(η-Cyclopentadienyl)imido Derivatives of Molybdenum and Tungsten‡

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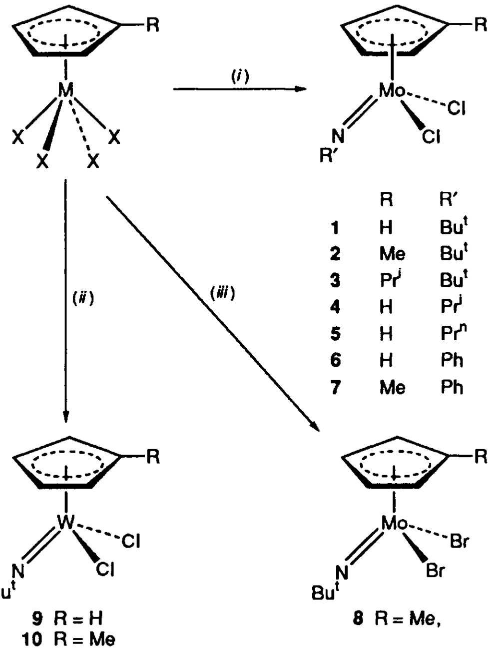
The new paramagnetic compounds [M(η-C_5H_4R)X_2(NR′)] (M = Mo, X = Cl, R′ = Bu^t, R = H, Me or Pr^i; M = Mo, X = Cl, R = H, R′ = Pr^i, Pr^n or Ph; M = Mo, X = Cl, R = Me, R′ = Ph; M = Mo, X = Br, R = Me, R′ = Bu^t; M = W, X = Cl, R′ = Bu^t, R = H or Me) have been prepared and the crystal structure of [Mo(η-C_5H_5)Cl_2(NBu^t)] has been determined. The new diamagnetic molybdenum(IV) compounds of general formula [Mo(η-C_5H_4R)Cl(L)(NR′)] where L = ethene, propene, styrene, but-2-yne or carbon monoxide have been synthesised. The mercury-bridged compounds [{Mo(η-C_5H_4R)(C_2H_4)(NBu^t)}$_2$(μ-Hg)] (R = H or Me) have also been obtained, together with the compound [Mo(NBu^t)Cl_2(PMe_3)$_3$]. The crystal structures of [Mo(η-C_5H_4Me)Cl(C_2H_4)(NBu^t)], [{Mo(η-C_5H_5)(C_2H_4)(NBu^t)}$_2$(μ-Hg)] and [Mo(NBu^t)Cl_2(PMe_3)$_3$] have been determined.

The purpose of the studies described herein was to develop the chemistry of molybdenum and tungsten compounds containing the ligand combination of η-cyclopentadienyl and imido groups, *i.e.* the general class of compounds [M(η-C_5H_5)$_x$$X_z$(L)(NR)$_y$], where X donates one electron to and requires one electron from the metal, and L donates a two-electron pair to the metal centre. This paper is the first of a series on the chemistry of compounds in the designated class with molybdenum and tungsten.

There are already a substantial number of transition-metal–imide–cyclopentadienyl compounds where the transition metal is Ti, Zr or Hf,[1–7] V, Nb or Ta,[8–24] Cr, Mo or W,[25–49] Mn or Re,[50–54] Ru[55], Co or Fe,[56] Os,[57,58] Ir,[59–61] Ni,[62] U[63–65] or Th.[64] During the course of this work the compounds [M(η-C_5R_5)Cl_3(NBu^t)] (R = H, M = Mo or W; R = Me, M = Mo) were synthesised by Sundermeyer[40,41] by treatment of [M(η-C_5R_5)Cl(NBu^t)$_2$] with HCl, and the crystal structure of [Mo(η-C_5Me_5)Cl_3(NBu^t)] reported. Also, niobium, tantalum[15] and rhenium[66] compounds which are close analogues of compounds **1**–**10** presented in this paper have been described. A preliminary report of part of this work has appeared.[67]

Results and Discussion

Synthesis and Characterization of [M(η-C_5H_4R)X_2(NR′)].—Treatment of the η-cyclopentadienyl tetrahalide compounds [M(η-C_5H_4R)X_4][68] with three equivalents of the appropriate primary amine NH_2R' affords the imido compounds [M(η-C_5H_4R)X_2(NR′)] (M = Mo, X = Cl, R′ = Bu^t, R = H **1**, Me **2** or Pr^i **3**; M = Mo, X = Cl, R = H, R′ = Pr^i **4**, Pr^n **5** or Ph **6**; M = Mo, X = Cl, R = Me, R′ = Ph **7**; M = Mo, X = Br, R = Me, R′ = Bu^t **8**; M = W, X = Cl, R′ = Bu^t, R = H **9** or Me **10**) in *ca.* 50% yield (see Scheme 1). Compounds **1**–**10** are yellow-brown, moderately air-sensitive solids. They are insoluble in light petroleum, but soluble in toluene, tetrahydrofuran (thf), diethyl ether, dichloromethane and acetone. The reaction failed to give tractable products when bulky amines such as cyclohexylamine or 2,6-diisopropylaniline were employed.



Scheme 1 (*i*) NH_2R' (3 mol) in toluene at room temperature (r.t.) for 1 h, 36–65%; (*ii*) NH_2Bu^t (3 mol) in toluene at r.t. for 30 min, R = H, 35% or Me, 70%; (*iii*) NH_2Bu^t (3 mol) at r.t. for 30 min, 70%

Most of the compounds **1**–**10** could be readily crystallized by cooling saturated toluene solutions of the compounds to −80 °C. The analytical and spectroscopic data which characterize the new compounds are given in Table 1 or in ref. 67 and these data are not discussed further except where the interpretation is not straightforward.

The crystal structure of [Mo(η-C_5H_5)Cl_2(NBu^t)] **1** has been determined[67] and the molecular structure is shown in Fig. 1 together with selected distances and angles for the two crystallographically independent molecules (the metric data for the two crystallographically independent molecules of **1** in the asymmetric unit are equivalent within experimental error and so just one of the two sets of data is discussed). The Mo–N–C linkage [Mo(1)–N(1)–C(6) 170.1(2)°] is nearly linear, consistent

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‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: $\mu_B \approx 9.274\,02 \times 10^{-24}$ J T^{-1}, $\mu_N \approx 5.050\,79 \times 10^{-27}$ J T^{-1}, atm ≈ 101 325 Pa, mmHg ≈ 133.322 Pa, eV ≈ $1.602\,18 \times 10^{-19}$ J.

Table 1 Analytical and spectroscopic data

Compound and analysis[a]	NMR data[b]
3 $[Mo(\eta\text{-}C_5H_4Pr^i)Cl_2(NBu^t)]$[c] C, 41.7 (41.8); H, 5.8 (5.8); N, 4.05 (4.05)	
4 $[Mo(\eta\text{-}C_5H_5)Cl_2(NPr^i)]$[d] C, 33.1 (33.25); H, 4.1 (4.2); N, 4.7 (4.85)	
7 $[Mo(\eta\text{-}C_5H_4Me)Cl_2(NPh)]$[e] C, 43.0 (42.8); H, 3.5 (3.6); N, 4.1 (4.15)	
10 $[W(\eta\text{-}C_5H_4Me)Cl_2(NBu^t)]$[f] C, 29.6 (29.7); H, 4.1 (4.0); N, 3.4 (3.45)	
11 $[Mo(\eta\text{-}C_5H_5)Cl(C_2H_4)(NBu^t)]$[g] C, 45.2 (44.7); H, 6.3 (6.1); N, 4.8 (4.7); Cl, 12.3 (12.0)	^1H: 5.30 (5 H, s, C_5H_5), 2.78–2.89 (1 H, m, C_2H_4), 2.52–2.62 (1 H, m, C_2H_4), 2.17–2.26 (1 H, m, C_2H_4), 1.95–2.04 (1 H, m, C_2H_4), 0.87 (9 H, s, Bu^t) $^{13}C\text{-}\{^1H\}$ DEPT (C_6D_6): 102.5 (C_5H_5), 49.1, 38.5 (2 × C_2H_4), 28.9 (CMe_3)
12 $[Mo(\eta\text{-}C_5H_4Me)Cl(C_2H_4)(NBu^t)]$[h] C, 46.7 (46.5); H, 6.7 (6.6); N, 4.5 (4.5)	^1H: ($CD_3C_6D_5$): 5.43, 5.36, 5.25, 4.49 (4 × 1 H, 4 × virtual q, *J* 2.1 Hz, C_5H_4Me), 2.55–2.75 (2 H, m, C_2H_4), 2.13–2.21 (1 H, m, C_2H_4), 1.75 (3 H, s, C_5H_4Me), 1.65–1.73 (1 H, m, C_2H_4), 0.92 (9 H, s, Bu^t) $^{13}C\text{-}\{^1H\}$ (C_6D_6): 105, 101, 97.6, 97.1 (4 × CH of C_5H_4Me), 71 (CMe_3), 49, 39 (2 × C_2H_4), 29 (CMe_3), 14 (C_5H_4Me)
13 $[Mo(\eta\text{-}C_5H_4Pr^i)Cl(C_2H_4)(NBu^t)]$[i] C, 49.8 (49.8); H, 7.4 (7.2); N, 4.1 (4.15)	^1H: 5.45, 5.35, 5.25, 4.70 (4 × 1 H, 4 × virtual q, *J* 2.4 Hz, $C_5H_4Pr^i$), 2.8 (2 H, m, C_2H_4 and $CHMe_2$), 2.7 (1 H, m, C_2H_4), 2.1 (1 H, m, C_2H_4), 1.9 (1 H, m, C_2H_4), 1.1 (3 H, d, *J* 7.5 Hz, $CHMe_2$), 0.92 (9 H, s, Bu^t), 0.89 (3 H, d, *J* 7.5 Hz, $CHMe_2$)
14 $[Mo(\eta\text{-}C_5H_5)Cl(PhCH{=}CH_2)(NBu^t)]$[j] C, 55.3 (54.9); H, 6.8 (6.0); N, 3.7 (3.8)	^1H: 7.65 (2 H, d, *J* 7.3, C_6H_5) (i), 7.38 (2 H, d, *J* 7.2 Hz, C_6H_5) (ii), 7.25 (3 H, m, C_6H_5) (i), 7.20–6.85 (multiplet partially obscured by solvent, C_6H_5) (ii), 5.37 (5 H, s, C_5H_5) (a), 5.32 (5 H, s, C_5H_5) (b), 5.24 (5 H, s, C_5H_5) (c), 5.13 (5 H, s, C_5H_5) (d), 4.6 (1 H, m, C_2H_3Ph) (w), 3.3 (1 H, m, C_2H_3Ph) (w), 2.55 (1 H, m, C_2H_3Ph) (w), 4.08 (1 H, m, C_2H_3Ph) (x), 2.87 (1 H, m, C_2H_3Ph) (x), 2.75 (1 H, m, C_2H_3Ph) (x), 4.01 (1 H, m, C_2H_3Ph) (y), 3.50 (1 H, m, C_2H_3Ph) (y), 2.23 (2 H, m, C_2H_3Ph) (y and z), 3.45 (1 H, m, C_2H_3Ph) (z), 3.09 (1 H, m, C_2H_3Ph) (z), 0.91 (9 H, s, Bu^t) (d), 0.86 (9 H, s, Bu^t) (c), 0.66 (9 H, s, Bu^t) (b), 0.58 (9 H, s, Bu^t) (a)[k]
19 $[Mo(\eta\text{-}C_5H_5)Cl(CO)(NBu^t)]$[l] C, 40.8 (40.6); H, 4.8 (4.8); N, 4.6 (4.7)	^1H: 5.04 (5 H, s, C_5H_5), 1.15 (9 H, s, Bu^t) $^{13}C\text{-}\{^1H\}$ (C_6D_6): 98.4 (C_5H_5), 72.9 (CMe_3), 30.18 (CMe_3)

