# Novel Bis(imido) Complexes of Molybdenum(VI): Precursors to New Alkene Metathesis Catalysts

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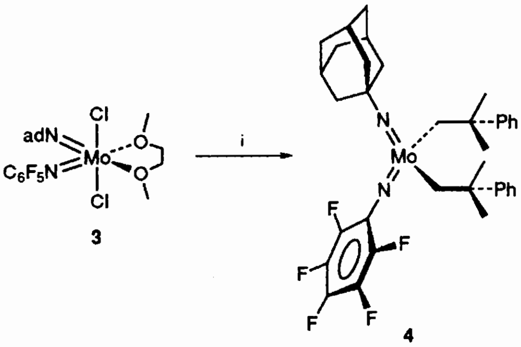
Novel four- and six-coordinate mixed-imido complexes of molybdenum are described and the structures of [Mo(Nad)($NC_6F_5$)$Cl_2$(dme)] (ad = adamantyl) and [Mo(Nad)($NC_6F_5$)($CH_2CMe_2Ph$)$_2$] are reported.

Organoimido (NR) complexes of molybdenum are relatively abundant and are of considerable technological significance.[1] Whilst numerous molybdenum imido complexes containing more than one imido ligand are known, derivatives containing different imido ligands at the same metal centre remain rare. We decided to explore routes to such complexes for two reasons: first, organoimido complexes are crucial intermediates in the synthesis of well-defined alkylidene metathesis catalysts,[2] and second, the presence of electronically and sterically disparate imido groups at the same metal centre would allow an opportunity to probe the bonding in the [Mo($NR^1$)($NR^2$)] fragment where, in a pseudo-tetrahedral geometry, the imido ligands necessarily engage in a competition for the available metal d$\pi$-symmetry orbitals.[1,3]

Here we describe two convenient routes to novel four- and six-coordinate mixed-imido complexes of molybdenum, starting from readily available $Na_2MoO_4$ (Scheme 1). The six-coordinate complexes can be prepared conveniently on a large scale either by (i) simultaneous addition of the two amines ($R^1NH_2$ and $R^2NH_2$) to a stirred suspension of $Na_2MoO_4$ in dme (dme = 1,2-dimethoxyethane) under the conditions outlined in Scheme 1, or (ii) in the case of *tert*-butylimido containing products, *via* treatment of the bis(*tert*-butylimido) complex **1** with an appropriate amine or aniline in dme at 70 °C. The synthetic procedure is quite general and can be extended to any number of new mixed imido complexes of the type [Mo($NR^1$)($NR^2$)$Cl_2$(dme)]. For example, the amines $H_2NR^1$ and $H_2NR^2$ can be selected from 2-*tert*-butylaniline, 2,6-dichloroaniline, pentafluoroaniline, 2,6-diisopropylaniline, *tert*-butylamine and 1-adamantamine. We also note here a third method of accessing the mixed imido species, *via* an inter-metal exchange of the imido ligands of [Mo($NR^1$)$_2Cl_2$(dme)] and [Mo($NR^2$)$_2Cl_2$(dme)] in refluxing dme over a period of 1 h. This exchange is not as facile as for four-coordinate complexes of the type [Mo(NR)$_2X_2$] (X = alkoxide),[4] presumably as a result of the greater coordinative saturation in the six-coordinate species, but nevertheless it does provide an alternative approach to the mixed imido complexes of interest.

By way of example, [Mo(Nad)($NC_6F_5$)$Cl_2$(dme)]† **3** is prepared from the admixture of 1-adamantamine and pentafluoroaniline, chlorotrimethylsilane, triethylamine and $Na_2MoO_4$ in dimethoxyethane. Simple recrystallisation from the reaction solvent affords red crystalline **3** in 75% isolated yield. Crystals suitable for X-ray analysis were grown from diethyl ether at −20 °C; the molecular structure is shown in Fig. 1. The structure‡ contains two molecules in the asymmetric unit, only one of which is shown. Of particular interest are the bond parameters associated with the imido ligands, and it is useful to compare these between the two crystallographically independent molecules. The Mo–N distances for the adamantylimido ligands are 1.716(3) and 1.715(3) Å, whilst those for the pentafluorophenylimido groups are longer at 1.759(3) and 1.775(3) Å. Two factors are likely to contribute to these bond length differences: (i) the more electron-releasing adamantylimido ligand would be expected to be capable of forming stronger $\pi$-interactions with metal d$\pi$-symmetry orbitals, and (ii) the metal–nitrogen $\pi$-interactions in the Mo–N($C_6F_5$) fragment are likely to be diminished due to



