A Versatile Route to Well-defined Molybdenum Metathesis Catalysts *via* Mixed Imido Precursors: The Molecular Structure of $\mathrm{[Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(N\text{-}Bu^t)(CH_2CMe_3)_2]}$

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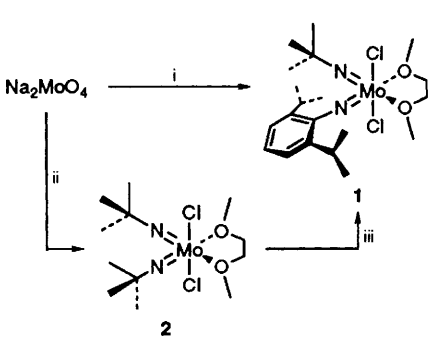
The four-coordinate bis(imido) dialkyl complex $\mathrm{[Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(N\text{-}Bu^t)(CH_2CMe_3)_2]}$ is readily converted to well-defined alkylidene metathesis catalysts upon treatment with alcoholic or phenolic activators.

Four-coordinate molybdenum alkylidene complexes of the type $\mathrm{[Mo(NR)(CHR')(OR'')_2]}$ are of considerable technological importance due to their role as well-defined ring-opening metathesis polymerisation (ROMP) initiators.[1] They offer a number of advantages over conventional initiator formulations, including: (*i*) their ability to promote 'living' metathesis polymerisations thereby allowing access to narrow molecular mass distribution polymers[2,3] and block copolymers,[4] (*ii*) their tolerance of a wide range of functionalities,[3] and (*iii*) a remarkable degree of microstructural control over the resultant polymer products.[5,6]

The synthesis of four-coordinate imido-alkylidene complexes is achieved *via* methodology developed by Osborn[7] and Schrock[8] which involves protonation of an imido ligand followed by an α-H-abstraction, with elimination of alkane, to give the stable alkylidene complex. Osborn found that, for *tert*-butylimido derivatives, the products are usually oils which can lead to substantial handling difficulties for polymerisations, and the methodology is restricted to alkoxides that are relatively electron-withdrawing. Schrock's approach employs precursors containing 2,6-diisopropylphenylimido ligands whose alkylidene products are, in general, more amenable to manipulation, and it is these that have found widespread applications in metathesis polymerisation. However, a drawback in the preparation of arylimido catalysts is the necessity for triflic acid ($\mathrm{HOSO_2CF_3}$), an expensive and potentially hazardous reagent, to 'protonate off' the much less basic arylimido ligand.

Here, we outline a development that circumvents these problems, making accessible a range of new arylimido derivatives without recourse to triflic acid, at the same time providing a convenient approach to the well-defined initiators directly from relatively stable dialkyl precursors. The new route exploits a greater propensity for protonation at the more basic imido nitrogen in mixed bis(imido) molybdenum(VI) complexes of the type $\mathrm{[Mo(NR^1)(NR^2)(R^3)_2]}$.

