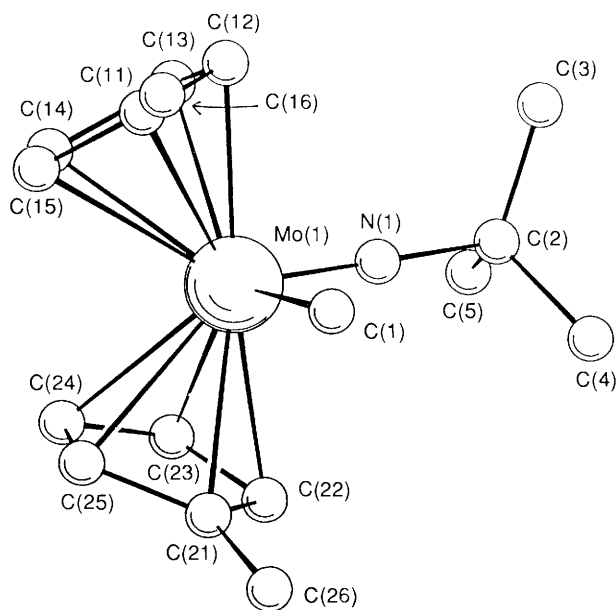


Fig. 3 Molecular structure of the $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Me})_2(\text{NBu}')\text{Me}]^+$ cation in **4-I**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) as follows: Mo(1)–N(1) 1.704(8), Mo(1)–C(1) 2.195(9), Mo(1)–C(11) 2.52(1), Mo(1)–C(12) 2.372(9), Mo(1)–C(13) 2.34(1), Mo(1)–C(14) 2.43(1), Mo(1)–C(15) 2.53(1), Mo(1)–C(21) 2.53(1), Mo(1)–C(22) 2.40(1), Mo(1)–C(23) 2.30(1), Mo(1)–C(24) 2.46(1), Mo(1)–C(25) 2.57, Mo(1)–C₅H₅scnt(1) 2.13, Mo(1)–C₅H₅scnt(2) 2.15, Mo(1)–N(1)–C(2) 176.4(7), N(1)–Mo(1)–C₅H₅scnt(1) 114.3, N(1)–Mo(1)–C₅H₅scnt(2) 112.9, C₅H₅scnt(1)–Mo(1)–C₅H₅scnt(2) 125.4 where C₅H₅scnt(1) and C₅H₅scnt(2) refer to the computed ring centroids for atoms C(11)–C(15) and C(21)–C(25), respectively.

that in effect the 18-electron rule is not violated in these complexes.

For example, the calculations for the vanadium imido complex predict two strong V–N π bonds in addition to the σ interaction. However, the nitrogen lone pair of b_2 symmetry (lying in the vanadium–ring centroids plane) competes with one of the linear combinations offered up by the cyclopentadienyl rings for the same metal acceptor orbital. This results in a metal–ligand non-bonding orbital which has negligible (1%) vanadium character and approximately equal contribution from the NPh and C₅H₅ ligands. We have carried out similar calculations on the model complex $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NH})]$ and obtained a similar distribution for the second highest occupied molecular orbital (HOMO) (Fig. 2). For the molybdenum nitrosyl species the HOMO is ligand based (largely NO and C₅H₅ character) with almost no metal contribution and so, in effect, an 18-electron count for Mo is achieved.¹¹

The photoelectron spectrum of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{NBu}')]$ (Fig. 2) shows two low lying ionization-energy (E_i) bands. The first (5.92 eV) is assigned to ionization of the metal d electrons occupying an a_1 orbital, the second (6.61 eV) to the b_2 ionization of electrons localized principally on the nitrogen and cyclopentadienyl rings. This E_i value for the b_2 orbital is strikingly low for a ligand-based ionization, indeed it is comparable with that of ferrocene, and some anti-bonding characteristics may well be inferred. We conclude that the structure and photoelectron spectra of **1c** suggest that the imido ligand b_2 lone pair competes strongly with the cyclopentadienyl ligands and is substantially involved in metal–nitrogen bonding at the expense of metal–ring bonding.

For purposes of comparison, we have prepared the indenyl compound $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Pr}^i)(\eta^3\text{-C}_9\text{H}_7)(\text{NBu}')]$ **3** by photolysis of a mixture of $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Pr}^i)(\text{NBu}')(\eta\text{-C}_2\text{H}_4)\text{Cl}]$ and lithium indenide in thf (tetrahydrofuran). The indenyl ligand is well-known to slip readily from penta- to tri-hapto coordina-

tion in response to electronic pressure at the metal centre. Comparison of the quaternary carbon chemical shifts of the indenyl ligand in **3** with those of other η^3 -indenyl complexes¹² are entirely consistent with the presence of an η^3 -indenyl ligand in **3**. The complex **3** is, therefore, valence isoelectronic with the precursor $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Me})(\text{NBu}')(\eta\text{-C}_2\text{H}_4)\text{Cl}]$ and has a four-electron donor imido ligand.