[a] Analytical data given as found (calc.) %. For **1**: C, 35.6 (35.7); H 4.8 (4.65); N, 4.6 (4.6). For **2**: C, 37.9 (37.9); H, 5.1 (5.1); N, 4.4 (4.4). For **5**: C, 33.5 (33.25); H, 4.3 (4.2); N, 4.8 (4.85). For **6**: C, 40.4 (40.9); H, 3.0 (3.1). For **8**: C, 29.7 (29.6); H, 4.0 (4.0); N, 3.3 (3.45). For **9**: C, 27.65 (27.65); H, 3.45 (3.6); N, 3.4 (3.6). For **15**: C, 36.2 (36.6); H, 5.0 (5.0); N, 3.8 (3.9). For **16**: C, 38.0 (38.5); H, 5.3 (5.3); N, 3.7 (3.75). For **17**: C, 49.35 (48.5); H, 6.5 (6.3); N, 4.4 (4.35). For **18**: C, 52.7 (52.7); H, 5.0 (4.7); N, 4.1 (4.1). For **20**: C, 33.8 (33.5); H, 7.5 (7.8); N, 3.0 (3.00). [b] IR spectra recorded as pressed CsI pellets. IR data for **1**, **2**, **5–8**, **11**, **15–18** and **20** are given in ref. 67. NMR spectra referenced relative to residual protio solvent resonance (^1H) or solvent resonance (^{13}C). NMR data given as (as appropriate): intensity, multiplicity (coupling constant), assignment. In C_6D_6 unless stated otherwise. [c] ν(Mo–N) 1360, ν(M–Cl) 280, 300, 330, 385 cm^{-1}. [d] ν(Mo=N) 1315, ν(M–Cl) 310, 350, 390 cm^{-1}. [e] ν(Mo=N) 1313, ν(M–Cl) 310, 340, 360 cm^{-1}. [f] ν(W=N) 1363, ν(M–Cl) 300, 320, 340 cm^{-1}. [g] ν(Mo=N) 1355, ν(M–Cl) 340, 370 cm^{-1}. [h] ν(Mo=N) 1360, ν(M–Cl) 310, 340, 380 cm^{-1}; *C*Me resonance of $\eta\text{-}C_5H_4Me$ ring was not observed. [i] ν(Mo=N) 1358, ν(M–Cl) 280, 310 cm^{-1}. [j] ν(Mo=N) 1360, ν(M–Cl) 287, 428 cm^{-1}. [k] Complete assignment of the resonances attributable to each isomer was not possible; however, the partial connectivities shown have been confirmed by a ^1H–^1H shift correlation experiment. The quoted peak intensities are 'normalized' for each isomer. a–d Refer to the four possible isomers; w–z also refer to the four isomers but cannot be related to a–d; i and ii are two multiplets which are coupled and belong to one of the isomers a–d. [l] ν(Mo=N) 1363, ν(M–CO) 1962, (M–Cl) 300 cm^{-1}.

Table 2 Selected structural parameters of some 4d and 5d half-sandwich cyclopentadienylimido compounds

Compound	M=N bond length (Å)	M–Cl bond length (Å)	M–N–C angle (°)	Ref.
1 $[Mo(\eta\text{-}C_5H_5)Cl_2(NBu^t)]$	1.712(2) 1.719(3)	2.367(1) 2.370(2) 2.361(1) 2.364(1)	170.1(2) 171.6(3)	This work
$[Nb(\eta\text{-}C_5H_5)Cl_2(NMe)]$	1.752(2)	2.355(1)	163.4(3)	16
$[Nb(\eta\text{-}C_5H_5)Cl_2(NBu^t)]$	1.744(3) 1.752(3)	2.354(1) 2.358(2)	172.5(3) 170.0(3)	16
$[Nb(\eta\text{-}C_5H_5)Cl_2(NC_6H_3Pr^i_2\text{-}2,6)]$	1.761(6)	2.338(2)	165.6(5)	16
$[Ta(\eta\text{-}C_5Me_5)Cl_2(NC_6H_3Pr^i_2\text{-}2,6)]$	1.780(5)	2.345(2)	171.4(5)	16
$[Re(\eta\text{-}C_5Me_5)Cl_2(NBu^t)]$	1.709(3)	2.3850(8) 2.3772(8)	170.5(2)	66

with the formation of a molybdenum–nitrogen triple bond, and the Mo(1)–N(1) bond length [1.712(2) Å] is within the range commonly observed for such bonds.[69] The metal–nitrogen distances and angles in the related 4d and 5d compounds $[Nb(\eta\text{-}C_5H_5)Cl_2(NMe)]$, $[Nb(\eta\text{-}C_5H_5)Cl_2(NBu^t)]$, $[Nb(\eta\text{-}C_5H_5)Cl_2(NC_6H_3Pr^i\text{-}2,6)]$, $[Ta(\eta\text{-}C_5Me_5)Cl_2(NC_6H_3Pr^i\text{-}2,6)]$ and $[Re(\eta\text{-}C_5Me_5)Cl_2(NBu^t)]$ are given for comparison in Table 2. They all have nearly linear M–N–C angles, consistent with formal metal–nitrogen triple bonds. In all these complexes the imido group can act as a four-electron donor to the metal centre without formal violation of the 18-electron rule. The small deviation of the Mo–N–C linkage of the imide from linearity is towards the $\eta\text{-}C_5H_5$ ring suggesting that the primary interaction of one of the nitrogen lone pairs is with a metal orbital *trans* to the ring.[15,69] The observed shortening in $M\equiv N$ bond lengths with increase in atomic number for the structurally analogous complexes $[M(\eta\text{-}C_5H_5)Cl_2(NBu^t)]$ (M = Nb, Mo or Re) presumably reflects the same trend in

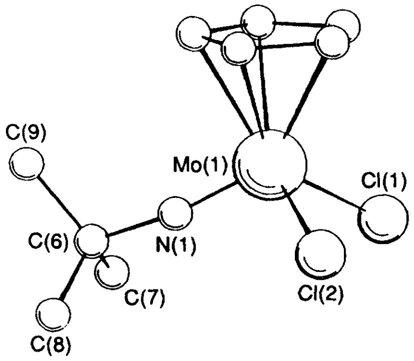


Fig. 1 Molecular structure of $[Mo(\eta-C_5H_5)Cl_2(NBu^t)]$ **1**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Mo(1)–N(1) 1.712(2), Mo(2)–N(2) 1.719(3), Mo(1)–Cl(1) 2.367(1), Mo(2)–Cl(3) 2.370(2), Mo(1)–Cl(2) 2.361(1), Mo(2)–Cl(4) 2.364(1), Mo(1)–C(1) 2.339(3), Mo(2)–C(11) 2.331(4), Mo(1)–C(2) 2.411(4), Mo(2)–C(12) 2.326(5), Mo(1)–C(3) 2.429(4), Mo(2)–C(13) 2.340(5), Mo(1)–C(4) 2.349(5), Mo(2)–C(14) 2.418(4), Mo(1)–C(5) 2.334(5), Mo(2)–C(15) 2.414(5), Mo(1)–$Cp_{cent(1)}$ 2.05, Mo(2)–$Cp_{cent(2)}$ 2.05, Mo(1)–N(1)–C(6) 170.1(2) and Mo(2)–N(2)–C(16), 171.6(3), where $Cp_{cent(1)}$ and $Cp_{cent(2)}$ refer to the computed η-cyclopentadienyl ring carbons centroids for Mo(1) and Mo(2) respectively. There are two crystallographically independent molecules in the asymmetric unit

covalent radii, namely, 1.57 (Nb), 1.56 (Mo) and 1.44 Å (Re). In contrast, the metal–chlorine bond lengths (Table 2) show an increase with increasing atomic number (an explanation for this is offered later).

