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FOUR COORDINATE MOLYBDENUM ALKENE AND ALKYNE COMPLEXES BEARING ANCILLARY IMIDO LIGANDS*

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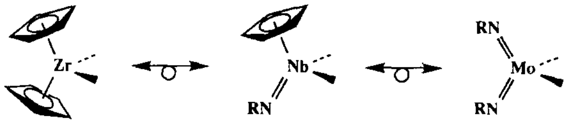
Abstract—Four coordinate molybdenum alkene complexes of the type $Mo(NR)_2(PMe_3)(CH_2CH_2R')$ [R = Bu^t, R′ = H (**2a**); R′ = Me (**2b**); R = adamantyl, R′ = H (**2c**)] have been synthesised by treatment of $Mo(NR)_2Cl_2(dme)$ [R = Bu^t (**1a**); R = adamantyl (**1b**) with two equivalents of RMgCl (R = Et, *n*-Pr) in diethylether. The molecular structure of **2b** is reported [triclinic, space group $P\bar{1}$, $a = 9.312(2)$, $b = 9.723(2)$, $c = 11.203(2)$ Å, $\alpha = 78.85(2)$, $\beta = 88.23(2)$, $\gamma = 85.94(2)°$, $U = 992.5(4)$ Å^3, $Z = 2$, $T = 293$ K]. The alkyne derivatives $Mo(NR)_2(PMe_3)(R'C{\equiv}CR'')$ [R = Bu^t, R′ = R″ = Ph (**3a**); R = Bu^t, R′ = Ph, R″ = H (**3b**); R = adamantyl, R′ = R″ = Ph (**3c**)] are prepared from **2a** and **2c** by prolonged warming at 60–70°C in heptane in the presence of one equivalent of the alkyne. The molecular structure of **3a** [orthorhombic, space group *Pbca* (No. 61), $a = 13.980(3)$, $b = 15.333(6)$, $c = 24.989(7)$ Å, $U = 5356(3)$ Å^3, $Z = 8$, $T = 120$ K] reveals an analogous pseudo-tetrahedral geometry to that found for **2b**. The relationship of these complexes to known zirconocene derivatives is discussed.

Recent studies have provided strong evidence for an 'isolobal' relationship between bent metallocenes of the group 4 elements, half-sandwich imido complexes of the group 5 metals and bis(imido) complexes of the group 6 metals;[1-3] this is illustrated for the Zr → Nb → Mo series above. The relationship derives from the similar 1σ,2π bonding characteristics of the mono-anionic cyclopentadienyl and di-anionic imido ligands and is useful for identifying new molecular systems potentially capable of metallocene-like reactivity.



(I) (II) (III)

'Single-faced' π-ligands such as carbenes, alkenes and two-electron alkynes provide good probes of the relationship since in a 'bent metallocene' environment these ligands show a strong orientation preference with respect to the 1σ,2π donor groups.[4,5] Here, we describe the synthesis and characterisation of some four coordinate, bis(imido) alkene and alkyne complexes of molybdenum that have direct analogues in zirconocene chemistry.

RESULTS AND DISCUSSION

Alkene derivatives

A convenient synthesis of the four coordinate ethene or propene complexes is provided by treat-

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* Dedicated to Professor John E. Bercaw on the occasion of his 50th birthday. There lies a veritable ability to inspire.

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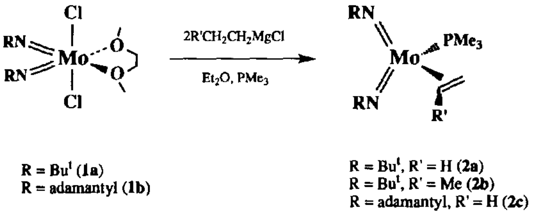
ment of the six coordinate dimethoxyethane (dme) adducts, Mo(NR)$_2$Cl$_2$(dme)[6] (R = *t*-butyl or adamantyl), with two equivalents of ethyl or *n*-propylmagnesium chloride in the presence of trimethylphosphine (eq. 1). The *t*-butylimido derivatives are somewhat easier to purify than the adamantylimido complex (**2c**) due to their tendency to crystallise more readily from pentane solution. It should be noted that if the imido ligands possess aryl substituents, e.g. 2,6-diisopropylphenyl, then five coordinate bis(phosphine) derivatives of the type Mo(NR)$_2$(PMe$_3$)$_2$(C$_2$H$_3$R′) (R′ = H, Me) result,[2a,7] a consequence of the orientational flexibility of the aryl group.



(1)

^{1}H and ^{13}C NMR data (Table 1) for the ethene derivatives (**2a,c**) show that the two ends of the ethene ligand are inequivalent, implying that the ethene C—C vector aligns in the plane perpendicular to that containing the metal centre and imido nitrogens. Moreover, the *endo* methylene hydrogens of the ethene ligand, i.e. those adjacent to the phosphine ligand, experience a substantial coupling to the PMe$_3$ phosphorus nucleus. This orientation is analogous to that adopted by 'single-faced' π-ligands in a bent metallocene environment.[4] There is no broadening of the resonances of the ethene hydrogens to >80°C indicating a substantial barrier to ethene ligand rotation and thereby a strong electronic preference for this metallocene-like orientation.

