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Preliminary Communication

Synthesis, structural characterisation and reactivity of the d^2 pseudo-metallocene complex $\text{Mo}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2(\text{PMe}_3)_2$ *

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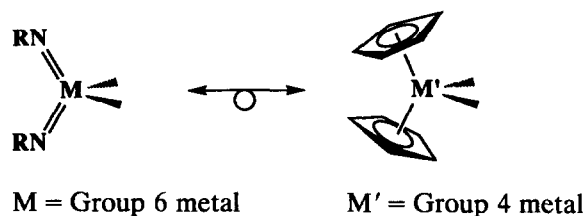
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Abstract

The d^2 bis(imido) complex $[\text{Mo}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2(\text{PMe}_3)_2]$ has been prepared by treatment of $[\text{Mo}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{Cl}_2(\text{dme})]$ with one equivalent of magnesium in the presence of an excess of PMe_3 . A molecular structure determination has revealed a pseudo-tetrahedral geometry with inter-ligand bond angles comparable with those in the d^2 metallocene $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{PMe}_3)_2]$. Preliminary reactivity studies are reported.

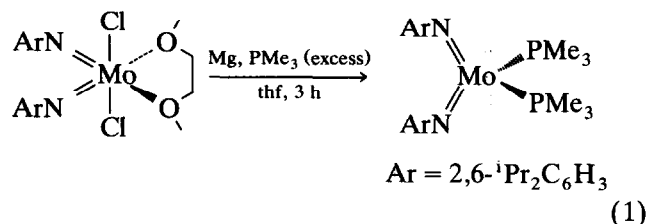
There is increasing evidence in support of a pseudo-isolobal relationship between bis(imido) metal complexes of the Group 6 metals and bent metallocenes of the Group 4 triad (below) [1–3], a relationship which is derived from the similar $1\sigma, 2\pi$ bonding characteristics of imido and cyclopentadienyl ligands [5].



The relationship was first pointed out by Schrock for bis(arylimido) complexes of tungsten [1] and later

for some rhenium analogues [2], where metallocene-like orientations of ancillary π -bonded groups were noted. Our studies have focused on the relationship between half-sandwich niobium imido complexes [4–8] and zirconocenes; for example in recent reports we have described the d^2 bis(phosphine) complex $[(\eta\text{-C}_5\text{Me}_5)\text{-Nb}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2(\text{PMe}_3)_2]$, which is isolobal with the synthetically versatile metallocene derivatives $[(\eta\text{-C}_5\text{H}_5)_2\text{M}(\text{PR}_3)_2]$ ($\text{M} = \text{Ti}$, $\text{PR}_3 = \text{PMe}_3$ [9]; $\text{M} = \text{Zr}$, $\text{PR}_3 = \text{PMe}_3$ or PMe_2Ph [10]). For purposes of comparison we were interested in extending this series to the second row bis(imido)molybdenum analogues, and report below the synthesis, structural characterisation and some preliminary reactivity studies of $[\text{Mo}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2(\text{PMe}_3)_2]$ (1).

Compound 1 was prepared *via* treatment of $[\text{Mo}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\text{Cl}_2(\text{dme})]$ [11] with one equivalent of magnesium in thf in the presence of an excess of trimethylphosphine (eqn. (1)), and was isolated in the form of extremely air and moisture sensitive dark green cubes from cold (-30°C) pentane solutions.



Room temperature ^1H NMR data are consistent with a highly symmetrical structure in which the two imido ligands are equivalent. A single resonance at δ 1.03 ppm is attributable to the bound PMe_3 ligand, broadened due to rapid exchange with free phosphine. Consistently, addition of an excess of PMe_3 leads to a marked broadening of the phosphine methyl resonance, with an associated shift of this signal towards that of free PMe_3 , and addition of an excess of $\text{P}(\text{CD}_3)_3$ causes a decrease in intensity of the phosphine resonance, which is again shifted towards that of free PMe_3 .