The centroid of the $\eta-C_5H_5$ ring in complex **1** is displaced from the projection of the metal atom onto the least-squares plane of the ring by 0.106 [Mo(1)] and 0.122 Å [Mo(2)]. This may be due to the *trans* influence of the imide, and compares with values of 0.143 and 0.083 Å for the two independent molecules of $[Nb(\eta-C_5H_5)Cl_2(NBu^t)]$, and with 0.115, 0.048 and 0.165 Å for $[Nb(\eta-C_5H_5)Cl_2(NMe)]$, $[Nb(\eta-C_5H_5)Cl_2(NC_6H_3Pr^i{}_2\text{-}2,6)]$ and $[Ta(\eta-C_5Me_5)Cl_2(NC_6H_3Pr^i{}_2\text{-}2,6)]$ respectively. There is some evidence for puckering of the $\eta-C_5H_5$ ring of compound **1**. The angle between the planes defined by C(1), C(4), C(5), and C(1), C(2), C(3), C(4) is 2.86°, and that between those defined by C(11), C(12), C(13), and C(11), C(13), C(14), C(15) is 3.18°. These values are small compared to the distortion reported for $[Re(\eta-C_5Me_5)Cl_2(NBu^t)]$ (8.3°), and may be comparable to experimental error. However, the ring carbon bond lengths in the two molecules of **1** do not show any variation consistent with an 'allyl–ene' distortion of the type described for the analogous niobium, tantalum and rhenium compounds mentioned above. The reason for this difference is unclear.

If the imide ligand is assumed to donate four electrons to the metal centre, the complexes **1**–**10** can be considered as formally having 17 valence electrons and, therefore, are paramagnetic. The magnetic susceptibility of complex **2** has been determined and gives the value of 1.51 μ_B, which is close to the spin-only value for one unpaired electron (1.73 μ_B), consistent with the presence of a single unpaired electron. The ESR spectrum of **2** was recorded in toluene at 20 K and the observed resonance is assignable to the presence of one unpaired electron, with an isotropic *g* value of 1.996. The six-line pattern (coupling constant = 3.5 mT) of satellites observed is consistent with the superposition of spectra due to electron spin coupling to the $I = \frac{5}{2}$ ^{95}Mo and ^{97}Mo nuclei (16 and 9% abundance respectively). The magnetic moments of the two isotope nuclei are −0.9099 and −0.9290 μ_N respectively,[70] hence the splitting of the hyperfine lines due to the two isotopes is within the observed linewidth of this spectrum. Compounds **1**–**10** are volatile and sublime at *ca.* 70 °C and 10^{-3} mmHg and the photoelectron spectra of **2**, **4**, **8** and **9** could be determined. These and related experiments and calculations will be discussed in detail elsewhere.[71] Here only those results pertinent to the present discussions are referred to. The photoelectron spectrum of $[Mo(\eta-C_5H_4Me)Cl_2(NBu^t)]$ **2** displays a band at low-ionisation energy (7.1 eV) possessing a high degree of metal d orbital character. Extended-Hückel calculations suggests that the orbital from which this ionisation arises is metal based and has significant metal–chlorine antibonding character. This interpretation is consistent with the ESR data, and is in accord with the observed M–Cl bond length trends listed in Table 2. Moreover, Fenske–Hall calculations on the model 16-electron niobium complex $[Nb(\eta-C_5H_5)Cl_2(NMe)]$ indicate that the lowest unoccupied molecular orbital for this molecule [and therefore presumably the singly occupied highest occupied molecular orbital (HOMO) in **1**–**10**] is predominantly metal based d_{z^2} in character.[15,72] The photoelectron spectrum of the dibromo compound $[Mo(\eta-C_5H_4Me)Br_2(NBu^t)]$ **8** shows a shift of all ionisations (including that from the HOMO) to lower ionisation potential compared to **2**, due mainly to the lower electronegativity of bromine compared to chlorine.

Table 3 Cyclic voltammetric data*

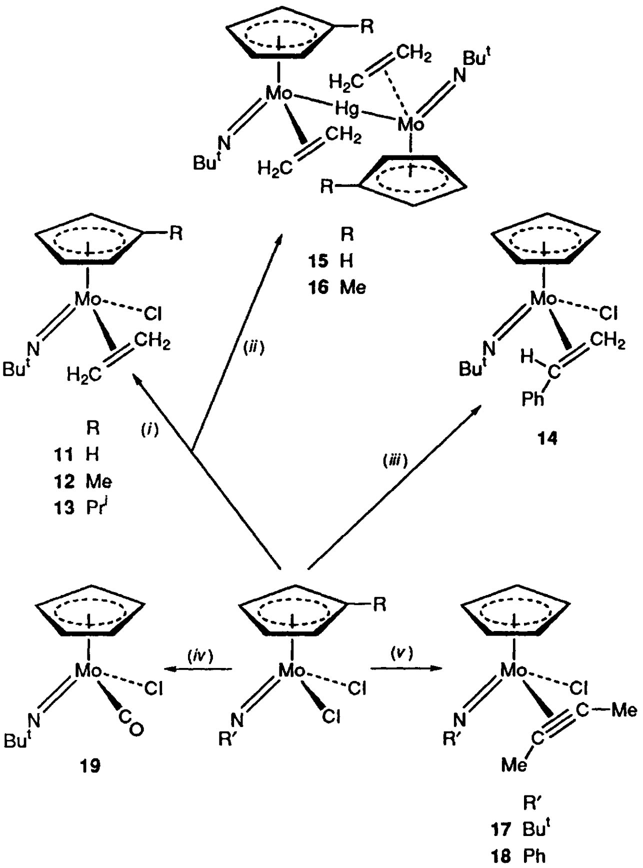
Compound	Reduction Potential/V	Oxidation Potential/V
2 $[Mo(\eta-C_5H_4Me)Cl_2(NBu^t)]$	−1.45	+0.20
4 $[Mo(\eta-C_5H_5)Cl_2(NPr^i)]$	−1.44	+0.27
5 $[Mo(\eta-C_5H_5)Cl_2(NPr^n)]$	−1.45	+0.25
6 $[Mo(\eta-C_5H_5)Cl_2(NPh)]$	−1.26	+0.23

* Obtained in 0.1 mol dm^{-3} $[NBu_4]PF_6$ supporting electrolyte in thf. Potentials are quoted relative to the $[Fe(\eta-C_5H_5)_2]$–$[Fe(\eta-C_5H_5)_2]^+$ couple.

Cyclic voltammetric studies of compounds **2** and **4**–**6** show oxidation behaviour consistent with an EC mechanism operating. The redox potentials all quoted relative to the $[Fe(\eta-C_5H_5)_2]$–$[Fe(\eta-C_5H_5)_2]^+$ couple, are recorded in Table 3. These data show that the effect of interchanging the alkylimide ligands on the reduction potential is small. However, in complex **6** the reduction potential shifts by *ca.* 200 mV, indicative of the differing π-donating ability of the phenylimide ligand.

Reactivity Studies of $[Mo(\eta-C_5H_4R)Cl_2(NR')]$.—Treatment of $[Mo(\eta-C_5H_4R)Cl_2(NBu^t)]$ (R = H **1**, Me **2** or Pr^i **3**) in thf solution with potassium graphite (KC_8) or, in some cases, with sodium amalgam, under 1 atm of ethene afforded the air- and moderately photo-sensitive compounds $[Mo(\eta-C_5H_4R)Cl(C_2H_4)(NBu^t)]$ (R = H **11**, Me **12** or Pr^i **13**) in *ca.* 50% yield (see Scheme 2). They were prepared in multigram quantities. The compounds are soluble in light petroleum and crystallise from this solvent at −20 °C as golden crystals.

The crystal structure of $[Mo(\eta-C_5H_4Me)Cl(C_2H_4)(NBu^t)]$ **12** has been determined[67] and the molecular structure is shown in Fig. 2 together with selected bond lengths and angles. The Mo–N–C angle [172.3(5)°] is nearly linear, and the Mo≡N bond length of 1.704(6) Å, is close to that in the parent compound **1** [1.712(2) Å]. The C–C bond length of the co-ordinated ethene ligand is 1.40(1) Å, which is considerably longer than of free ethene (1.34 Å). The centroid of the C_5 ring is displaced by 0.145 Å from the projection of the molybdenum atom onto the least-squares plane of the ring. This compares with 0.106 Å and 0.122 for **1**, and values of 0.083–0.165 Å observed in the compounds $[M(\eta-C_5R_5)Cl_2(NR')]$ (M = Nb, R = H, R' = Bu^t, Me or $C_6H_3Pr^i{}_2\text{-}2,6$; M = Ta, R = Me, R' = $C_6H_3Pr^i{}_2\text{-}2,6$), suggesting that there is a *trans* influence of imide and alkene ligands on the metal to C_5-ring bonding. Also, the carbons of the ethene ligand and the chlorine atom are coplanar. The frontier orbitals of the imide and cyclopentadienyl ligands are somewhat analogous. This leads to a formal isolobal analogy between a $M(\eta-C_5R_5)(NR')$ fragment and a valence isoelectronic $M'(\eta-C_5R_5)_2$ fragment[15] which, in this instance,



Scheme 2 (*i*) Potassium graphite (KC_8) in thf with ethene (1 atm) for 2 h, 35–50%; (*ii*) Na/Hg in thf with ethene (1 atm) for 2 h, R = H, 50% or Me, 16%; (*iii*) Na/Hg in thf with styrene at r.t. for 40 min, isomeric mixture, 33%; (*iv*) Na/Hg in thf and carbon monoxide (1 atm) for 2.5 h, 5%; (*v*) Na/Hg in thf and but-2-yne at r.t. for 2.5 h, R' = Bu^t, 47% or Ph 20%