The ^{1}H NMR resonances for the propene ligand of **2b** are considerably more complicated due to extensive ^{1}H–^{1}H and ^{1}H–^{31}P couplings. However, only one isomer is observed implying that just one of the two possible alkene orientations in the 'equatorial' binding plane is favoured. The precise orientation was established by an X-ray structure determination which showed it to be the *exo* isomer in which the methyl substituent of the propene ligand lies on the side of the molecule remote to the PMe$_3$ group. The *endo* olefinic carbon also shows substantial coupling (*ca* 10 Hz) to the phosphorus nucleus. In all cases, **2a–c**, the ^{13}C NMR shifts and C—H coupling constants for the alkene ligands are consistent with considerable back donation from the d^2 metal centre.

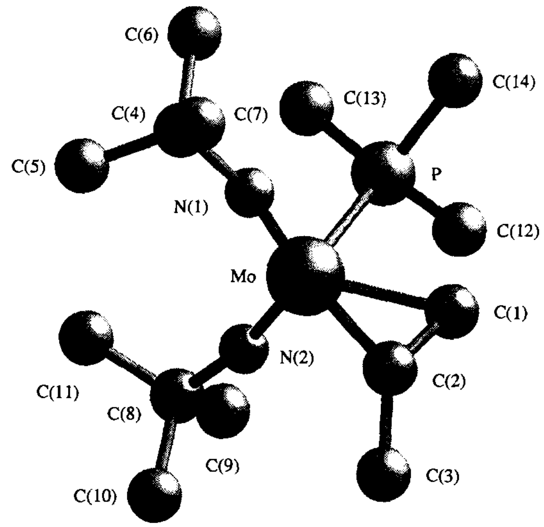


Fig. 1. Molecular structure of **2b**, without H atoms and with key atoms labelled.

Molecular structure of 2b

The molecular structure of **2b** is shown in Fig. 1 and crystal data are given in Table 2. Bond lengths and angles are collected in Table 3. The molecular parameters associated with **2b** have been discussed in detail previously and will not be reiterated here. Key bond distances and angles are collected in Table 4 for comparison with the 'isolobal' zirconocene complex Cp$_2$Zr(PMe$_3$)(C$_2$H$_4$)[8] and their alkyne analogues. It can be seen that the alkene and phosphine metal–ligand bond distances are greater for the zirconocene complex, a lengthening that is not wholly compensated for by the greater ionic radius of Zr compared with Mo. While the longer Zr—P distance could be a consequence of the greater steric congestion within the metal coordination sphere of a Cp$_2$M fragment, the greater C—C distance for the ethylene ligand attached to Zr implies enhanced metal → ligand back donation, an observation consistent with the lower electronegativity of the earlier transition metal centre. The alkenes bind asymmetrically to the metal centres of both complexes, most probably reflecting the close proximity of the PMe$_3$ ligand to one end of the alkene. The similar alignments of the C—C axes, in the same plane as the Mo—P vector provides strong support for the metallocene-like nature of the frontier orbitals for the [Mo(NBu^t)$_2$] fragment, an observation in accord with recent SCF-X$_\alpha$-SW calculations by Schrock and co-workers on the model [W(NH)$_2$] fragment.[2e]

A convenient way of illustrating the orientation of the alkene ligand in a pseudo-tetrahedral complex is using a triad representation[5] in which the