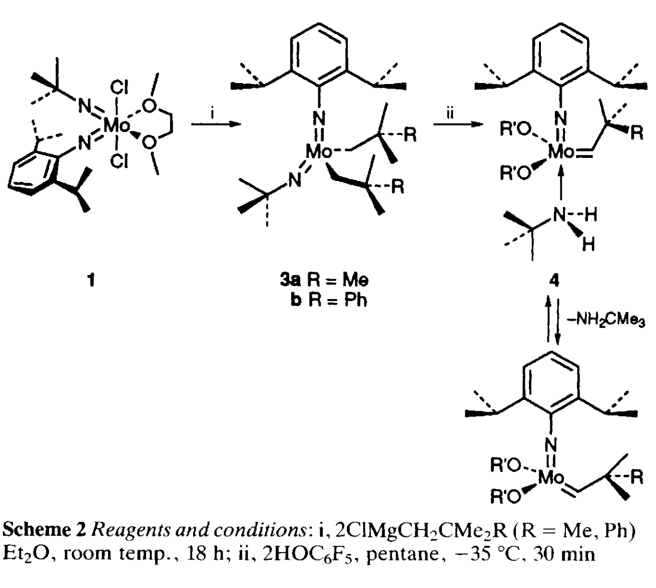
The starting point for the synthesis of 2,6-diisopropylphenylimido derivatives is the mixed bis(imido) complex $\mathrm{[Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(N\text{-}Bu^t)Cl_2(dme)]}$ **1** (dme = 1,2-dimethoxyethane) which can be accessed conveniently by either of the two routes shown in Scheme 1. The direct route from $\mathrm{Na_2MoO_4}$ involves sequential addition of *tert*-butylamine and $\mathrm{H_2N\text{-}2,6\text{-}Pr^i_2C_6H_3}$ in equimolar proportions to give a mixture of **1**, $\mathrm{[Mo(N\text{-}Bu^t)_2Cl_2(dme)]}$ **2** and the bis(arylimido) derivative $\mathrm{[Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2Cl_2(dme)]}$ in an approximate 3:1:2 ratio. The minor components can be effectively removed after one recrystallisation affording analytically pure, red crystalline **1** in *ca.* 35% overall yield. Alternatively, treatment of **2** with 1 equiv. of $\mathrm{H_2N\text{-}2,6\text{-}Pr^i_2C_6H_3}$ in refluxing dme for 1 h affords **1** in 60% yield after work-up. The ready availability of $\mathrm{Na_2MoO_4}$, and the amenability of this reaction to scale-up, makes large quantities of **1** conveniently accessible *via* either method. Also, the synthetic approach outlined here is quite general and can be used to prepare any number of new mixed imido complexes of the type $\mathrm{[Mo(NR^1)(NR^2)Cl_2(dme)]}$.[9]



Scheme 1 *Reagents and conditions*: i, $\mathrm{H_2N\text{-}Bu^t}$, $\mathrm{H_2N\text{-}2,6\text{-}Pr^i_2C_6H_3}$, $\mathrm{8Me_3SiCl}$, $\mathrm{4Et_3N}$, dme, 70 °C, 18 h; ii, $\mathrm{H_2N\text{-}Bu^t}$ 2 equiv., $\mathrm{8Me_3SiCl}$, $\mathrm{4Et_3N}$, dme, 70 °C, 18h; iii, $\mathrm{H_2N\text{-}2,6\text{-}Pr^i_2C_6H_3}$, dme, 70 °C, 1 h

Treatment of **1** with 2 equiv. of neopentyl- or neophylmagnesium chloride in diethyl ether affords the four-coordinate dialkyl complexes **3** (Scheme 2). Crystals of **3a** suitable for an X-ray structure determination were grown from acetonitrile at room temp. The molecular structure† is shown in Fig. 1 and selected bond lengths and angles are given in the caption. The metal–nitrogen bond distances of 1.737(2) Å [Mo–N(1)] and 1.759(2) Å [Mo–N(2)] are consistent with bond lengths generally found for alkyl- and aryl-imido ligands attached to molybdenum[10] while the M–N–C angles of 156.2(1)° [Mo–N(1)–C(1)] and 157.9(1)° [Mo–N(2)–C(15)] lie at the low end of the range (150–180°) observed for terminal imido ligands in related bis(imido) systems.[9] A striking feature of the structure is the presence of two α-agostic interactions involving a hydrogen on each of the neopentyl methylene carbons. These result in metal–hydrogen contacts of 2.35 Å [Mo···H(10a)] and 2.44 Å [Mo···H(5a)] and $\mathrm{Mo\text{-}C\text{-}H_\alpha}$ angles of 91.1 and 98.0° respectively, comparable with the weak multiple agostic interactions found in $\mathrm{[Nb(C_5H_5)(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(CH_2CMe_3)_2]}$.[11]

We envisaged that, for the mixed imido dialkyl complexes **3a** and **3b**, the more basic *tert*-butylimido nitrogen would be selectively protonated over the less basic arylimido nitrogen



Scheme 2 *Reagents and conditions*: i, $\mathrm{2ClMgCH_2CMe_2R}$ (R = Me, Ph) $\mathrm{Et_2O}$, room temp., 18 h; ii, $\mathrm{2HOC_6F_5}$, pentane, −35 °C, 30 min