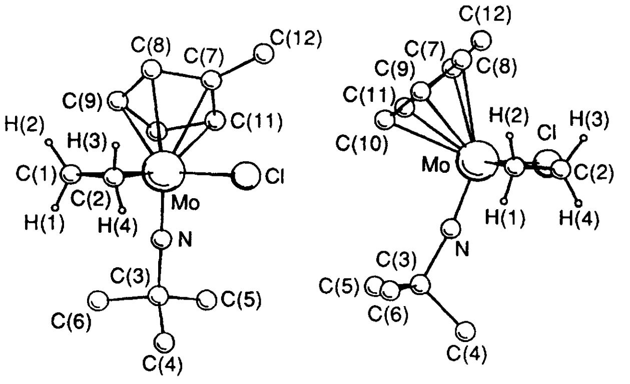


Fig. 2 Two views of the molecular structure of [Mo(η-C_5H_4Me)Cl(C_2H_4)(NBu^t)] **12**. Hydrogen atoms bonded to the η-C_5H_4Me and Bu^t groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Mo–N 1.704(6), Mo–C(1) 2.215(8), Mo–C(2) 2.190(9), C(1)–C(2) 1.40(1), Mo–Cp$_{cent}$ 2.07 and Mo–N–C(3) 172.3(5), where Cp$_{cent}$ refers to the computed η-cyclopentadienyl ring carbons centroid

is reflected in the virtual coplanarity of the metal atom, ethene carbon atoms and the chloride ligand in **12**, as shown in Fig. 2. Thus the maximum deviation of C(1), C(2) or Cl from the least-squares plane defined by these atoms is 0.003 Å, and the ethene ligand is rotated (about the vector linking the metal atom and the mid-point of the C–C bond) by only 0.38° with respect to this plane. In addition, the angles between this plane and the metal–ring centroid and metal–nitrogen vectors are 126.7 and 105.0° respectively. If the imide and cyclopentadienyl ligand frontier orbitals were exactly demanding of the metal centre orbitals, these two angles might be expected to be approximately equal.

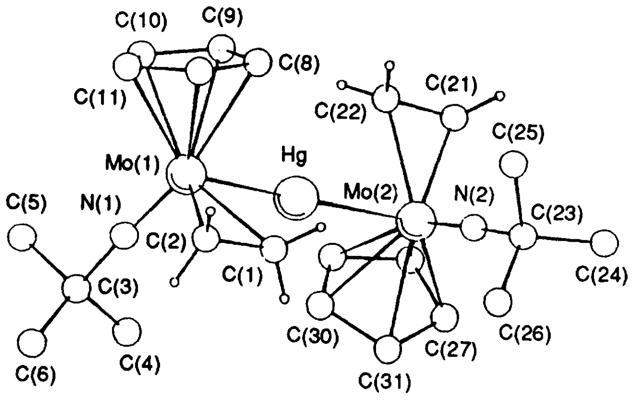


Fig. 3 Molecular structure of [{Mo(η-C_5H_5)(C_2H_4)(NBu^t)}$_2$(μ-Hg)] **15**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mo(1)–N(1) 1.75(2), Mo(2)–N(2) 1.72(3), Mo(1)–C(1) 2.28(3), Mo(2)–C(21) 2.17(3), Mo(1)–C(2) 2.18(3), Mo(2)–C(22) 2.26(2), Mo(1)–Cp$_{cent(1)}$ 2.05, Mo(2)–Cp$_{cent(2)}$ 2.01, Mo(1)–Hg 2.692(2), Mo(2)–Hg 2.773(2), C(1)–C(2) 1.427(5), C(21)–C(22) 1.426(5), Mo(1)–N(1)–C(3) 175.9(20), Mo(2)–N(2)–C(23) 177.0(18) and Mo(1)–Hg–Mo(2) 175.8(1), where Cp$_{cent(1)}$ and Cp$_{cent(2)}$ refer to the computed η-cyclopentadienyl ring carbons centroids for Mo(1) and Mo(2) respectively

Interesting comparisons can be drawn between the structure of complex **12** and that of the related crystallographically characterized niobium propene complex [Nb(η-C_5H_5)(PMe_3)(C_3H_6)($NC_6H_3Pr^i_2$-2,6)].[17] There are few other crystallographically characterized compounds containing imide and olefin ligands. The M=N bond length in **12** [1.704(6) Å] is shorter than in its parent dichloride compound **1** [1.712(2) Å]; this is in contrast to the niobium propene compound, in which the Nb=N bond [1.793(11) Å] is longer than in its parent compound, [Nb(η-C_5H_5)Cl_2($NC_6H_3Pr^i_2$-2,6)] [1.704(6) Å]. This observation has been attributed to the lowering of the metal oxidation state on formation of the Nb^{III} species.[17] Comparisons can also be made between the geometries of the alkene ligands with respect to the chloride or phosphine ligands in the two complexes. The near coplanarity of the ancillary ligand (Cl or PMe_3) with the M(η-C_2) fragment in both cases is indicative of the nature of the metallocene-like frontier molecular orbitals offered by the M(η-C_5H_5)(NR') fragment.

The ^{1}H NMR spectrum of complex **12** is consistent with a structure in solution essentially similar to that found in the crystals. No broadening of the alkene ligand resonances in the ^{1}H spectrum was detected on heating the sample to 355 K, indicating a high energy barrier to alkene rotation. This is also illustrative of the pseudo-metallocene character of the frontier orbitals offered by the Mo(η-C_5H_4R)(NR') fragment; metallocene-like frontier orbitals would constrain the olefin to lie within the inter-ring 'wedge', with no low-energy pathway to out-of-plane rotation.[73]

The ^{1}H and ^{13}C NMR spectra of compounds **11** and **13** are closely similar to those of **12** suggesting that they are related structurally. The IR spectra of **11**–**13** show absorptions assignable to ν(Mo–Cl) in the region below 400 cm^{-1} and absorptions tentatively assignable to ν(Mo=N) at around 1360 cm^{-1} (Table 1). The assignment of metal–nitrogen stretches is not straightforward due to extensive coupling of these modes to the rest of the molecule.[38]

Reduction of compounds **1** and **2** with sodium amalgam under 1 atm of ethene afforded not only the ethene chloride compounds [Mo(η-C_5H_5)Cl(C_2H_4)(NBu^t)] **11** and [Mo(η-C_5H_4Me)Cl(C_2H_4)(NBu^t)] **12**, but also the mercury-bridged dimolybdenum species [{Mo(η-C_5H_5)(C_2H_4)(NBu^t)}$_2$(μ-Hg)] **15** and [{Mo(η-C_5H_4Me)(C_2H_4)(NBu^t)}$_2$(μ-Hg)] **16** respectively. The relative proportions and absolute yields of the two products were very variable. The crystal structure of complex **15** has been determined[67] and the molecular structure is shown in Fig. 3 together with selected bond distances and angles. The structure features near-linear M=N–C vectors [175.9(20), 177.0(18)°] and Mo=N bond lengths of 1.75(2) and 1.72(3) Å. The maximum deviations of the alkene carbon atoms or mercury atom from the appropriate $Mo(\eta-C_2)Hg$ planes are 0.075 [about Mo(1)] and 0.087 Å [about Mo(2)], again illustrating the close similarity between the frontier orbitals offered by the $M(\eta-C_5R_5)(NR')$ fragment and those of the $M(\eta-C_5R_5)_2$ fragment. The $Mo(\eta-C_2)Hg$ planes lie at angles of 122.61 and 127.67° to the metal–ring centroid vectors, and at angles of 101.05 and 98.78° to the metal–nitrogen vectors [for Mo(1) and Mo(2) respectively]. Again, the reasons why these angles are not equal may be ascribed to a combination of steric and electronic effects.

There is also evidence for *trans* influence causing a lengthening of the metal–ring carbon bonds *trans* to the imide ligand; the displacements of the centroids are 0.154 and 0.211 Å, comparable with that for complex **12** (0.145 Å). The structure also displays some evidence of C_5-ring puckering; the angle between the planes defined by C(9), C(10), C(11), and C(7), C(8), C(9), C(11) is 3.51°, whilst that between the planes defined by C(28), C(29), C(30), and C(27), C(28), C(30), C(31) is 8.70°. The latter is a surprisingly large distortion, although partial pseudo-translational disorder in the crystal, and the consequent need to apply distance and angle restraints to the carbon atoms of the ring,[67] necessitate a degree of caution in interpreting this result. The Mo–Hg–Mo vector is linear, the bond length being *ca.* 2.7 Å which is comparable with those in $[\{W(\eta-C_5H_5)(CO)_3\}_2(\mu-Hg)]$ (2.75 Å) and $[\{Re(NC_6H_3Pr^i{}_2-2,6)_3\}_2(\mu-Hg)]$ (2.62 Å).[74,75]

The ^1H NMR spectrum of complex **15** displays resonances attributable to *tert*-butyl and alkenyl protons, and also two distinct cyclopentadienyl ring C–H resonances, separated by 2.16 Hz at an instrument operating frequency of 300 MHz (for ^1H). Measurement of the spectrum at 200 MHz reveals a peak separation of 1.47 Hz showing that the splitting of the two lines is not a consequence of simple scalar coupling. A possible interpretation is that the four possible stereoisomers of the molecule may display two different spectra, namely that due to the (*R,R*) and (*S,S*) molecules, and that due to the (*R,S*) and (*S,R*) molecules. The presence of only one set of *tert*-butyl and olefinic resonances may be due to accidental degeneracies and broad linewidths. The $^{13}C-\{^1H\}$ DEPT (distortionless enhancement by polarization transfer) spectrum shows, in addition to *tert*-butyl and olefinic resonances, a single signal attributable to the η-cyclopentadienyl ring carbons; the reason for this discrepancy is obscure. The ^1H NMR spectrum of complex **16** shows just one set of four virtually coupled quartets for the methylcyclopentadienyl ring, one *tert*-butyl resonance, and one set of two olefinic resonances, consistent with the proposed structure.