Table 1. NMR data

Compound	Assignment	Chem. shifts (ppm), multiplicity, coupling constants (Hz) ^{1}H[a]	^{13}C[b]	^{31}P[c]
2a	$CH_2{=}\mathit{CH}_2$ (*exo*)	2.26 (td, $^3J_{HH}$ 11.6, $^3J_{PH}$ 1.6)	20.96 (t, $^1J_{CH}$ 156.1)	
	$\mathit{CH}_2{=}CH_2$ (*endo*)	1.16 (td, $^3J_{HH}$ 11.6, $^3J_{PH}$ 8.2)	31.76 (td, $^1J_{CH}$ 152.4, $^2J_{PC}$ 9.9)	
	$NC\mathit{Me}_3$	1.37 (s)	33.70 (q, $^1J_{CH}$ 125.8)	
	$N\mathit{C}Me_3$		64.78 (s)	
	$P\mathit{Me}_3$	1.13 (d, $^2J_{PH}$ 8.8)	19.10 (qd, $^1J_{CH}$ 132.7, $^1J_{PC}$ 24.7)	22.55 (s)
2b	$CH_2{=}\mathit{CH}Me$	3.23 (tqd, $^3J_{HH}$ 10.8, 6.3, $^3J_{PH}$ 1.4)[d]	39.93 (d, $^1J_{CH}$ 147.7)	
	$CH_2{=}CH\mathit{Me}$	2.24 (d, $^3J_{HH}$ 6.3)	27.46 (q, $^1J_{CH}$ 124.4)	
	$\mathit{CH}_2{=}CHMe$	1.22 (ddd, $^3J_{HH}$ 10.8, $^2J_{HH}$ 5.4, $^3J_{PH}$ 5.2)[d]	37.42 (td, $^1J_{CH}$ 147.9, $^2J_{PC}$ 9.5)	
		1.02 (ddd, $^3J_{HH}$ 10.8, $^2J_{HH}$ 5.4, $^3J_{PH}$ 5.2)[d]		
	$NC\mathit{Me}_3$	1.36 (s)	34.06 (q, $^1J_{CH}$ 125.1)	
		1.34 (s)	33.86 (q, $^1J_{CH}$ 125.1)	
	$N\mathit{C}Me_3$		65.32 (s), 65.03 (s)	
	$P\mathit{Me}_3$	1.12 (d, $^2J_{PH}$ 8.7)	19.51 (qd, $^1J_{CH}$ 127.6, $^1J_{PC}$ 28.2)	22.00 (s)
2c	$CH_2{=}\mathit{CH}_2$ (*exo*)[e]	2.31 (t, $^3J_{HH}$ 12.0)	21.22 (t, $^1J_{CH}$ 152.6)	
	$\mathit{CH}_2{=}CH_2$ (*endo*)[e]	1.2[f]	32.14 (td, $^1J_{CH}$ 150.2, $^2J_{PC}$ 9.5)	
	Ad, C_α		65.7 (s)	
	Ad, $C_\beta H$	1.93 (m,[g] br)	48.1 (t, $^1J_{CH}$ 130.4)	
	Ad, $C_\gamma H$	2.02 (m,[g] br)	30.5 (d, $^1J_{CH}$ 131.7)	
	Ad, $C_\delta H$	1.58 (AB quartet, br)	36.8 (t, $^1J_{CH}$ 126.2)	
	$P\mathit{Me}_3$	1.21 (d, $^2J_{PH}$ 9.2)	20.10 (qd, $^1J_{CH}$ 129.3, $^1J_{PC}$ 28.3)	
3a	*o*-C_6H_5	8.09,[h] 7.04	132.02,[h] 125.40	
	m-C_6H_5	7.22, 7.15	128.34,[h] 128.49	
	p-C_6H_5	7.05, 6.95	124.00,[h] 127.39	
	ipso-C_6H_5		148.53,[h] 137.58	
	$NC\mathit{Me}_3$	1.40 (s)	33.94 (q, $^1J_{CH}$ 126.0)	
	$N\mathit{C}Me_3$		65.88 (s)	
	$PhC{\equiv}\mathit{C}Ph$ (*exo*)		149.41 (d, $^2J_{PC}$ 2.3)	
	$Ph\mathit{C}{\equiv}CPh$ (*endo*)		154.62 (d, $^2J_{PC}$ 18.7)	
	$P\mathit{Me}_3$	1.13 (d, $^2J_{PH}$ 9.2)	19.05 (qd, $^1J_{CH}$ 130.4, $^1J_{PC}$ 28.2)	16.18 (s)
3b	*o*-C_6H_5	8.17 (d, $^3J_{HH}$ 6.8)	132.59 (d, $^1J_{CH}$ 158.3)	
	m-C_6H_5	7.35 (t, $^3J_{HH}$ 7.6)	128.41[i]	
	p-C_6H_5	7.13 (t, $^3J_{HH}$ 7.6)	127.58[i]	
	ipso-C_6H_5		137.73 (d, $^3J_{PC}$ 3.0)	
	$NC\mathit{Me}_3$	1.36 (s)	34.00 (q, $^1J_{CH}$ 126.0)	
	$N\mathit{C}Me_3$		65.47 (s)	
	$PhC{\equiv}\mathit{CH}$	8.58 (d, $^3J_{PH}$ 14.8)	138.25 (dd, $^1J_{CH}$ 187.7, $^2J_{PC}$ 23.6)	
	$Ph\mathit{C}{\equiv}CH$		153.03 (s, br)	
	$P\mathit{Me}_3$	1.20 (d, $^2J_{PH}$ 9.6)	19.10 (qd, $^1J_{CH}$ 129.8, $^1J_{PC}$ 29.4)	20.29 (s)
3c	*o*-C_6H_5	7.62, 6.93	132.4, 125.6	
	m-C_6H_5	7.19, 7.14	128.5, 128.0	
	p-C_6H_5	7.03, 6.96	127.1, 123.2	
	ipso-C_6H_5		148.9,[h] 137.6	
	$PhC{\equiv}\mathit{C}Ph$ (*exo*)		149.3 (d, $^2J_{PC}$ 5.0)	
	$Ph\mathit{C}{\equiv}CPh$ (*endo*)		153.1 (d, $^2J_{PC}$ 19.0)	
	Ad, C_α		66.6 (s)	
	Ad, $C_\beta H$	1.77 (m,[g] br)	48.4 (t, $^1J_{CH}$ 128.9)	
	Ad, $C_\gamma H$	2.00 (m,[g] br)	31.2 (d, $^1J_{CH}$ 131.3)	
	Ad, $C_\delta H$	1.61 (AB quartet, br)	37.4 (t, $^1J_{CH}$ 127.8)	
	$P\mathit{Me}_3$	1.45 (d, $^2J_{PH}$ 9.6)	20.3 (qd, $^1J_{CH}$ 129.7, $^1J_{PC}$ 27.5)	

[a] Recorded in C_6D_6 at 400 MHz.
[b] Recorded in C_6D_6 at 100.58 MHz.
[c] Recorded in C_6D_6 at 161.9 MHz, referenced to aq. H_3PO_4 (external).
[d] $^3J_{PH}$ couplings assigned by ^{31}P decoupling experiments.
[e] Assignments aided by heteronuclear ^{1}H–^{13}C correlation experiments.
[f] Obscured by PMe_3 resonance.
[g] Small couplings evident but unresolved.
[h] Resonances that can be clearly assigned to the *exo* phenyl substituent.
[i] Coincident with C_6D_6 resonance.