Crystals of 1 suitable for an X-ray structure determination were grown from a saturated diethyl ether solution maintained at -30°C . The structure of one independent molecule is shown in Fig. 1, and the bond lengths and angles in the Mo environment are included in the Figure caption. The molecules show a rather

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* Dedicated to Professor M.F. Lappert on the occasion of his 65th birthday.

distorted tetrahedral arrangement with mean * N–Mo–N and P–Mo–P bond angles of $137.3(7)^\circ$ and $97.1(2)^\circ$, respectively. The mean Mo–N separation of $1.805(12)$ Å, and the associated Mo–N–C angle $171.3(9)^\circ$, are consistent with linear imido units bound to molybdenum through pseudo triple bonds. These molecular parameters are comparable with those for a tungsten analogue, $[\text{W}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2(\text{PMePh}_2)_2]$, whose structure was recently determined by Schrock and co-workers [12]. There is also a close correlation with the inter-ligand angles found in the isolobal d^2 complex $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{PMe}_3)_2]$ [9], $92.9(1)^\circ$ for P–Ti–P and $133.2(5)^\circ$ for the ring centroid–Ti–ring centroid angle.

The results of some preliminary reactivity studies on **1** are shown in Scheme 1. The ready dissociation of PMe_3 allows related tertiary phosphine derivatives to be obtained by simple ligand exchange, as shown for the PMe_2Ph derivative **2**. Treatment of **1** with diphenylacetylene affords the four coordinate ‘metallocene-like’ acetylene complex **3**; the crystal structure of the tert-butylimido analogue has been determined [13]. Reactions with ethylene or propylene do not result in displacement of PMe_3 but rather in the formation of unusual, formally ‘20-electron’, five-coordinate complexes **4**. It was envisaged that a potentially chelating

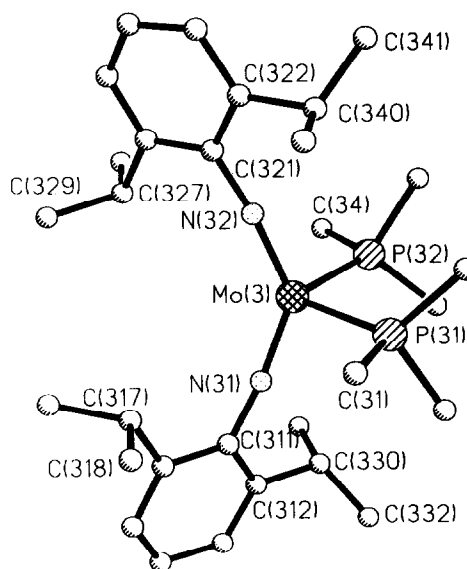
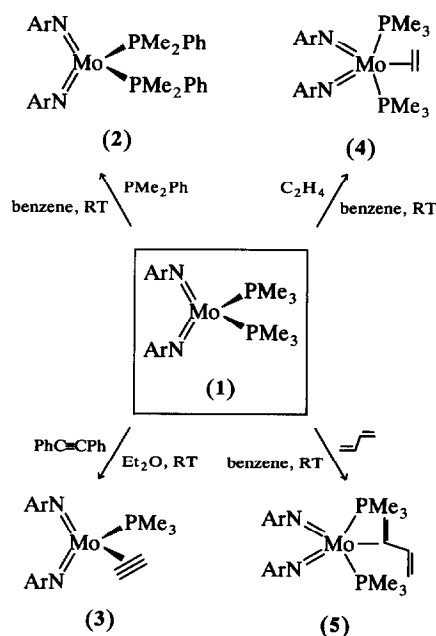


Fig. 1. Molecular structure of the unique molecule of $[\text{Mo}(\text{N-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2(\text{PMe}_3)_2]$ (**1**). Key dimensions: Mo(3)–P(31) $2.400(4)$, Mo(3)–P(32) $2.405(5)$, Mo(3)–N(31) $1.805(13)$, Mo(3)–N(32) $1.797(10)$ Å; P(31)–Mo(3)–N(31) $98.9(3)$, P(31)–Mo(3)–N(32) $110.1(3)$, P(32)–Mo(3)–P(31) $96.9(2)$, P(32)–Mo(3)–N(31) $109.0(4)$, P(32)–Mo(3)–N(32) $98.5(4)$, N(31)–Mo(3)–N(32) $137.1(5)$, Mo(3)–N(31)–C(311) $169.8(9)$, Mo(3)–N(32)–C(321) $172.3(9)^\circ$.