A preliminary study of the reactivity of **1a** has shown that treatment with methyl iodide afforded the orange salt $\{[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Me})_2(\text{NBu}')\text{Me}]\text{I}\}$ **4-I** in 61% yield in which methylation has taken place at the metal rather than at the nitrogen 'lone pair'. The complex **4-I** is soluble in water and addition of NaBF₄ afforded the corresponding salt $\{[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Me})_2(\text{NBu}')\text{Me}]\text{BF}_4\}$ **4-BF₄**. The X-ray structure of **4-I** has been determined and the cationic part is shown in Fig. 3.[†] The cation consists of a bent $\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Me})_2$ fragment bonded to a methyl group and to a near-linear NBu' moiety $[\text{Mo}(1)\text{-N}(1)\text{-C}(2) = 176.2(7)^\circ]$. The metal nitrogen distance $[\text{Mo}(1)\text{-N}(1) = 1.704(8) \text{ \AA}]$ is consistent with the imido ligand acting as a strong electron donor to the d^0 metal centre. The metal–carbon bond lengths to the cyclopentadienyl rings are long compared with most other bis(cyclopentadienyl)molybdenum species, as are the metal–(ring centroid) distances. Thus, the structure of **4-I** suggests that in this complex the *tert*-butyl imido ligand is also acting as a strong electron donor (at the expense of metal–ring bonding). The $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Me})_2(\text{NBu}')\text{Me}]^+$ cation is valence isoelectronic with $[\text{W}(\eta\text{-C}_5\text{Me}_5)_2(\text{O})\text{Me}]^+$,^{3c} and $[\text{Ta}(\eta\text{-C}_5\text{Me}_5)_2(\text{H})(\text{E})]$ (E = O or NPh).¹³ Interestingly, the X-ray structure of $[\text{Ta}(\eta\text{-C}_5\text{Me}_5)_2(\text{H})(\text{NPh})]$ apparently shows no unusual features for the $\text{Ta}(\eta\text{-C}_5\text{Me}_5)_2$ unit and the Ta–N bond is long compared with that expected for a four-electron donor imido ligand.

Finally, removal of the NBu' group of **1a** may readily be effected by treatment of a cold (-70°C) thf solution of **1a** with HCl gas, which gives the green dichloride $[\text{Mo}(\eta\text{-C}_5\text{H}_4\text{Me})_2\text{Cl}_2]$ ¹⁴ in good yield.

We thank the SERC for a studentship (to P. C. K.).

Received, 26th May 1992; Com. 2/02712G

References

- Ch. Elschenbroich and A. Salzer, *Organometallics*, VCH, Cambridge, 1989, p. 316.
- P. B. Hitchcock, M. F. Lappert and W.-P. Leung, *J. Chem. Soc., Chem. Commun.*, 1987, 1282.
- (a) M. L. H. Green, A. H. Lynch and M. G. Swanwick, *J. Chem. Soc., Dalton Trans.*, 1972, 1445; (b) N. D. Silavwe, M. Y. Chiang and D. R. Tyler, *Inorg. Chem.*, 1985, **24**, 4219; (c) G. Parkin and J. E. Bercaw, *Polyhedron*, 1988, **7**, 2053.
- (a) J. A. Marsella, K. Folting, J. C. Huffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1981, **103**, 5596; (b) P. T. Wolzanski, R. S. Threlkel and J. E. Bercaw, *J. Am. Chem. Soc.*, 1979, **101**, 218.
- (a) P. Jernakoff, G. L. Geoffroy, A. L. Rheingold and S. J. Geib, *J. Chem. Soc., Chem. Commun.*, 1987, 1610; (b) R. Freer, Part II Thesis, Oxford University, 1989.
- (a) M. L. H. Green, G. Hogarth, P. C. Konidaris and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1990, 3781; (b) M. L. H. Green, P. C. Konidaris, P. Mountford and S. J. Simpson, *J. Chem. Soc., Chem. Commun.*, 1992, 256.
- M. L. H. Green and J. T. James, unpublished results.
- W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley Interscience, New York, 1988.
- F. A. Cotton and P. Legzdins, *J. Am. Chem. Soc.*, 1968, **90**, 6232; J. L. Calderon, F. A. Cotton and P. Legzdins, *J. Am. Chem. Soc.*, 1969, **91**, 2528; F. A. Cotton and Rusholme, *J. Am. Chem. Soc.*, 1972, **94**, 402.
- J. H. Osborne, A. L. Rheingold and W. C. Trogler, *J. Am. Chem. Soc.*, 1985, **107**, 7945.
- J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.

- 12 F. H. Köhler, *Chem. Ber.*, 1974, **107**, 570; M. H. Chisholm, M. J. Hampden-Smith, J. C. Huffman, J. D. Martin and K. A. Stahl, *Polyhedron*, 1988, **7**, 1991.
 - 13 G. Parkin, A. van Asselt, D. J. Leahy, L. Whinnery, N. G. Hua, R. W. Quan, L. M. Henling, W. P. Schaefer, B. D. Santarsiero and J. E. Bercaw, *Inorg. Chem.*, 1992, **31**, 82.
 - 14 G. J. S. Adams, Part II Thesis, Oxford University, 1976.
 - 15 M. C. Burla, M. Cannalli, G. Cascarno, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, *J. Appl. Crystallogr.*, 1989, **22**, 389.
 - 16 D. J. Watkin, J. R. Carruthers and P. W. Betteridge, *CRYSTALS User Guide*, Chemical Crystallography Laboratory, University of Oxford, 1985.
 - 17 K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2290.
 - 18 D. N. Williams, J. P. Mitchell, A. D. Poole, U. Siemeling, W. Clegg, D. C. R. Hockless, P. A. O'Neil and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1992, 739; W. A. Herrmann, G. Weichselbaumer, R. A. Paciello, R. A. Fischer, E. Herdtweck, J. Okuda and D. W. Marz, *Organometallics*, 1990, **9**, 489.
-