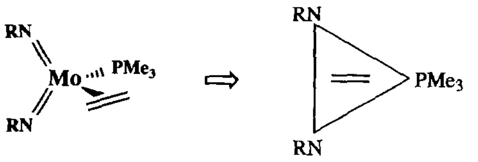
Table 2. Crystallographic experimental details

Compound	**2b**	**3a**
Chemical formula	$MoPN_2C_{14}H_{33}$	$MoPN_2C_{25}H_{37}$
M_r	356.3	492.5
Crystal dimensions (mm)	0.25 × 0.35 × 0.5	1.0 × 0.2 × 0.2
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	Pbca
a (Å)	9.312(2)	13.980(3)
b (Å)	9.723(2)	15.333(6)
c (Å)	11.203(2)	24.989(7)
α (°)	78.85(2)	
β (°)	88.23(2)	
γ (°)	85.94(2)	
V (Å^3)	992.5(4)	5356(3)
D_c (g cm^{-3})	1.19	1.22
F(000)	376	2064
Radiation, MoK_α $\bar{\lambda}$ (Å)	0.71073	0.71073
[Graphite monochromated]		
Absorption coeff μ (cm^{-1})	7.3	5.6
Data collection		
Diffractometer	AFC6-S	AFC6-S
Scan method	2θ–ω	ω
2θ (max)	55°	55°
Temperature (K)	293	120
No. of reflections measured	4945	8099
No. of independent reflections	4555	4722
No. of "observed" reflections	3839	2344
$F \geqslant n\,\sigma(F) : n$	4	2
No. of parameters refined	149	262
Absorption correction[a]	empirical	empirical
t_{min}/t_{max} transmission	0.908, 1.00	0.92, 1.00
(h, k, l) min	−12, −12, −14	0, 0, 0
(h, k, l) max	12, 0, 14	17, 16, 30
R (wR) %[b]	4.56 (6.44)	5.85 (6.73)
Goodness of fit	1.55	1.08
Max shift : error	0.004	0.001
Largest difference peak/hole (e Å^{-3})	0.92, −0.65	0.72, −1.07
Anisotropic atoms	All non-H[c]	All non-H
Hydrogen atoms	Riding, fixed U_{iso}	Riding, fixed U_{iso}

[a] TEXSAN, Molecular Structure Cooperation, Texas (1991).

[b] SHELXTL PLUS, G. M. Sheldrick, University of Göttingen & Siemens plc (1990).

[c] Except one highly thermally active ^{t}Bu group [C(8)—C(11)] which was constrained to vibrate as a regular tetrahedron.



molecule is viewed along the alkene–metal axis with the two imido ligands and phosphine defining a plane beneath the metal (see above). The ethene ligand aligns its C—C axis so as to point towards the weakest π-donor ligand, the PMe_3 group, an orientation that arises from the presence of the two strong π-donating imido ligands. Such representations can be used more generally to assess the relative π-donor capacities of different ligands.[5]

Alkyne derivatives

The closely related alkyne derivatives are readily accessed via displacement of the ethene ligands of **2a,c** (eq. 2).

Table 3. Bond lengths (Å) and bond angles (°) for **2b**

Mo(1)—P(1)	2.446(1)	Mo(1)—N(1)	1.771(3)
Mo(1)—N(2)	1.772(4)	Mo(1)—C(1)	2.238(4)
Mo(1)—C(2)	2.188(4)	P(1)—C(12)	1.800(6)
P(1)—C(13)	1.811(6)	P(1)—C(14)	1.808(6)
N(1)—C(4)	1.452(5)	N(2)—C(8)	1.450(6)
C(1)—C(2)	1.431(7)	C(2)—C(3)	1.517(8)
C(4)—C(5)	1.537(7)	C(4)—C(6)	1.517(9)
C(4)—C(7)	1.517(7)	C(8)—C(9)	1.482(8)
C(8)—C(10)	1.482(9)	C(8)—C(11)	1.482(8)
P(1)—Mo(1)—N(1)	101.9(1)	P(1)—Mo(1)—N(2)	99.4(1)
N(1)—Mo(1)—N(2)	123.0(2)	P(1)—Mo(1)—C(1)	81.0(1)
N(1)—Mo(1)—C(1)	115.9(2)	N(2)—Mo(1)—C(1)	119.3(2)
P(1)—Mo(1)—C(2)	118.5(1)	N(1)—Mo(1)—C(2)	108.1(2)
N(2)—Mo(1)—C(2)	106.5(2)	C(1)—Mo(1)—C(2)	37.7(2)
Mo(1)—P(1)—C(12)	116.3(3)	Mo(1)—P(1)—C(13)	114.7(2)
C(12)—P(1)—C(13)	101.8(3)	Mo(1)—P(1)—C(14)	116.0(2)
C(12)—P(1)—C(14)	104.1(3)	C(13)—P(1)—C(14)	102.0(3)
Mo(1)—N(1)—C(4)	162.9(3)	Mo(1)—N(2)—C(8)	168.2(3)
Mo(1)—C(1)—C(2)	69.3(2)	Mo(1)—C(2)—C(1)	73.0(3)
Mo(1)—C(2)—C(3)	115.9(3)	C(1)—C(2)—C(3)	119.0(4)
N(1)—C(4)—C(5)	109.8(4)	N(1)—C(4)—C(6)	108.7(4)
C(5)—C(4)—C(6)	109.6(4)	N(1)—C(4)—C(7)	109.2(4)
C(5)—C(4)—C(7)	110.6(4)	C(6)—C(4)—C(7)	108.8(4)
N(2)—C(8)—C(9)	110.6(4)	N(2)—C(8)—C(10)	109.1(4)
C(9)—C(8)—C(10)	109.1(5)	N(2)—C(8)—C(11)	109.7(4)
C(9)—C(8)—C(11)	109.2(5)	C(10)—C(8)—C(11)	109.1(5)