The reduction of complex **1** with sodium amalgam in the presence of styrene afforded a yellow oily solid. The ^1H NMR spectrum of the product showed resonances consistent with the presence of four isomers of $[Mo(\eta-C_5H_5)Cl(PhCH{=}CH_2)(NBu^t)]$ **14**, with structures based on that of compound **11** in which the styrene ligand takes up the four possible co-ordination geometries, *i.e.* with the phenyl group up or down with respect to the C_5 ring or adjacent to the Cl or the NBu^t ring. A partial assignment of the ^1H NMR spectrum of **14** was assisted by a $^1H-^1H$ shift correlation experiment (COSY-45). Separation of the isomers of the product **14** could not be achieved through column chromatography, sublimation or fractional crystallization. We note that the compound $[Nb(\eta-C_5H_5)(PMe_3)(C_3H_6)(NC_6H_3Pr^i{}_2-2,6)]$ also exists as a mixture of four isomers and selective crystallization of only one isomer was possible.[17]

The reduction of a solution of **1** with sodium amalgam in the presence of an excess of but-2-yne afforded two products which were crystallized from light petroleum. The major (yellow) product **17** was separated from the minor (red) product by crystal picking. Trace contamination with the minor product prevented isolation of an analytically pure sample of the major product. Both products were volatile. The major (yellow) product, $[Mo(\eta-C_5H_5)Cl(C_2Me_2)(NBu^t)]$ **17**, was isolated in *ca.* 50% yield. Its IR spectrum showed bands assignable to ν(Mo–Cl) at 280 cm^{-1} and a band at 1357 cm^{-1} is tentively assigned to the M=NR moiety. There is also a band at 1858 cm^{-1} assignable to the ν(C≡C) stretching mode of a co-ordinated alkyne. Electron-counting procedures require the alkyne ligand of **17** to donate only two electrons to the metal centre.[76]

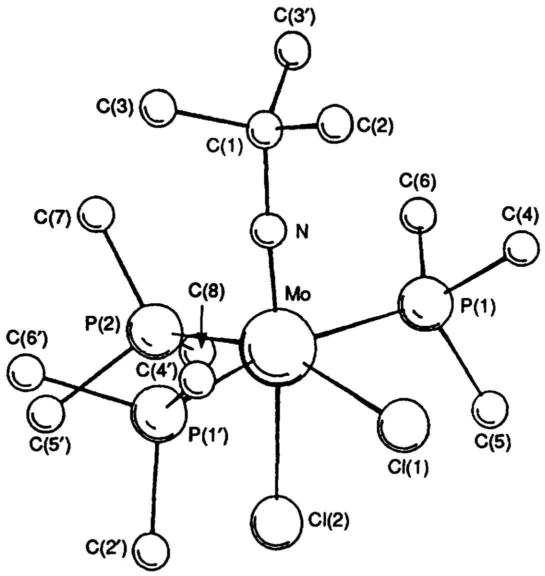


Fig. 4 Molecular structure of $[Mo(NBu^t)Cl_2(PMe_3)_3]$ **20**. Hydrogen atoms are omitted for clarity

The minor product of the reaction was formed in insufficient quantity for full characterization. The ^1H NMR spectrum showed resonances assignable to η-cyclopentadienyl, *tert*-butyl and alkyne methyl group resonances: it may be a mercury-bridged compound $[\{Mo(\eta-C_5H_5)(C_2Me_2)(NBu^t)\}_2(\mu-Hg)]$ analogous to **15** and **16**.

Reduction of a solution of **6** in the presence of but-2-yne afforded the yellow phenylimide butyne compound $[Mo(\eta-C_5H_5)Cl(C_2Me_2)(NPh)]$ **18** as the only isolated product in *ca.* 20% yield. Compounds **17** and **18** may be compared to $[Ta(NC_6H_3Pr^i{}_2-2,6)(OC_6H_3Pr^i{}_2-2,6)(py)_2(RC{\equiv}CR)]$ (py = pyridine),[77] $[Nb(\eta-C_5R_5)(PMe_3)(RC{\equiv}CR)(NC_6H_3Pr^i{}_2-2,6)]$,[16,17] $[WCl_2(NPh)(PhC{\equiv}CPh)(PMe_3)_2]$,[76] $[W(NC_6H_3-Pr^i{}_2-2,6)_2(PMe_2Ph)(HC{\equiv}CSiMe_3)]$[78] and $[Mo(NC_6H_4Me-4)\{C_2(CO_2Me)_2\}(S_2CNEt_2)_2]$,[79] which also possess both an alkyne and an imide ligand co-ordinated to the metal centre.

The reduction of complex **1** with sodium amalgam under 1 atm of carbon monoxide afforded green microcrystals of $[Mo(\eta-C_5H_5)Cl(CO)(NBu^t)]$ **19** in very low yield, and the reduction of **2** with sodium amalgam in the presence of an excess of trimethylphosphine afforded the air-stable compound $[Mo(NBu^t)Cl_2(PMe_3)_3]$ **20** in low yield. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a thf solution.

The molecular structure of complex **20** is shown in Fig. 4, selected bond lengths and angles are given in Table 4 and fractional atomic coordinates for the non-hydrogen atoms are listed in Table 5. The structure features a short metal–nitrogen bond [1.717(5) Å] and a near-linear metal–nitrogen–carbon unit [176.8(5)°], consistent with the imide ligand acting as a four-electron donor. This enables the molecule to achieve an 18-electron configuration. The compound is isostructural with $[W(NPh)Cl_2(PMe_3)_3]$,[80] and selected metric data for this complex and **20** are compared in Table 6.

Both compounds feature a *mer* configuration of phosphine

Table 4 Selected bond lengths (Å) and angles (°) for $[Mo(NBu^t)Cl_2(PMe_3)_3]$ **20** with estimated standard deviations (e.s.d.s) in parentheses

Mo–Cl(1)	2.508(2)	Mo–Cl(2)	2.552(2)
Mo–N	1.717(5)	Mo–P(1)	2.516(1)
Mo–P(2)	2.475(2)	N–C(1)	1.459(9)
Cl(1)–Mo–Cl(2)	84.21(8)	P(1)–Mo–P(1′)	166.24(7)
N–Mo–Cl(1)	102.5(2)	P(2)–Mo–Cl(1)	159.84(8)
N–Mo–Cl(2)	173.2(2)	P(2)–Mo–Cl(2)	75.62(7)
P(1)–Mo–Cl(1)	83.13(3)	P(2)–Mo–N	97.6(2)
P(1)–Mo–Cl(2)	88.88(3)	P(2)–Mo–P(1)	96.29(3)
P(1)–Mo–N	91.91(4)		

Table 5 Fractional atomic coordinates for the non-hydrogen atoms of $[Mo(NBu^t)Cl_2(PMe_3)_3]$ **20** with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Mo	0.000 0	0.762 71(3)	0.002 3(2)
Cl(1)	0.000 0	0.707 8(2)	−0.181 6(3)
Cl(2)	0.000 0	0.941 7(1)	−0.072 6(3)
N	0.000 0	0.649 0(4)	0.066 7(5)
P(1)	0.186 7(1)	0.757 52(9)	−0.020 2(3)
P(2)	0.000 0	0.875 6(1)	0.153 9(3)
C(1)	0.000 0	0.549 5(5)	0.115 9(3)
C(2)	0.000 0	0.468 4(5)	0.034 9(8)
C(3)	−0.093 6(4)	0.540 2(5)	0.182 8(5)
C(4)	0.226 9(5)	0.640 1(5)	−0.079 2(7)
C(5)	0.237 1(6)	0.851 4(6)	−0.106 8(6)
C(6)	0.272 8(5)	0.762 3(6)	0.089 7(8)
C(7)	0.000 0	0.812 6(7)	0.275 1(7)
C(8)	0.104 1(5)	0.962 4(6)	0.169 3(6)

Table 6 Comparison of selected structural data for $[Mo(NBu^t)Cl_2(PMe_3)_3]$ **20** and $[W(NPh)Cl_2(PMe_3)_3]$

Bond length/Å	$[Mo(NBu^t)Cl_2(PMe_3)_3]$	$[W(NPh)Cl_2(PMe_3)_3]$
M=N	1.717(5)	1.755(3)
$M–Cl_{axial}$	2.552(2)	2.501(1)
$M–Cl_{equatorial}$	2.508(2)	2.491(1)
$M–P_{ipso}$	2.475(2)	2.453(1)
M–P	2.516(1)	2.483(1)
M=N–C	176.8(5)	179.5(3)

ligands, and a *cis* disposition of chlorine atoms. The structure of complex **20** shows evidence of the *trans* influence of the imide and phosphine ligands in the differing lengths of the metal–chlorine bonds (that *trans* to the imide ligand is elongated by 0.04 Å), and in the lengths of the metal–phosphine bonds (that *trans* to chlorine is 0.041 Å shorter than that *trans* to phosphorus). Similar trends are observed in the metal–phosphorus bond lengths of $[W(NPh)Cl_2(PMe_3)_3]$, although, surprisingly, the metal–chlorine bonds are apparently equal. Similar structural motifs are observed in the related compounds $[W(O)Cl_2(PMe_2Ph)_3]$, $[W(O)Cl_2(PMePh_2)_3]$, $[W(O)Cl_2(PEt_2Ph)_3]$, $[W(O)Cl_2(PMe_3)_3]$ and $[ReNCl_2(PEt_2Ph)_3]$.[81] The formation of compound **20** from **2** illustrates the strength and inertness of the metal–nitrogen multiple bond (in the series of complexes under study here) since it remains intact whilst the cyclopentadienyl ring is detached.

In conclusion, the new compounds and reactions are summarised in Schemes 1 and 2. The molybdenum–imide fragment is able to survive under a variety of reaction conditions and may be described as inert.

Experimental

Where necessary, reactions were performed under an inert atmosphere of dinitrogen using a dual nitrogen/vacuum line. Unless otherwise stated, reactions were performed in Schlenk vessels, sealed at the B24 cone by rubber 'Suba-Seals', or glass caps. Liquids were transferred through stainless steel cannulae (0.5–2 mm diameter) by excess dinitrogen pressure. Filtration was achieved either by using such cannulae modified to take a paper or glass filter at one end, or by use of a glass frit covered with a bed of oven-dried Celite (Koch-Light). Chromatography was performed on columns of deactivated alumina (6% w/w water) made up with light petroleum (b.p. 40–60 °C) under dinitrogen.

