

Four Coordinate Bis(imido) Alkene Complexes of Molybdenum(IV): Relatives of the Zirconocene Family

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The unusual four coordinate bis(imido) alkene complexes $[\text{Mo}(\text{NBU}^t)_2(\text{CH}_2=\text{CHR})(\text{PMe}_3)]$ ($\text{R} = \text{H}, \text{Me}$) have been synthesised *via* treatment of $[\text{Mo}(\text{NBU}^t)_2\text{Cl}_2(\text{dme})]$ ($\text{dme} = \text{dimethoxyethane}$) with two equivalents of $\text{RCH}_2\text{CH}_2\text{MgCl}$ ($\text{R} = \text{H}, \text{Me}$) in the presence of PMe_3 ; the molecular structure of the propene derivative is reported.

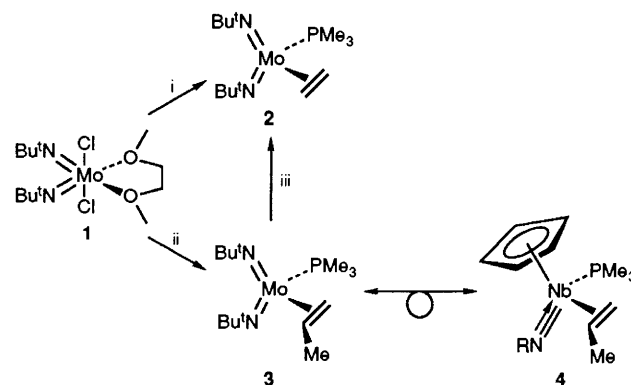
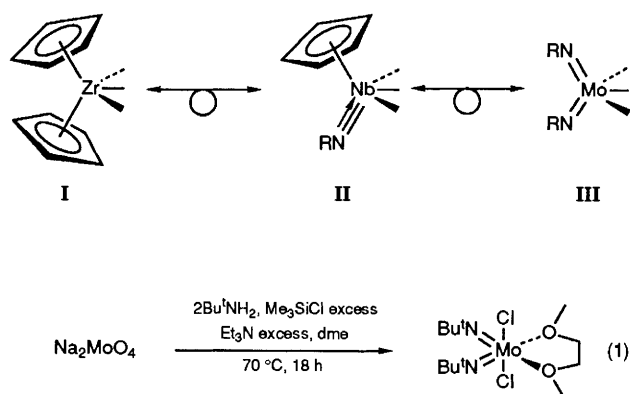
Recent years have witnessed much renewed interest in the coordination and organometallic chemistry of transition metal complexes containing imido ligands.¹ Our studies have focused on the half-sandwich niobium system²⁻⁴ for which we have been exploring the potentially useful isolobal relationship with zirconocene derivatives² (**I** and **II** below). This derives from the similarities between the symmetry properties of the frontier orbitals of the imido and cyclopentadienyl ligands, both of which interact with a metal *via* $1\sigma + 2\pi$ donor interactions.

Such a relationship can also be extended to non-cyclopentadienyl bis(imido) species (**III**) of the group 6 metals.^{2,5} For example, Schrock and coworkers have described a 'metallocene-like' tungsten oxametallacyclopropane complex, $[\text{W}(\text{N}-2,6\text{-Pr}_i^2\text{C}_6\text{H}_3)_2(\eta^2\text{-O=CMe}_2)(\text{PMe}_2\text{Ph})]$, supported by 2,6-diisopropylphenylimido ligands.⁵ For this particular imido ligand, flexibility in the orientation of the aryl substituent also allows access to a five-coordinate manifold as found for the simple alkene derivatives.⁵ In order to obtain a direct analogue of the 'metallocene-like' niobium species $[\text{Nb}(\eta\text{-C}_5\text{H}_5)(\text{N}-2,6\text{-Pr}_i^2\text{C}_6\text{H}_3)(\text{CH}_2=\text{CHMe})(\text{PMe}_3)]$ described recently,³ we have investigated the bis(*tert*-butylimido)molyb-

denum system where we envisaged that the reduced flexibility of the *tert*-butylimido groups would help to maintain a four-coordinate metal environment.

The starting point for these studies is the six-coordinate dme adduct $[\text{Mo}(\text{NBU}^t)_2\text{Cl}_2(\text{dme})]$ **1** ($\text{dme} = \text{dimethoxyethane}$) which may be synthesised conveniently on a large scale and in excellent yield using a slightly modified synthetic procedure[†] to that described by Schrock and coworkers⁶ [eqn. (1)].