Table 4. Comparison of key structural parameters for 'isolobal' zirconocene and bis(imido)molybdenum complexes

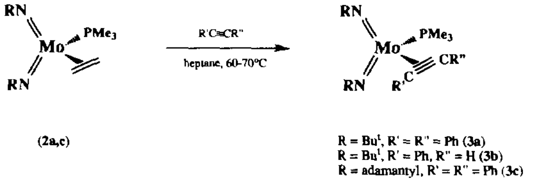
Parameter	$Mo(NBu^t)_2(PMe_3)$ (C_2H_6) (**2b**)	$(C_5H_5)_2Zr(PMe_3)$ (C_2H_4)[8]	$Mo(NBu^t)_2(PMe_3)$ (PhC≡CPh) (**3a**)	$(C_5H_5)_2Zr(PMe_3)$ (PhC≡CPh)[10]
M—X (Å)	1.771(3)[a] 1.772(4)[a]	2.22[b]	1.761(7)[a] 1.759(7)[a]	—
M—P (Å)	2.446(1)	2.693(2)	2.465(3)	2.70(1)
M—C(*endo*)[c] (Å)	2.238(4)	2.373(8)	2.158(9)	2.25(4)
M—C(*exo*)[d] (Å)	2.188(4)	2.344(8)	2.081(8)	2.20(4)
C(*exo*)—C(*endo*) (Å)	1.431(7)	1.486(8)	1.31(1)	1.36(6)
X—M—X (°)	123.0(2)[a]	129.3[b]	117.6(3)[a]	127.4[b]

[a] $X = NBu^t$.

[b] $X = C_5H_5$ ring centroid.

[c] C(*endo*) refers to the metal-bound olefinic or acetylenic carbon closest to the PMe_3 ligand.

[d] C(*exo*) refers to the metal-bound olefinic or acetylenic carbon furthest from the PMe_3 ligand.



(**2a,c**)

$R = Bu^t$, R' = R" = Ph (**3a**)
$R = Bu^t$, R' = Ph, R" = H (**3b**)
R = adamantyl, R' = R" = Ph (**3c**)

(2)

^1H and ^{13}C NMR data for **3a** and **3c** show that the phenyl substituents of the acetylene ligand are inequivalent, again implying that the alkyne ligands align in the plane perpendicular to that containing the metal and imido nitrogens. For the diphenylacetylene complexes **3a** and **3c** the acetylenic carbons resonate in the range 145–155 ppm which is intermediate between the ranges typically observed for two-electron (110–120 ppm) and four-electron alkyne ligands (190–210 ppm), as noted by Tem-

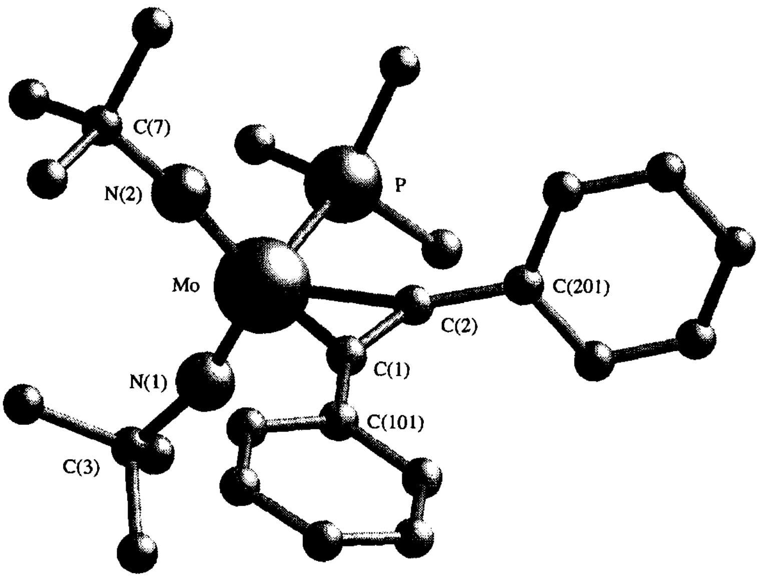
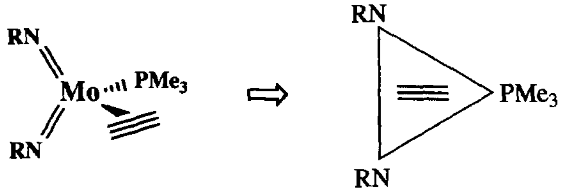


Fig. 2. Molecular structure of **3a**, without H atoms and with key atoms labelled.

pleton and Ward.[9] This may reflect, at least to some extent, partial donation of electron density from the orthogonal π-system of the alkyne ligands, since in a pseudo-tetrahedral environment, π-donor ligands compete with each other for the available empty metal $d\pi$ symmetry orbitals. We note that similar intermediate shifts are also a feature of bis(cyclopentadienyl)metal derivatives, e.g. $(C_5H_5)_2Zr(PhC{\equiv}CPh)(PMe_3)$ (156.4, 141.6),[10] $(Me_3SiC_5H_4)_2Nb(PhC{\equiv}CPh)Cl$ (156.1, 140.1 ppm),[11] and $(C_5H_5)_2NbH(Me_3SiC{\equiv}CSiMe_3)$ (160.0, 149.3).[12] Analogously to the alkene derivatives, the acetylenic carbon atom adjacent to the PMe_3 ligand shows the more substantial coupling to phosphorus (*ca* 20 Hz).