Toluene and diglyme (2-methoxyethyl ether) were distilled from sodium, thf and benzene from potassium, and diethyl ether and light petroleum (b.p. 40–60 °C) from Na/K alloy. Distillation was conducted under dinitrogen. Dichloromethane was distilled under dinitrogen from phosphorus pentaoxide. Acetonitrile was distilled under dinitrogen from calcium hydride. Chlorobenzene was dried over activated molecular sieves (4 Å). Dried solvents were stored over activated molecular sieves (4 Å) in flame-dried Young's ampoules. Solvents were degassed prior to use by repeated pumping and admission of dinitrogen. Deuteriated solvents were stored over molecular sieves (4 Å) for 1 week prior to use. Microanalyses were obtained either from the microanalytical department of this department, or from Analytische Laboratorien, Engelskirchen, Germany.

The IR spectra were recorded on either Mattson 'Polaris' FTIR, Perkin-Elmer 1710 FTIR or Perkin-Elmer 457 grating spectrometers. Samples were prepared as pressed CsI discs unless otherwise stated. The NMR spectra were recorded on a Brüker AM 300 instrument; ^1H spectra at 300.13 MHz and ^{13}C at 75.5 MHz. Spectra were referenced internally by using the residual protio solvent resonance or the solvent resonance (^{13}C). Chemical shifts (δ) are expressed in ppm, and coupling constants in Hz. Mass spectra were measured either on an AEI MS 302 mass spectrometer, or were obtained by Dr. Ballantine at the SERC facility at the University of Swansea (for FAB). The ESR spectra were recorded on a Varian E 109 instrument.

Cyclic voltammograms were measured using an Oxford Instruments potentiostat connected to a Rikadenki XY recorder. Magnetic measurements were made on a Johnson Matthey Chemicals magnetic susceptibility balance.

The compounds bis[tricarbonyl(η-cyclopentadienyl)molybdenum], bis[tricarbonyl(η-methylcyclopentadienyl)molybdenum],[7] tetrachloro(η-cyclopentadienyl)molybdenum[68] and tetrachloro(η-methylcyclopentadienyl)molybdenum[68] were prepared as described.

Preparations.—*Bis*[*tricarbonyl*(η-*isopropylcyclopentadienyl*)-*molybdenum*]. Molybdenum hexacarbonyl (20.3 g, 0.075 mol) was treated with sodium isopropylcyclopentadienide (10 g, 0.075 mol) in diglyme. Subsequent oxidation with iron(II) sulfate (31 g, 0.075 mol) and work-up as described[82] afforded the product. Yield, 20.5 g (93%).

Tetrachloro(η-*isopropylcyclopentadienyl*)*molybdenum*. Bis[tricarbonyl(η-isopropylcyclopentadienyl)molybdenum] (29.2 g, 0.051 mol) was treated with phosphorus pentachloride (42.4 g, 0.20 mol), as described for tetrachloro(η-methylcyclopentadienyl)molybdenum.[68] Yield, 24.2 g (71%).

$[Mo(\eta\text{-}C_5H_4R)Cl_2(NBu^t)]$ (R = H **1**, Me **2** *or* Pr^i **3**). A typical reaction is described. Tetrachloro(η-cyclopentadienyl)molybdenum (11.4 g, 0.038 mol) suspended in toluene (200 cm^3) was treated with *tert*-butylamine (12.0 cm^3, 0.114 mol) in toluene (50 cm^3) added dropwise with stirring over 1 h. The initially red suspension became yellow-brown. The mixture was stirred for 1 h and filtered. The solvent was removed under reduced pressure and the resulting brown solid **1** was recrystallized from thf at −80 °C. Yield, 5 g (44%). For **2**, purification was by sublimation (10^{-2} mmHg, *ca.* 100 °C), or by recrystallization from toluene at −80 °C. Yield, 4.4 g (36%). For **3**, final purification was effected by sublimation. Yield, *ca.* 2.5 g (50%).

Dichloro(η-*cyclopentadienyl*)(*isopropylimido*)*molybdenum* **4** *and dichloro*(η-*cyclopentadienyl*)(n-*propylimido*)*molybdenum* **5**. Tetrachloro(η-cyclopentadienyl)molybdenum (5.0 g, 16.5 mmol) suspended in toluene (100 cm^3) was treated with isopropylamine (4.2 cm^3, 0.043 mol) dropwise with stirring over 15 min. The initially red suspension became yellow-brown. The mixture was stirred for 15 min and filtered. The solution was concentrated under reduced pressure and cooled to −80 °C. The resulting brown crystals of **4** were filtered off at −80 °C, washed with toluene (5 cm^3), light petroleum (10 cm^3) and dried *in vacuo*. Yield, 3 g (60%).

Compound **5** was prepared similarly from tetrachloro(η-cyclopentadienyl)molybdenum (0.7 g, 2.3 mmol) and *n*-propylamine (0.6 cm^3, 6.93 mmol). The mixture was stirred for 45 min, and filtered. The solvent was removed under reduced pressure and the resulting greenish brown solid **5** was purified by recrystallization from thf–pentane (1:1) at −80 °C. Yield, 300 mg (45%).

Dichloro(η-*cyclopentadienyl*)(*phenylimido*)*molybdenum* **6** *and dichloro*(η-*methylcyclopentadienyl*)(*phenylimido*)*molybdenum* **7**. Tetrachloro(η-cyclopentadienyl)molydenum (0.5 g, 1.65 mmol) suspended in toluene (100 cm^3) was treated with aniline (0.5 cm^3, 5 mmol) dropwise with stirring over 20 min. The initially red suspension became yellow-brown. The mixture was stirred for 15 min, allowed to settle and filtered. The solution was concentrated under reduced pressure and cooled to −20 °C. The resulting brown crystals of **6** were filtered at −20 °C, washed three times with toluene (2 cm^3) and dried *in vacuo*. Yield, 0.25 g (50%).

Compound **7** was prepared similarly from tetrachloro(η-methylcyclopentadienyl)molybdenum (1.00 g, 3.15 mmol) and aniline (0.9 cm^3, 9.5 mmol). Yield, 0.7 g (65%).

(tert-*Butylimido*)*dibromo*(η-*methylcyclopentadienyl*)*molybdenum* **8**. Tetrabromo(η-methylcyclopentadienyl)molybdenum (500 mg, 1.01 mmol) in toluene (50 cm^3) was treated with *tert*-butylamine (0.33 cm^3) in toluene (50 cm^3) dropwise over 30 min with stirring. The initially black suspension became yellow. The mixture was stirred for 15 min, then filtered. Solvent was removed under reduced pressure and the yellow-orange solid recrystallized from thf–pentane (3:2) at −30 °C. Yield, *ca.* 300 mg (70%). Final purification was effected by sublimation (10^{-2} mmHg, 70 °C).

(tert-*Butylimido*)*dichloro*(η-*cyclopentadienyl*)*tungsten* **9** *and* (tert-*butylimido*)*dichloro*(η-*methylcyclopentadienyl*)*tungsten* **10**. Tetrachloro(η-cyclopentadienyl)tungsten (550 mg, 1.41 mmol) in toluene (30 cm^3) was treated with *tert*-butylamine (0.5 cm^3, 4.7 mmol) in toluene (30 cm^3) added dropwise over 30 min with stirring. The initially dark red suspension became dark yellow-green. The mixture was filtered, solvent was removed under reduced pressure and the product was recrystallized from thf–pentane (1:1) at −20 °C, yielding blue-green crystals of **9**. Yield, *ca.* 200 mg (35%).

Compound **10** was prepared similarly from tetrachloro(η-methylcyclopentadienyl)tungsten (500 mg, 1.24 mmol) in toluene (30 cm^3) and *tert*-butylamine (0.4 cm^3, 3.8 mmol) in toluene (30 cm^3). The initially red suspension became dark red. The mixture was stirred for 2 h and filtered. Slow removal of solvent under reduced pressure yielded analytically pure red crystals. Yield, 350 mg (70%).

(tert-*Butylimido*)*chloro*(η-*cyclopentadienyl*)(η-*ethene*)*molybdenum* **11**. (*tert*-Butylimido)dichloro(η-cyclopentadienyl)molybdenum (500 mg, 1.65 mmol) in thf (50 cm^3) under 1 atm of ethene was treated with sodium amalgam (0.08 g Na, 2 equivalents) in a dropwise manner over 15 min with stirring. The mixture was stirred for 2 h. The initially brown solution turned deep yellow and a white precipitate formed. The solution was decanted, solvent was removed under reduced pressure and the product extracted with light petroleum (100 cm^3). Concentration and cooling to −20 °C yielded orange-red crystals which were filtered, washed with cold (−20 °C) light petroleum (2 cm^3) and dried *in vacuo*. Yield, 250 mg (50%).

(tert-*Butylimido*)*chloro*(η-*ethene*)(η-*methylcyclopentadienyl*)*molybdenum* **12** *and* (tert-*butylimido*)*chloro*(η-*ethene*)(η-*isopropylcyclopentadienyl*)*molybdenum* **13**. (*tert*-Butylimido)dichloro(η-methylcyclopentadienyl)molybdenum (500 mg, 1.57 mmol) in thf (100 cm^3) under 1 atm of ethene was treated with potassium graphite (KC$_8$, 250 mg, 1 equivalent) over 10 min with stirring. The mixture was stirred for a further 10 min and the initially brown solution became yellow-orange. The mixture was filtered, solvent was removed under reduced pressure, the product was extracted into light petroleum and concentrated. Cooling to −20 °C yielded orange-red crystals which were filtered at −20 °C, washed once with cold (−20 °C) light petroleum (2 cm^3) and dried *in vacuo*. Yield, 200 mg (40%).