* Selected spectroscopic data for **1**: ^1H NMR (400 MHz, C_6D_6 , 298 K): 1.03 [18H, s(br) ($\nu_{1/2}$ 36 Hz), PMe_3], 1.32 [24H, d (3J 7.2), CHMe_2], 3.73 [4H, sept. (3J 6.8), CHMe_2], 6.91 [2H, t (3J 7.6), $p\text{-Ar}$], 7.19 [4H, d (3J 9.2), $m\text{-Ar}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6 , 298 K): 22.31 [br, PMe_3], 25.17 [$\text{CH}(\text{CH}_3)_2$], 26.43 [CHMe_2], 117.75 [$p\text{-Ar}$], 122.78 [$m\text{-Ar}$], 135.74 [$o\text{-Ar}$], 155.45 [$ipso\text{-Ar}$]. Elemental Anal. for $\text{MoP}_2\text{N}_2\text{C}_{30}\text{H}_{52}$: Found (required): %C 59.98 (60.18); %H 8.69 (8.77); %N 4.40 (4.68).

Crystal data for $\text{C}_{30}\text{H}_{52}\text{N}_2\text{P}_2\text{Mo}$: $M = 598.6$, monoclinic, $C2/c$, $a = 25.848(6)$, $b = 25.848(3)$, $c = 21.340(3)$ Å, $\beta = 107.72(2)^\circ$, $V = 13581(4)$ Å³, $Z = 16$, $F(000) = 5088$, $\mu = 4.99$ cm^{−1}, $D_c = 1.17$ g cm^{−3}, $T = 293$ K. Intensity data were measured on a Rigaku AFC6S diffractometer from a rather small, weakly diffracting green, prismatic crystal of **1**. The structure was solved by Patterson methods and refined with 4121 observed ($F \geq 2\sigma(F)$), from the 8874 total unique reflections recorded, using Shelxtlplus [14]. The apparently identical a and b unit cell dimensions were very carefully checked and thorough searches made for higher symmetry, but none were found and the lattice symmetry of these crystals is seen to be monoclinic upon satisfactory refinement. [$R = 0.060$, $R_w = 0.067$ with 387 parameters refined]. The complex crystallizes with one complete molecule in a general position (Fig. 1) and two half molecules with the Mo atoms on sites of 2-fold symmetry. The three ‘molecules’ have very similar geometries and the mean values of the molybdenum atom core coordination have been given in the text. All molecules show high thermal vibrations in the ^iPr groups of the imido ligands and accordingly some restraints were applied to the geometry of these groups in the refinement. Lists of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

diene such as butadiene might be capable of trapping out a mono-phosphine derivative, but again a five-coordinate complex, this time incorporating an η^2 -butadiene ligand, is obtained. These five coordinate species are non metallocene-like, and arise as a conse-



Scheme 1.

quence of the greater space around the metal in these arylimido derivatives as compared with that in bis(cyclopentadienyl) metal species, which are sterically more hindered in the immediate vicinity of the metal centre. Nevertheless, it has been found that four coordination in bis(imido) derivatives can be maintained if the arylimido ligands are replaced by tert-butyylimido groups [3]. Finally, it is worth noting some differences in reactivity of **1** compared with its half-sandwich niobium imido analogue [(η -C₅Me₅)Nb(N-2,6-ⁱPr₂C₆H₃)₂(PMe₃)₂]: whereas the niobium compound reacts smoothly with carbon monoxide to afford a stable mono-carbonyl derivative, **1** reacts instantaneously to give an intractable mixture of products. In contrast, **1** does not react with dihydrogen even upon prolonged warming at 120°C, unlike [(η -C₅Me₅)Nb(N-2,6-ⁱPr₂C₆H₃)₂(PMe₃)₂] which reacts smoothly at 60°C to give the stable dihydride [(η -C₅Me₅)Nb(N-2,6-ⁱPr₂C₆H₃)₂(PMe₃)(H)₂] [7].

The products outlined in Scheme 1 will be described in detail elsewhere.

Acknowledgements

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