**Scheme 2** *Reagents and conditions*: i, $2ClMgCH_2CMe_2Ph$, $Et_2O$, room temp. 18 h

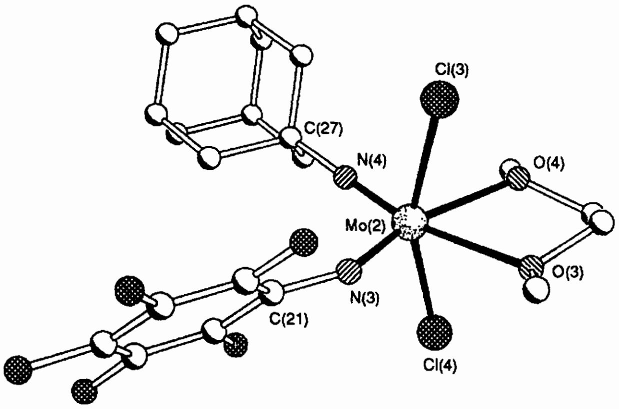
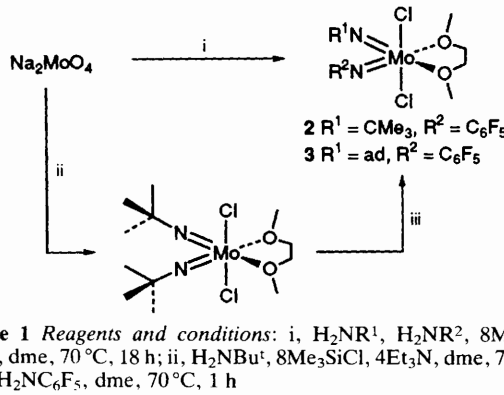


**Fig. 1** Structure of one of the two crystallograpically independent molecules of **3**, without H atoms and with key atoms labelled. Selected bond lengths (Å) and angles (°) for this and the other molecule: Mo(2)–N(3) 1.775(3), 1.759(3); Mo(2)–N(4) 1.715(3), 1.716(3); Mo(2)–O(3) 2.337(2), 2.354(2); Mo(2)–O(4) 2.372(2), 2.367(2); Mo(2)–Cl(3) 2.4006(12), 2.3841(12); Mo(2)–Cl(4) 2.3969(11), 2.4049(12); N(3)–C(21) 1.374(4), 1.373(4); N(4)–C(27) 1.447(4), 1.450(4); N(3)–Mo(2)–N(4) 105.23(13), 104.20(13); O(3)–Mo(2)–O(4) 70.04(8), 69.80(8); Cl(3)–Mo(2)–Cl(4) 157.71(3), 158.44(3); Mo(2)–N(3)–C(21) 152.0(2), 160.0 (2); Mo(2)–N(4)–C(27) 172.6(2), 162.8(2).



**2** $R^1$ = $CMe_3$, $R^2$ = $C_6F_5$
**3** $R^1$ = ad, $R^2$ = $C_6F_5$

**Scheme 1** *Reagents and conditions*: i, $H_2NR^1$, $H_2NR^2$, $8Me_3SiCl$, $4Et_3N$, dme, 70 °C, 18 h; ii, $H_2NBu^t$, $8Me_3SiCl$, $4Et_3N$, dme, 70 °C, 18 h; iii, $H_2NC_6F_5$, dme, 70 °C, 1 h π-bonding between the nitrogen and the *ipso*-carbon of the aromatic ring. For example, whereas the adamantylimido N–C distance, at 1.449(4) Å (avg.), is within the normal range for an alkyl substituent attached to nitrogen, the pentafluorophenylimido N–C distance of 1.374(4) Å is indicative of substantial multiple bond character between nitrogen and carbon The metal–oxygen distance for the dme oxygen lying. approximately *trans* to the pentafluorophenylimido ligand is shorter, 2.346(2) Å (avg.), than the Mo–O distance [2.370(2) Å (avg.)] for the oxygen *trans* to the adamantylimido group, reflecting a greater *trans*-influence for the more electron-releasing adamantylimido ligand.