Compound **13** was prepared similarly from (*tert*-butylimido)dichloro(η-isopropylcyclopentadienyl)molybdenum (1 g, 2.90 mmol) in thf (150 cm^3) under 1 atm of ethene and potassium graphite (0.5 g, 1 equivalent) over 15 min at −30 °C. Yield, 350 mg (35%).

(tert-*Butylimido*)*chloro*(η-*cyclopentadienyl*)(η-*styrene*)*molybdenum* **14**. (*tert*-Butylimido)dichloro(η-cyclopentadienyl)molybdenum (500 mg, 1.65 mmol) in thf (50 cm^3) and styrene (0.5 cm^3) was treated with sodium amalgam [0.08 g sodium (2 equivalents) in 2 cm^3 mercury] dropwise with stirring over 20 min. The mixture was stirred for a further 20 min. The initially red solution became yellowish red and a white suspension formed. The mixture was filtered, solvent was removed under reduced pressure and the yellow oily solid extracted with light petroleum (2 × 50 cm^3) and cooled to −20 °C. Filtration afforded an oily yellow solid. Yield, 200 mg (33%).

Bis[(tert-*butylimido*)(η-*cyclopentadienyl*)(η-*ethene*)*molybdenio*]*mercury* **15**. (*tert*-Butylimido)dichloro(η-cyclopentadienyl)molybdenum (0.5 g, 1.65 mmol) in thf (50 cm^3) under 1 atm of ethene was treated with sodium amalgam [0.08 g sodium (2 equivalents) in 2 cm^3 mercury] dropwise with stirring over 0.5 h. The mixture was stirred for 1.5 h, and the initially red solution became bright yellow and a pale precipitate formed. The solution was filtered, solvent was removed under reduced pressure and the yellow oily solid extracted with light petroleum (50 cm^3) yielding a dark yellow solution. Cooling to −20 °C yielded very dark yellow crystals which were filtered off, washed with cold light petroleum (1 cm^3) and dried *in vacuo*. Yield, 300 mg (50%).

Bis[(tert-*butylimido*)(η-*ethene*)(η-*methylcyclopentadienyl*)-*molybdenio*]*mercury* **16**. (*tert*-Butylimido)dichloro(η-methylcyclopentadienyl)molybdenum (0.50 g, 1.58 mmol) in thf (50 cm^3) under 1 atm of ethene was treated with sodium amalgam [0.075 g sodium (2 equivalents) in 2 cm^3 mercury] dropwise with stirring over 0.5 h. The mixture was stirred for 15 min and the initially red solution became bright yellow and a pale precipitate formed. Filtration and subsequent work-up yielded both *tert*-(butylimido)chloro(η-ethene)(η-methylcyclopentadienyl)molybdenum and the title compound, which were separated by fractional crystallization from light petroleum. Yield of **16**, 100 mg (16%).

(tert-*Butylimido*)(η^2-*butyne*)*chloro*(η-*cyclopentadienyl*)*molybdenum* **17**. (*tert*-Butylimido)*dichloro*(η-*cyclopentadienyl*)*molybdenum* (500 mg, 1.65 mmol) and butyne (*ca.* 2 cm^3) in thf (100 cm^3) were treated with sodium amalgam [0.08 g sodium (2 equivalents) in 2 cm^3 mercury] dropwise with stirring over 30 min. The mixture was stirred for 2 h. The initially brownish solution became reddish-yellow and a white precipitate formed. The solution was filtered, solvent was removed under reduced pressure and the reddish yellow oily solid extracted with light petroleum (50 cm^3). The resulting yellow extracts were concentrated and cooled to −20 °C yielding both red and yellow (major product) microcrystals. The yellow product was separated manually. Yield, 250 mg (47%).

(η^2-*Butyne*)*chloro*(η-*cyclopentadienyl*)(*phenylimido*)*molybdenum* **18**. Dichloro(η-cyclopentadienyl)(phenylimido)molybdenum (500 mg, 1.54 mmol) and butyne (*ca.* 1 cm^3, excess) in thf (50 cm^3) were treated with sodium amalgam [0.071 g sodium (2 equivalents) in 2 cm^3 mercury] dropwise with stirring over 15 min. The mixture was stirred for a further 10 min. The initially brownish solution became yellow and a white precipitate formed. The solution was filtered, solvent was removed under reduced pressure and the reddish-yellow oily solid extracted with light petroleum (3 × 50 cm^3). The resulting yellow extracts were concentrated and cooled to −20 °C yielding orange microcrystals. Final purification was effected by sublimation. Yield, *ca.* 100 mg (20%).

(tert-*Butylimido*)*carbonyl*(*chloro*)(η-*cyclopentadienyl*)*molybdenum* **19**. (*tert*-Butylimido)dichloro(η-cyclopentadienyl)molybdenum (500 mg, 1.65 mmol) in thf (100 cm^3) under 1 atm of carbon monoxide was treated with sodium amalgam [0.04 g sodium (1 equivalent) in 2 cm^3 mercury] dropwise with stirring over 30 min. The mixture was stirred for a further 2 h. The initially yellow-brown solution became yellow and a white precipitate formed. The solution was filtered, solvent was removed under reduced pressure and the yellow oily solid extracted with toluene (50 cm^3). The extract was concentrated and cooled to −80 °C. Green crystals formed which were filtered off at −80 °C, washed with toluene (3 × 5 cm^3) at −80 °C and dried *in vacuo*. Yield, 20 mg (5%).

(tert-*Butylimido*)*dichloro*[*tris*(*trimethylphosphine*)]*molybdenum* **20**. (*tert*-Butylimido)dichloro(η-methylcyclopentadienyl)molybdenum (0.5 g, 1.57 mmol) in thf (50 cm^3) and trimethylphosphine (0.5 cm^3, 3 equivalents) were treated with sodium amalgam [0.075 g sodium (2 equivalents) in 2 cm^3 mercury], added dropwise with stirring over 45 min. The mixture was stirred for a further 30 min and the initially yellow-brown solution became deep red and a white precipitate formed. The mixture was filtered, solvent was removed under reduced pressure and the red oily solid was extracted with toluene (2 × 50 cm^3). The deep red extracts were concentrated and cooled to −20 °C, and the resulting purple microcrystals filtered off, washed with cold toluene (2 × 1 cm^3) and dried *in vacuo*. Yield, 200 mg (25%). Recrystallization by slow evaporation of a thf solution of **20** afforded single crystals suitable for X-ray diffraction analysis.

Crystal Structure Determination of $[Mo(NBu^t)Cl_2(PMe_3)_3]$ **20**.—*Crystal data.* $C_{13}H_{36}Cl_2MoNP_3$, $M = 466.20$, crystal size 0.2 × 0.3 × 0.3 mm, orthorhombic, space group $Cmc2_1$, $a = 13.382(7)$, $b = 13.166(7)$, $c = 13.057(2)$ Å, $U = 2300.4$ $Å^3$, $Z = 4$, $D_c = 1.346$ g cm^{-3}, $\mu = 9.91$ cm^{-1}, $F(000) = 968$, Mo-Kα ($\lambda = 0.710\,69$ Å); $2 < 2\theta < 50°$, scan mode ω–2θ, total unique data 1235, observations $[I > 3\sigma(I)]$ 1130, variables 106, observations/variables 10.7, Chebyshev parameters 14.4, −9.93, 11.7, $R_{merge} = 0.044$, $R = \Sigma(|F_o - F_c|)/\Sigma|F_o| = 0.031$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|]^{\frac{1}{2}} = 0.033$.

A crystal of complex **20** was sealed in a Lindemann glass capilliary under N_2 and transferred to the goniometer head of an Enraf–Nonius CAD4 diffractometer. Unit-cell parameters were calculated from the setting angles of 25 reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections.

The data were corrected for Lorentz and polarisation effects and an empirical absorption correction[83] based on azimuthal scan data was applied. Equivalent reflections were merged and systematically absent reflections rejected. The molybdenum atom positions were determined by direct methods. Subsequent Fourier-difference syntheses revealed the positions of all other non-hydrogen atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in estimated positions (C–H 0.96 Å) with fixed isotropic thermal parameters (1.3 × the equivalent isotropic, thermal parameter of the carbon atom to which they were bonded) and refined riding their supporting carbon atoms. A Chebyshev weighting scheme[84] was applied and the data were corrected for the effects of anomalous dispersion and isotropic extinction (*via* an overall isotropic extinction parameter[85]) in the final stages of refinement. All crystallographic calculations were performed using the CRYSTALS suite[86] on a MicroVAX 3800 computer in the Chemical Crystallography Laboratory, Oxford. Neutral-atom scattering factors were taken from the usual sources.[87]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