[†] The modified procedure employs Na_2MoO_4 instead of $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ and triethylamine base. Typically, solutions of triethylamine (27.07 cm³, 194.25 mmol), chlorotrimethylsilane (55.47 cm³, 437.06 mmol), and *tert*-butylamine (10.21 cm³, 97.13 mmol) in 1,2-dimethoxyethane (*ca.* 20 cm³ each solution) are added sequentially to a stirred suspension of Na_2MoO_4 (10 g, 48.6 mmol) in 1,2-dimethoxyethane (100 cm³) at room temp. The reaction mixture is then heated at 70 °C for 12 h to leave a pale-yellow solution and a white precipitate. The solution is filtered from the solid and the solvent is then removed under reduced pressure to afford analytically pure $[\text{Mo}(\text{NBU}^t)_2\text{Cl}_2(\text{dme})]$ (yield 15.35 g, 98%).



Scheme 1 Reagents and conditions: i, EtMgCl, Et₂O, PMe₃, 25°C, 3 h; ii, PrⁿMgCl, Et₂O, PMe₃, 25°C, 3 h; iii, C₂H₄, 1 equiv., benzene, 60°C, 10 h

Treatment of **1** with two equivalents of ethyl or n-propylmagnesium chloride in diethyl ether in the presence of trimethylphosphine affords on work-up yellow pentane-soluble crystals of **2** and **3**, respectively (Scheme 1).[‡] Monitoring of the reaction of **1** with n-propylmagnesium chloride by GC-MS reveals that propane is formed indicating that the reaction proceeds *via* β-elimination from an intermediate di-n-propyl species. Complexes **2** and **3** may be warmed in hydrocarbon solvent at 100°C for several days without decomposition but both are unstable to air and moisture. Complex **3** is found to convert readily into **2** upon treatment with one equivalent of ethylene at 60°C for 10 h, reflecting the greater steric congestion in the propene derivative.

The molecular structure of **3** has been determined[§] and is shown in Fig. 1. The molecule is pseudotetrahedral with mean N-Mo-N and N-Mo-P angles of 123.0 and 100.7°, respectively, while the angles subtended at the molybdenum by the C(1)-C(2) centroid and the NBU^t and PMe₃ ligands are 113.8(mean) and 99.5(1)°. The Mo, P, C(1) and C(2) atoms lie in the pseudoplane (mean deviation 0.041 Å) which bisects the N-Mo-N angle (deviation from orthogonality 0.4°). The Mo-N-C angles, 168.3(3) and 162.6(3) Å, lie within the range

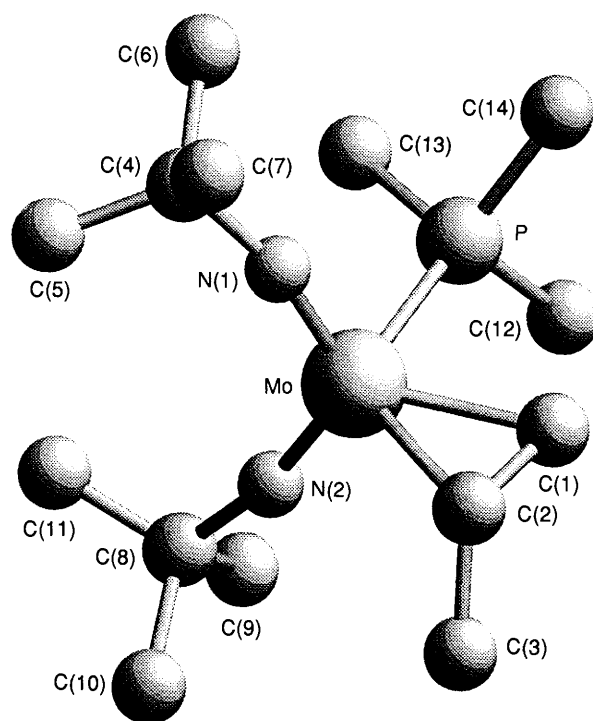


Fig. 1 Molecular structure of [Mo(NBU^t)₂(CH₂=CHMe)(PMe₃)] **3**. Key dimensions: Mo-P 2.445(1), Mo-N(1) 1.774(3), Mo-N(2) 1.765(3), Mo-C(1) 2.228(4), Mo-C(2) 2.182(3), C(1)-C(2) 1.418(6), C(2)-C(3) 1.521(7) Å; P-Mo-N(1) 101.7(1), P-Mo-N(2) 99.7(1), N(1)-Mo-N(2) 123.0(1)°.

[‡] Satisfactory elemental analyses have been obtained.