An important difference between the two molecules lies in the angles at the imido nitrogens. In one of the molecules, these are comparable, being 160.0(2)° for ad–N–Mo (ad = adamantyl) and 162.8(2)° for $C_6F_5$–N–Mo. However, in the second molecule, ad–N–Mo is 172.6(2)° whereas $C_6F_5$–N–Mo is 152.0(2)°. This quite wide range of bond angles for molecules contained within the same crystal structure provides a useful indicator of the 'softness' of this angle for quasi-linear, terminal imido ligands. It is, therefore, doubtful that imido ligands in general with angles at nitrogen down to 150° are electronically perturbed to any great extent, but more likely arise as a consequence of inter-ligand steric interactions and crystal packing forces.

Four-coordinate dialkyl derivatives can be prepared *via* treatment of the dichloro complexes $[Mo(NR^1)(NR^2)Cl_2(dme)]$ with an appropriate Grignard reagent in diethyl ether. An example is shown in Scheme 2, where the mixed imido complex **3** reacts with two equivalents of neophylmagnesium chloride ($ClMgCH_2CMe_2Ph$) to give $[Mo(Nad)(NC_6F_5)(CH_2CMe_2Ph)_2]$ **4**, isolable as golden yellow crystals. The molecular structure of **4** has been determined§ and is shown in Fig. 2. In this complex the angles at the imido nitrogens are virtually identical, 156.5(2)° at the adamantylimido nitrogen, compared with 156.1(2)° at the pentafluorophenylimido nitrogen. These are at the low end of the range typically found (150–180°) for quasi-linear terminal imido ligands, while the Mo–N distances of 1.723(2) (Mo–Nad) and 1.773(2) Å (Mo–$NC_6F_5$) are comparable with the bond lengths observed for the adamantyl- and pentafluorophenyl-imido ligands in **3**. There is no evidence for close contacts of any hydrogens with the metal centre.

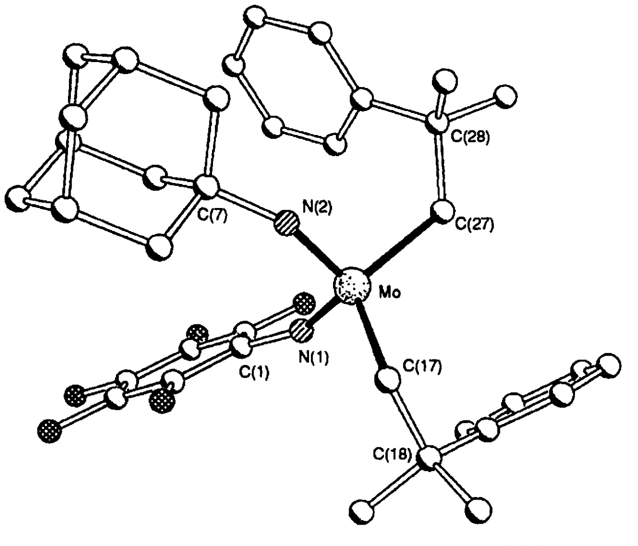


**Fig. 2** Molecular structure of **4**, without H atoms and with key atoms labelled. Selected bond lengths (Å) and angles (°): Mo–N(1) 1.773(2), Mo–N(2) 1.723(2), Mo–C(17) 2.138(2), Mo–C(27) 2.136(2), N(1)–C(1) 1.373(3), N(2)–C(7) 1.453(3); N(1)–Mo–N(2) 111.03(9), C(17)–Mo–C(27) 117.62(10), Mo–N(1)–C(1) 156.1(2), Mo–N(2)–C(7) 156.6(2), Mo–C(17)–C(18) 117.7(2), Mo–C(27)–C(28) 124.7(2).

An important application of this synthetic approach lies in making available new alkene metathesis catalysts *via* Osborn's alcoholysis methodology.[5] Here, the more basic adamantylimido nitrogen is selectively protonated by the alcohol to afford alkylidene catalysts containing the highly electron-withdrawing pentafluorophenylimido substituent. New alkylidene complexes derived in this manner and their metathesis activity will be outlined in future reports.