Molecular structure of **3a**

Crystals of **3a** suitable for an X-ray structure determination were grown from heptane by slow cooling of a solution from 60°C to room temperature. The molecular structure is shown in Fig. 2 and crystal data are given in Table 2. Bond lengths and angles are collected in Table 5. The molecule is pseudo-tetrahedral, with an N—Mo—N angle of 117.6(3)° and N—Mo—P angle of 100.7(3), and 'metallocene-like' with the acetylenic carbons lying in the same plane as the Mo and P atoms (the deviation of the P atom from the Mo—C(1)—C(2) plane is 0.11 Å); a triad representation of the molecule illustrating the alkyne orientation is shown below.



The *ipso*-carbon atoms of the acetylene phenyl substituents also lie in the Mo—C(1)—C(2) plane. The phenyl rings, however, are tilted out of this plane; the ring defined by atoms C(101)—C(106) is twisted by 23.7° while the ring defined by atoms C(201)—C(206) is twisted by 104.9°. This uneven distortion and the asymmetrical coordination of the acetylene [Mo—C(1) 2.081(8) Å, Mo—C(2) 2.158(9) Å] are both likely consequences of the steric constraints imposed by the PMe_3 ligand. The C(1)—C(2) bond length of 1.31(1) Å is indicative of substantial back donation but is not as marked as for the zirconocene analogue (Table 4).

The Mo—N—C angles of 162.8(6) and 171.6(7)° lie within the range of quasi-linear imido units, while the Mo—N bond distances of 1.761(7) and 1.759(7) Å are comparable with those found in **2b**, though slightly elongated compared with monoimido molybdenum complexes,[13] a consequence of the competition that exists between the two imido groups for the available metal orbitals in a pseudo-tetrahedral geometry.

In summary, the structures of **2b** and **3a** lend strong support for the 'isolobal' relationship between zirconocenes and four coordinate bis (imido) complexes of molybdenum. Apart from relatively minor deviations in inter-ligand bond

Table 5. Bond lengths (Å) and bond angles (°) for **3a**

Mo—C(1)	2.081(8)	Mo—C(2)	2.158(9)
Mo—N(1)	1.759(7)	Mo—N(2)	1.761(7)
Mo—P	2.465 (3)	C(1)—C(2)	1.306(12)
C(1)—C(101)	1.446(12)	C(2)—C(201)	1.473(11)
C(101)—C(102)	1.411(11)	C(101)—C(106)	1.428(11)
C(102)—C(103)	1.367(13)	C(103)—C(104)	1.373(13)
C(104)—C(105)	1.388(13)	C(105)—C(106)	1.367(12)
C(201)—C(202)	1.408(12)	C(201)—C(206)	1.421(11)
C(202)—C(203)	1.395(13)	C(203)—C(204)	1.392(12)
C(204)—C(205)	1.390(13)	C(205)—C(206)	1.384(12)
N(1)—C(3)	1.448(12)	C(3)—C(4)	1.506(14)
C(3)—C(5)	1.543(13)	C(3)—C(6)	1.514(15)
N(2)—C(7)	1.450(11)	C(7)—C(8)	1.509(17)
C(7)—C(9)	1.515(14)	C(7)—C(10)	1.515(18)
P—C(11)	1.806(11)	P—C(12)	1.824(9)
P—C(13)	1.795(10)		
C(1)—Mo—C(2)	35.8(3)	C(1)—Mo—N(1)	107.3(3)
C(2)—Mo—N(1)	120.3(3)	C(1)—Mo—N(2)	109.1(3)
C(2)—Mo—N(2)	119.1(3)	N(1)—Mo—N(2)	117.6(3)
C(1)—Mo—P	121.8(2)	C(2)—Mo—P	86.0(2)
N(1)—Mo—P	100.7(2)	N(2)—Mo—P	100.7(3)
Mo—C(1)—C(2)	75.3(6)	Mo—C(1)—C(101)	142.8(6)
C(2)—C(1)—C(101)	141.8(8)	Mo—C(2)—C(1)	68.9(5)
Mo—C(2)—C(201)	152.3(7)	C(1)—C(2)—C(201)	138.8(9)
C(1)—C(101)—C(102)	121.7(7)	C(1)—C(101)—C(106)	122.0(7)
C(102)—C(101)—C(106)	116.2(7)	C(101)—C(102)—C(103)	121.5(7)
C(102)—C(103)—C(104)	120.6(8)	C(103)—C(104)—C(105)	120.4(8)
C(104)—C(105)—C(106)	119.6(8)	C(101)—C(106)—C(105)	121.7(8)
C(2)—C(201)—C(202)	121.4(7)	C(2)—C(201)—C(206)	120.7(8)
C(202)—C(201)—C(206)	117.8(8)	C(201)—C(202)—C(203)	120.6(8)
C(202)—C(203)—C(204)	121.1(8)	C(203)—C(204)—C(205)	118.5(8)
C(204)—C(205)—C(206)	121.8(8)	C(201)—C(206)—C(205)	120.2(8)
Mo—N(1)—C(3)	162.8(6)	N(1)—C(3)—C(4)	108.6(8)
N(1)—C(3)—C(5)	109.7(8)	C(4)—C(3)—C(5)	109.1(8)
N(1)—C(3)—C(6)	109.2(8)	C(4)—C(3)—C(6)	110.4(9)
C(5)—C(3)—C(6)	109.8(9)	Mo—N(2)—C(7)	171.6(7)
N(2)—C(7)—C(8)	107.4(8)	N(2)—C(7)—C(9)	109.7(8)
C(8)—C(7)—C(9)	109.7(9)	N(2)—C(7)—C(10)	108.7(8)
C(8)—C(7)—C(10)	112.4(10)	C(9)—C(7)—C(10)	108.9(9)
Mo—P—C(11)	112.9(3)	Mo—P—C(12)	115.3(3)
C(11)—P—C(12)	103.0(5)	Mo—P—C(13)	116.7(4)
C(11)—P—C(13)	103.2(5)	C(12)—P—C(13)	104.1(5)