References

1 J. N. Armor, *Inorg. Chem.*, 1978, **17**, 203.
2 K. M. Doxsee, J. B. Farahi and H. Hope, *J. Am. Chem. Soc.*, 1991, **113**, 8889.
3 P. J. Walsh, F. J. Hollander and R. G. Bergman, *Organometallics*, 1993, **12**, 3705.
4 W. A. Herrmann, B. Menjon and E. Herdtweck, *Organometallics*, 1991, **10**, 2134.
5 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc.*, 1983, **105**, 7295.
6 C. T. Vroegop, J. H. Teuben, F. van Balhuis and J. G. M. van der Linden, *J. Chem. Soc., Chem. Commun.*, 1983, 550.
7 Y. Bai, H. W. Roesky, M. Noltemeyer and M. Witt, *Chem. Ber.*, 1992, **125**, 825.
8 J. M. Meyer, C. J. Curtis and J. E. Bercaw, *J. Am. Chem. Soc.*, 1983, **105**, 2651.
9 S. Gambarotta, A. Chiesi-Villa and C. Guastini, *J. Organomet. Chem.*, 1984, **270**, C49.
10 J. H. Osborne and W. C. Trogler, *Inorg. Chem.*, 1985, **24**, 3098.
11 N. Wiberg, H. W. Haring and U. Schubert, *Z. Naturforsch., Teil B*, 1980, **35**, 599.
12 J. H. Osborne, A. L. Rheingold and W. C. Trogler, *J. Am. Chem. Soc.*, 1985, **107**, 7945.
13 M. Veith, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 387.
14 M. Jolly, J. P. Mitchell and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1992, 1331.
15 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.
16 U. Siemeling and V. C. Gibson, *J. Organomet. Chem.*, 1992, **426**, C25.
17 A. D. Poole, V. C. Gibson and W. Clegg, *J. Chem. Soc., Chem. Commun.*, 1992, 237.
18 F. Preuss, H. Becker, J. Kaub and W. S. Sheldrick, *Z. Naturforsch., Teil B*, 1988, **43**, 1195.
19 E. A. Maata, *Inorg. Chem.*, 1984, **23**, 2560.
20 G. Parkin, A. van Asselt, D. J. Leahy, L. Whinnery, N. G. Hua, R. W. Quan, R. M. Henling, W. P. Schaefer, B. D. Santarsiero and J. E. Bercaw, *Inorg. Chem.*, 1992, **31**, 82.
21 I. Manners and P. Paetzold, *J. Chem. Soc., Chem. Commun.*, 1988, 183.
22 D. M. Antonelli, M. L. H. Green and P. Mountford, *J. Organomet. Chem.*, 1992, **438**, C4.
23 R. R. Schrock and J. D. Feldman, *J. Am. Chem. Soc.*, 1978, **100**, 3359.
24 C. D. Wood, S. J. McLain and R. R. Schrock, *J. Am. Chem. Soc.*, 1979, **101**, 3210.
25 H. Alper, J.-F. Petrignani, F. W. B. Einstein and A. C. Willis, *J. Am. Chem. Soc.*, 1983, **105**, 1701.
26 R. Korswagen, K. Wiederhammer and M. L. Ziegler, *Acta Crystallogr., Sect. B*, 1979, **35**, 2554.
27 I. Bernal, M. Draux, H. Brunner, B. Hoffmann and J. Wachter, *Organometallics*, 1986, **5**, 655.
28 J. J. D'Errico, L. Messerle and M. D. Curtis, *Inorg. Chem.*, 1983, **22**, 849.
29 L. Messerle and M. D. Curtis, *J. Am. Chem. Soc.*, 1982, **104**, 889.
30 M. R. Churchill and Y.-J. Li, *J. Organomet. Chem.*, 1986, **301**, 49.
31 F. W. B. Einstein, T. T. Jones, A. J. L. Hanlan and D. Sutton, *Inorg. Chem.*, 1982, **21**, 2585.
32 L. F. Dahl, P. D. Frisch and G. R. Gust, *J. Less-Common Met.*, 1974, **36**, 255.
33 W. G. Kita, J. A. McCleverty and D. Seddon, *J. Less-Common Met.*, 1974, **36**, 203.
34 N. Meijboom, C. J. Schaverien and A. G. Orpen, *Organometallics*, 1990, **9**, 774.
35 M. L. H. Green and K. J. Moynihan, *Polyhedron*, 1986, **5**, 921.
36 M. L. H. Green, G. Hogarth, P. C. Konidaris and P. Mountford, *J. Chem Soc., Dalton Trans.*, 1990, 3781.
37 J. Fletcher, G. Hogarth and D. A. Tocher, *J. Organomet. Chem.*, 1991, **403**, 345.

38 T. E. Glassman, M. G. Vale and R. R. Schrock, *Organometallics*, 1991, **10**, 4046.

39 T. E. Glassman, A. H. Liu and R. R. Schrock, *Inorg. Chem.*, 1991, **30**, 4723.

40 J. Sundermeyer, *Chem. Ber.*, 1991, **124**, 1977.

41 J. Sundermeyer, MSc Thesis, Wurtzburg, 1991, personal communication.

42 Y. Ma, P. Demou and J. Faller, *Inorg. Chem.*, 1991, **30**, 62.

43 M. B. O'Regan, A. H. Liu, W. C. Finch, R. R. Schrock and W. M. Davis, *J. Am. Chem. Soc.*, 1990, **112**, 4331.

44 R. R. Schrock, R. M. Kolodziej, A. H. Liu, W. M. Davis and M. G. Vale, *J. Am. Chem. Soc.*, 1990, **112**, 4338.

45 I. L. Eremenko, A. A. Pasynskii, E. A. Vas'utinskaya, A. S. Katugin, S. E. Nefedov, O. G. Ellert, V. M. Novotortsev, A. F. Shestakov, A. I. Yanovski and Y. T. Struchkov, *J. Organomet. Chem.*, 1991, **411**, 193.

46 G. Hogarth and P. C. Konidaris, *J. Organomet. Chem.*, 1990, **399**, 149.

47 G. Hogarth, J. Fletcher and D. A. Tocher, *J. Organomet. Chem.*, 1991, **405**, 207.

48 P. Legzdins, S. J. Rettig, K. J. Ross and J. E. Veltheer, *J. Am. Chem. Soc.*, 1991, **113**, 4361.

49 S. F. Pedersen and R. R. Schrock, *J. Am. Chem. Soc.*, 1982, **104**, 7483.

50 W. A. Herrmann, E. Herdtweck, M. Floel, J. Kulpe, U. Kusthardt and J. Okuda, *Polyhedron*, 1987, **6**, 1165.

51 C. F. Barrientos-Penna, F. W. B. Einstein, T. Jones and D. Sutton, *Inorg. Chem.*, 1982, **21**, 2578.

52 N. Wiberg, H. W. Haring, G. Huttner and P. Friedrich, *Chem. Ber.*, 1978, **111**, 2708.

53 W. A. Herrmann, D. W. Marz and E. Herdtweck, *J. Organomet. Chem.*, 1990, **394**, 285.

54 A. A. Danopoulos, G. Wilkinson and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 181.

55 Y. Chi, H.-F. Hsu, L.-K. Liu, S.-M. Peng and G.-H. Lee, *Organometallics*, 1992, **11**, 1763.

56 J. Muller, I. Sonn and T. Akhnoukh, *J. Organomet. Chem.*, 1991, **414**, 381.

57 R. W. Marshman, J. M. Shusta, S. R. Wilson and P. A. Shapley, *Organometallics*, 1991, **10**, 1671.

58 Y. Chi, D.-K. Hwang, S.-F. Chen and L.-K. Liu, *J. Chem. Soc., Chem. Commun.*, 1989, 1540.

59 D. S. Glueck, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1989, **111**, 2719.

60 D. S. Glueck, J. Wu, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1991, **113**, 2041.

61 W. D. McGhee, T. Foo, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 8544.

62 S. Otsuka, A. Nakamura and T. Yoshida, *Inorg. Chem.*, 1968, **7**, 261.

63 J. G. Brennan and R. A. Andersen, *J. Am. Chem. Soc.*, 1985, **107**, 514.

64 R. E. Cramer, F. Edelmann, A. L. Mori, S. Roth, J. W. Gilje, K. Tatsumi and A. Nakamura, *Organometallics*, 1988, **7**, 841.

65 J. G. Brennan, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1988, **110**, 4554.

66 W. A. Herrmann, G. Weichselbaumer, R. A. Paciello, R. A. Fischer, E. Herdtweck, J. Okuda and D. W. Marz, *Organometallics*, 1990, **9**, 489.

67 M. L. H. Green, P. C. Konidaris, P. Mountford and S. J. Simpson, *J. Chem. Soc., Chem. Commun.*, 1992, 256.

68 R. C. Murray, L. Blum, A. H. Liu and R. R. Schrock, *Organometallics*, 1985, **4**, 953; M. L. H. Green, J. D. Hubert and P. Mountford, *J. Chem. Soc., Dalton Trans.*, 1990, 3793.

69 W. A. Nugent and J. Mayer, *Metal-Ligand Multiple Bonds*, Wiley-Interscience, New York, 1988.

70 T.-T. Chang, *Phys. Rev.*, 1964, **136**, A1413.

71 J. C. Green and G. H. Maunder, unpublished work.

72 V. C. Gibson, D. N. Williams, W. Clegg and D. C. R. Hockless, *Polyhedron*, 1989, **8**, 1819.

73 J. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.

74 L.-C. Song, H. Yang, Q. Dong and Q.-M. Hu, *J. Organomet. Chem.*, 1991, **414**, 137.

75 D. S. Williams, J. T. Anhaus, M. H. Schofield, R. R. Schrock and W. M. Davis, *J. Am. Chem. Soc.*, 1991, **113**, 5840.

76 A. J. Neilson and D. C. Ware, *Polyhedron*, 1990, **9**, 603.

77 Y.-W. Chao, P. A. Wexler and D. E. Wigley, *Inorg. Chem.*, 1989, **28**, 3860.

78 D. S. Williams, M. H. Schofield, J. T. Anhaus and R. R. Schrock, *J. Am. Chem. Soc.*, 1990, **112**, 6728.

79 D. Devore and E. A. Maata, *Inorg. Chem.*, 1985, **24**, 2846.

80 D. C. Bradley, M. B. Hursthouse, K. M. Abdul-Malik, A. J. Nielson and R. L. Short, *J. Chem. Soc., Dalton Trans.*, 1983, 2651.

81 A. V. Butcher, J. Chatt, G. J. Leigh and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1972, 1064; E. Carmona, L. Sanchez, M. L. Poveda, R. A. Jones and J. G. Hefner, *Polyhedron*, 1983, **2**, 797; P. W. R. Corfield, R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

82 R. Birdwhistell, P. Hackett and A. R. Manning, *J. Organomet. Chem.*, 1978, **157**, 239.

83 A. C. T. North, D. C. Philips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

84 J. S. Rollet, *Computing Methods in Crystallography*, Pergamon Press, Oxford, 1965.

85 A. C. Larson, *Acta Crystallogr., Sect. A*, 1967, **23**, 664.

86 D. J. Watkin, J. R. Carruthers and P. W. Betteridge, *CRYSTALS User Guide*, Chemical Crystallography Laboratory, University of Oxford, 1985.

87 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

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