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## Footnotes

† Satisfactory elemental analyses have been obtained for compounds **2–4** *Selected spectroscopic data* for **2**: $^1H$ NMR ($C_6D_6$, 400 MHz, 298 K): δ 3.42 (s, 6H, $MeOCH_2$), 3.13 (s, 4H, $MeOCH_2$), 1.25 [s, 9H, $NC(CH_3)_3$].

For **3**: $^1H$ NMR ($C_6D_6$, 200 MHz, 298 K): δ 3.49 (s, 6H, $MeOCH_2$), 3.21 (s, 4H, $MeOCH_2$), 2.10 (m, 6H, $adCH_2$), 1.82 (m, 3H, adC*H*), 1.35 (m, 6H, $adCH_2$).

For **4**: $^1H$ NMR ($C_6D_6$, 400 MHz, 298 K): δ 1.86 (d, 2H, $^2J_{HH}$ 12.4 Hz, $CH_2CMe_2Ph$), 1.82 (m, 3H, adC*H*), 1.78 (d, 2H, $^2J_{HH}$ 12.4 Hz, $CH_2CMe_2Ph$), 1.75 (m, 6H, $adCH_2$), 1.50 (s, 6H, $CH_2CMe_2Ph$), 1.46 (s, 6H, $CH_2CMe_2Ph$), 1.39 (m, 6H, $adCH_2$).

‡ *Crystal data* for **3**: $C_{20}H_{25}Cl_2F_5MoN_2O_2$, $M$ = 587.26, monoclinic, space group $P2_1/n$, $a$ = 14.045 (3), $b$ = 12.823 (3), $c$ = 25.934 (5) Å, β = 92.86 (4)°, $U$ = 4665 (2) $Å^3$, $Z$ = 8, $D_c$ = 1.672 g $cm^{-3}$, $F(000)$ = 2368, μ(Mo-Kα) = 0.851 $mm^{-1}$, λ = 0.71073 Å. 9558 reflections ($2\theta_{max}$ = 50°) were measured by ω/θ scans and on-line profile fitting[6] at 160 K on a Stoe-Siemens diffractometer with a Cryostream cooler,[7] yielding 8232 unique data ($R_{int}$ = 0.0530), corrected semi-empirically for absorption. Structure solution was by direct methods, refinement by full-matrix least-squares analysis on $F^2$ for all independent reflections.[8] A riding model was used for isotropic H atoms, other atoms were anisotropic. $wR$ (all data) = $\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ = 0.0781, conventional $R$ [on $F$ values of 6336 reflections with $F_o^2 > 2\sigma(F_o^2)$] = 0.0283, goodness of fit $S$ = 1.058 on $F^2$ values for 663 parameters.

§ *Crystal data* for **4**: $C_{36}H_{41}F_5MoN_2$, $M$ = 692.65, triclinic, space group $P\bar{1}$, $a$ = 11.491 (4), $b$ = 11.780 (4), $c$ = 12.345 (5) Å, α = 100.22 (4)°, β = 93.30 (4)°, γ = 98.43 (4)°, $U$ = 1620.8 (11) $Å^3$, $Z$ = 2, $D_c$ = 1.419 g $cm^{-3}$, $F(000)$ = 716, μ(Mo-Kα) = 0.461 $mm^{-1}$. 7418 reflections were measured at 160 K, giving 5246 unique data ($R_{int}$ = 0.0181). $wR$ (all data) = 0.0728, conventional $R$ (4871 reflections) = 0.0260, $S$ = 1.046 for 413 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

## References

1 For examples, see: W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley Interscience, New York, 1988.
2 R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare and M. O'Regan, *J. Am. Chem. Soc.*, 1990, **112**, 3875.
3 V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1994, 1607.
4 M. Jolly, J. P. Mitchell and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1992, 1331.
5 G. Schoettel, J. Kress and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1989, 1062.
6 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
7 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.
8 G. M. Sheldrick, SHELXTL Manual, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1990; SHELXL-93, program for crystal structure refinement, University of Göttingen, 1993.