angles, the only substantial difference appears to be in the degree of back donation from the metal centres to the unsaturated hydrocarbon ligands. Such an effect is likely to lead to differences in the reactivities of the two systems, an aspect that we are presently exploring.

EXPERIMENTAL

General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry at Durham. NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400.0 MHz (^{1}H), 100.6 MHz (^{13}C) and 161.9 MHz (^{31}P); chemical shifts are referenced to the residual protio impurity of the deuterated solvent; IR spectra (Nujol mulls, CsI windows), Perkin–Elmer 577 and 457 grating spectrophotometers; mass spectra, VG 7070E [70 eV (*ca* 1.12×10^{17} J), 100 μA emission]. PMe_3 was prepared by a previously published procedure.[14] $Mo(NR)_2Cl_2(dme)$ [R = Bu^t(**1a**), adamantyl (**1b**)] were synthesised via a modification of the procedure described by Schrock and co-workers.[6] Anhydrous Na_2MoO_4 was purchased from Aldrich Chemical Co. and used as received. All other chemicals were obtained commercially and used as received unless stated otherwise.

Preparation of $Mo(NBu^t)_2Cl_2(dme)$ (**1a**)

Solutions of triethylamine (27.1 cm^3, 194.4 mmol), chlorotrimethylsilane (68 cm^3, 534.6 mmol) and *tert*-butylamine (10.2 cm^3, 97.2 mmol) in 1,2-dimethoxyethane (dme) (*ca* 20 cm^3 each solution) were added sequentially to a stirred suspension of anhydrous Na_2MoO_4 (10 g, 48.6 mmol) in dme (100 cm^3) at room temperature. The reaction mixture was then heated at 70°C for 12 h to afford a pale yellow solution and a large quantity of white precipitate. The solution was filtered from the solid which was then washed with diethylether (3 × 50 cm^3). The solvent was then removed from the combined filtrate and washings under reduced pressure to afford analytically pure, yellow crystalline $Mo(NBu^t)_2Cl_2(dme)$. Yield 15.4 g (79%). Found: C, 36.0; H, 7.2; N, 6.9. Calc. for $C_{12}H_{28}N_2O_2Cl_2Mo$: C, 36.1; H, 7.0; N, 7.0%.

Preparation of $Mo(NAd)_2Cl_2(dme)$ (**1b**)

To a stirred suspension of anhydrous Na_2MoO_4 (5.0 g, 24.3 mmol) in 1,2-dimethoxyethane (100 cm^3) were added, dropwise and sequentially, dme solutions of triethylamine (13.55 cm^3, 97.1 mmol in 15 cm^3 dme) and chlorotrimethylsilane (34 cm^3, 267 mmol in 30 cm^3 dme) at room temperature. A suspension of 1-adamantanamine (7.35 g, 48.6 mmol) in 1,2-dimethoxyethane (30 cm^3) was then added and the mixture warmed with stirring to 70°C. After 48 h at this temperature the mixture was allowed to cool to reveal a golden yellow solution over a pale precipitate. The solution was filtered from the solid which was then washed with diethylether (3 × 50 cm^3). The solvent was then removed under reduced pressure from the combined filtrate and washings to afford yellow $Mo(NAd)_2Cl_2(dme)$. Yield 8.2 g (61%). Found: C, 51.7; H, 7.5; N, 5.0. Calc. for $C_{24}H_{40}N_2O_2Cl_2Mo$: C, 51.9; H, 7.3; N, 5.0%.

Preparation of $Mo(NBu^t)_2(PMe_3)(C_2H_4)$ (**2a**)

Trimethylphosphine (1.0 cm^3, 10 mmol) was condensed onto a frozen (−196°) mixture of **1a** (2.0 g, 5 mmol) and diethylether (40 cm^3) in a glass ampoule fitted with a teflon stopcock. After warming the mixture to −78°C (dry-ice/acetone slush bath), a nitrogen atmosphere was introduced and EtMgCl (5.0 cm^3, 2 M solution in Et_2O) was added by syringe. The reaction mixture was then allowed to warm to room temperature with stirring and occasional venting. After 3 h at room temperature, the volatile components were removed under reduced pressure. Extraction of the residue with pentane (30 cm^3) afforded a dark purple–red solution which was concentrated and cooled to −30°C to give yellow crystals of **2a**. Yield 1.11 g (65%). Found: C, 45.6; H, 8.1; N, 9.1. Calc. for $C_{13}H_{31}N_2PMo$: C, 45.6; H, 8.2; N, 9.1%. IR: 1355s, 1285s, 1215s, 1135s, 1105s(br), 1020m(br), 950s(br), 890w, 845w, 800s, 670w.