Selected spectroscopic data for 2: ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 2.26 (td, 2H, ³J_{HH} 11.6 Hz, C₂H₄), 1.37 (s, 18H, NCM₃), 1.16 (td, 2H, ³J_{HH} 11.3 Hz, C₂H₄), 1.13 (d, 9H, ²J_{PH} 8.8 Hz, PMe₃). ¹³C NMR (C₆D₆, 100.6 MHz, 298 K): δ 64.78 (s, NCM₃), 33.70 (q, ¹J_{CH} 125.8 Hz, NCM₃), 31.76 (td, ¹J_{CH} 152.4 Hz, ²J_{PC} 9.9 Hz, C₂H₄), 20.96 (t, ¹J_{CH} 156.1 Hz, C₂H₄), 19.10 (qd, ¹J_{CH} 132.7, ¹J_{PC} 24.7 Hz, PMe₃). ³¹P NMR (C₆D₆, 101.26 MHz, 298 K, external ref. aq. H₃PO₄) δ 22.55 (s, PMe₃). For **3**: ¹H NMR (C₆D₆, 400 MHz, 298 K): δ 3.23 (tqd, 1H, ³J_{HH} 10.8, ³J_{HH} 6.3, ³J_{PH} 1.4 Hz, CH₂=CHMe),^a 2.24 (d, 3H, ³J_{HH} 6.3 Hz, CH₂=HMe), 1.36 (s, 9H, NCM₃), 1.34 (s, 9H, NCM₃), 1.22 (ddd, 1H, ³J_{HH} 10.8, ²J_{HH} 5.4, ³J_{PH} 5.2 Hz, CH₂=CHMe),^a 1.12 (d, 9H, ²J_{PH} 8.7 Hz, PMe₃) 1.02 (ddd, 1H, ³J_{HH} 10.8, ²J_{HH} 5.4, ³J_{PH} 5.2 Hz, CH₂=CHMe),^a ¹³C NMR (C₆D₆, 100.6 MHz, 298 K): δ 65.32 (s, NCM₃), 65.03 (s, NCM₃), 39.93 (d, ¹J_{CH} 148.6 Hz, CH₂=CHMe), 37.42 (t, ¹J_{CH} 148.8 Hz, CH₂=CHMe), 33.96 (qd, ¹J_{CH} 127.6 Hz, ¹J_{PC} 20.6 Hz, coincident signals due to NCM₃), 27.46 (q, ¹J_{CH} 125.1 Hz, CH₂=CHMe), 19.51 (qd, ¹J_{CH} 127.6, ¹J_{PC} 28.2 Hz, PMe₃). ³¹P NMR (C₆D₆, 101.26 MHz, 298 K, external ref. aq. H₃PO₄) δ 22.00 (s, PMe₃).

^a Coupling constants assigned *via* ¹H and ³¹P decoupling experiments.

[§] *Crystal data:* MoN₂PC₁₄H₃₃, *M* = 356.3. Triclinic, space group *P* $\bar{1}$, *a* = 9.312(2), *b* = 9.723(2), *c* = 11.203(2) Å, α = 78.852(15), β = 88.231(17), γ = 85.938(19)°, *V* = 992.5(3) Å³, *D*_c = 1.192 g cm⁻³, μ(Mo-Kα) = 0.73 mm⁻¹, *F*(000) = 376, *Z* = 2, *T* = 25°C, Rigaku AFC6S diffractometer, graphite-monochromated Mo-Kα X-radiation (λ = 0.7107 Å). Full-matrix least-squares refinement of 174 parameters, using 3802 reflections with *F*_o > 4σ(*F*_o) converged at *R*(*R*_w) = 0.0405(0.0598).

Atomic coordinates, bond lengths and angles, and atomic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

of 'linear' imido units while the Mo=N distances, at 1.774(3) and 1.765(3) Å, are slightly elongated compared with those typically observed in monoimido molybdenum complexes;⁷ this is a reflection of the competition which exists between the two imido groups for the available π-symmetry metal orbitals in a tetrahedral geometry.^{5,7} The C(1)-C(2) separation within the propene ligand, 1.418(6) Å, is consistent with considerable back donation from the d² metal centre and the alignment of the C(1)-C(2) axis in the same plane as the Mo-P vector is supportive of bent metallocene-like frontier orbitals for the [Mo(NBU^t)₂] fragment. Of the two possible isomers of **3**, one with the methyl substituent pointing towards the PMe₃ ligand (*endo*) and the other with the methyl directed away from the phosphine ligand (*exo*), only one isomer is observed in

solution by ^1H and ^{13}C NMR spectroscopy, and difference NOE (nuclear Overhauser effect) measurements are supportive of the *exo* geometry established in the solid state.

Thus, in conclusion an isolobal relationship can be drawn between **3**, the niobium propene complex **4**, and also well-established zirconocene derivatives of the type $[\text{Zr}(\eta\text{-C}_5\text{H}_5)_2(\text{CH}_2=\text{CHR})(\text{PMe}_3)]$.⁸ We envisage that a wide range of metallocene-like derivative chemistry should prove accessible for molybdenum complexes containing the $[\text{Mo}(\text{NBU}^t)_2]$ moiety.

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