Preparation of $Mo(NBu^t)_2(PMe_3)(C_2H_6)$ (**2b**)

Complex **2b** was obtained by an analogous procedure to that described above for **2a**, using *n*-PrMgCl. Quantities of reagents employed: trimethylphosphine (0.5 cm^3, 10 mmol), **1a** (2.0 g, 5 mmol), diethylether (40 cm^3), *n*-PrMgCl (5.0 cm^3, 2 M solution in Et_2O). The product was isolated as yellow crystals from a cold (−30°C) pentane solution. Yield 1.25 g (70%). Found: C, 47.0; H, 9.2; N, 7.7. Calc. for $C_{14}H_{33}N_2PMo$: C, 47.1; H, 9.4; N, 7.9%. IR: 1355m, 1305w, 1285m, 1260s, 1220s, 1185w, 1150w, 1110m, 1045w, 1020w, 950s, 900w, 845w, 800s, 670w, 575w(br).

Preparation of $Mo(NAd)_2(PMe_3)(C_2H_4)$ (**2c**)

Complex **2c** was obtained from **1b** by an analogous procedure to that described above for **2a**. Quantities of reagents employed: trimethylphosphine (0.2 cm^3, 2 mmol), **1b** (0.425 g, 0.77 mmol), diethylether (40 cm^3), EtMgCl (0.8 cm^3, 2 M solution in Et_2O). The product was isolated as yellow crystals from a cold (−30°C) pentane solution. Yield 0.15 g (39%). Found: C, 60.3; H, 9.1; N, 5.1. Calc. for $C_{25}H_{43}N_2PMo$: C, 60.2; H, 8.7; N, 5.6%. MS: *m/z* 499 (M^+), 471 ($M^+ - C_2H_4$). IR: 1570m, 1341m, 1310m, 1300s, 1288m, 1284m, 1240m(br), 1195s, 1175m, 1140s, 1098m, 1025w(br), 960s, 942s, 896w, 850w, 812m, 810w, 805w, 760w, 740w, 730w, 675m, 650w, 565w, 520w, 490w, 440w(br), 370m.

Preparation of $Mo(NBu^t)_2(PMe_3)(PhC{\equiv}CPh)$ (**3a**)

A thick-walled glass ampoule fitted with a teflon stopcock was charged with **2a** (0.5 g, 1.5 mmol), diphenylacetylene (0.27 g, 1.5 mmol) and heptane solvent (50 cm^3). The mixture was stirred at 60°C for 10 days to give an orange–brown solution. Slow cooling of this solution to room temperature afforded yellow needle crystals of **3a** which were isolated by filtration. Concentration of the mother liquor followed by cooling to −30°C gave a further quantity of yellow crystals. Overall yield, 0.70 g (95%). Found: C, 61.0; H, 7.6; N, 5.4. Calc. for $C_{25}H_{37}N_2PMo$: C, 61.0; H, 7.6; N, 5.7%. IR: 1730m, 1590m, 1565w, 1350s, 1305w, 1285m, 1255s(br), 1215s(br), 1170w, 1100m(br), 1065m, 1020m(br), 950s(br), 850w, 800s, 765m, 750s, 690s, 585m, 545m, 500m, 460w(br), 440w, 380w, 350w.

Preparation of $Mo(NBu^t)_2(PMe_3)(PhC{\equiv}CH)$ (**3b**)

The phenylacetylene complex **3b** was generated in an NMR tube experiment by treatment of **2a** (0.030 g, 0.09 mmol) with $PhC{\equiv}CH$ (0.009 g, 0.09 mmol). After warming the sample for 10 days at 60°C, the conversion of **2a** to **3b** was quantitative by NMR.

Preparation of $Mo(NAd)_2(PMe_3)(PhC{\equiv}CPh)$ (**3c**)

Diphenylacetylene (0.167 g, 0.94 mmol) in heptane (150 cm^3) was added to the crude solid product from a preparation of **2c** (0.522 g **1b**, 0.94 mmol). The mixture was heated with stirring at 70°C for 3 days to give a small amount of brown residue and a clear red solution. The solution was filtered, concentrated and cooled to −30°C over 2 days to give brown, crystalline **3c**. Overall yield 0.25 g (41%). Found: C, 68.3; H, 7.5; N, 4.5. Calc. for $C_{37}H_{49}N_2PMo$: C, 68.5; H, 7.6; N, 4.3%. IR: 1725m, 1590w, 1340m, 1305s, 1282m, 1255s, 1200s, 1172w, 1130w, 1090s, 1060w, 1020m, 950s, 920w, 910w, 880w, 840w, 810m, 800w, 760m, 755m, 730w, 710w, 690w, 682s, 410w(br), 360w.

X-Ray crystallography

Intensity data for crystals of **2b** and **3a** were measured on a Rigaku AFC6S diffractometer using graphite monochromated MoK_α X-radiation (λ = 0.71707 Å). The crystal of **3a** was measured at 120 K, cooled using a Cryostream N_2 flow device. In both cases the crystals were mounted in capillary tubes under nitrogen. A summary of the crystallographic data and experimental details is given in Table 2. Lists of atomic coordinates, bond lengths and angles and atomic displacement parameters have been deposited with the Cambridge Crystallographic Data Centre.*

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* Data for **2b** have been re-deposited due to further refinement of the *t*-butyl groups since ref. 2(c).