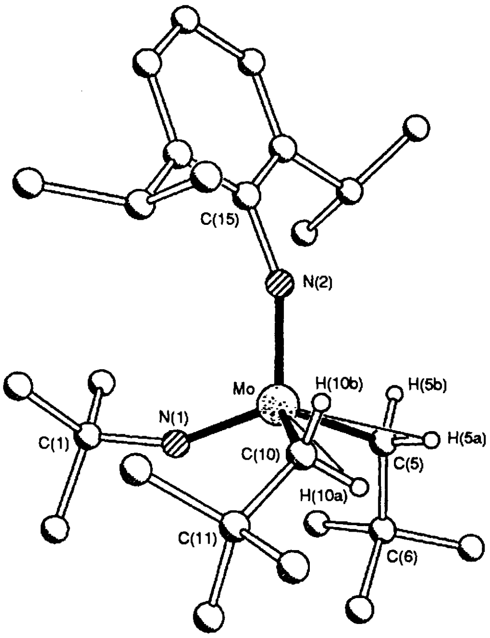


Fig. 1 Molecular structure of **3a**, with key atoms labelled. H atoms are omitted except for the α-CH_2 groups of the neopentyl ligands; agostic Mo–H interactions are shown as single lines. Selected dimensions (Å and °): Mo–N(1) 1.737(2), Mo–N(2) 1.759(2), Mo–C(5) 2.148(3), Mo–C(10) 2.140(3), N(1)–C(1) 1.467(3), N(2)–C(15) 1.398(3); N(1)–Mo–N(2) 111.07(10), C(5)–Mo–C(10) 113.65(11), Mo–N(1)–C(1) 156.19(13), Mo–N(2)–C(15) 157.89(13).

and thereby allow access to a range of new alkylidene species containing the desirable 2,6-diisopropylphenylimido ligand. Indeed, we find that **3a** and **3b** are excellent precursors to new alkylidene derivatives. For example, **3b** reacts with 2 equiv. of HOC_6F_5 in pentane at −35 °C to give $[Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(OC_6F_5)_2(H_2NBu^t)]$ **4** as a yellow microcrystalline solid in high yield. There is no evidence for protonation of the 2,6-diisopropylphenylimido functionality under these conditions. This preparation parallels the conversion of $[Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2(CH_2CMe_2Ph)_2]$ to $[Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(OSO_2CF_3)_2(dme)]$ using triflic acid.[8] However, the protonating agent pentafluorophenol is notably less acidic than triflic acid and is more easily handled.

A particular advantage of the approach outlined here is the potential it holds for generating well-defined, single-component, alkylidene metathesis catalysts *in situ* from robust dialkyl precursors thereby avoiding the need for extensive manipulations and storage of the alkylidene complexes themselves. An important area of application is in ring-opening metathesis polymerisation (ROMP) of cyclo-alkenes *via* reaction injection moulding (RIM). Well-defined, single-component initiators for the bulk polymerisation of dicyclopentadiene (DCPD) can be generated on the RIM timescale by combining the dialkyl procatalysts $[M(NR^1)(NR^2)(R^3)(R^4)]$ with alcoholic or phenolic activators, ROH (*e.g.* R = C_6F_5OH, $2,6\text{-}Cl_2C_6H_3OH$ and C_6H_5OH). The resultant alkylidenes are extremely active, resulting in essentially quantitative conversion of DCPD to thermoset poly-DCPD, and furthermore may offer opportunities to influence the microstructures of such thermoset polymers.

The Engineering and Physical Sciences Research Council and the Interdisciplinary Research Centre in Polymer Science and Technology (Leeds, Durham and Bradford Universities) are gratefully acknowledged for financial support.

Received, 8th August 1994; Com. 4/04842C

Footnotes

† *Crystal data* for **3a**: $C_{26}H_{48}MoN_2$, $M = 484.60$, triclinic, space group $P\bar{1}$, $a = 9.382\ (8)$, $b = 11.098\ (11)$, $c = 14.275\ (13)$ Å, $\alpha = 79.71\ (6)$, $\beta = 76.52\ (7)$, $\gamma = 74.67\ (5)°$, $U = 1383\ (2)$ Å^3, $Z = 2$, $D_c = 1.164$ g cm^{-3}, $F(000) = 520$, μ(Mo-Kα) = 0.487 mm^{-1}, $\lambda = 0.71073$ Å. 6217 reflections ($2\theta_{max} = 50°$) were measured by ω/θ scans and on-line profile fitting[12] at 160 K on a Stoe-Siemens diffractometer with a Cryostream cooler,[13] yielding 4857 unique data ($R_{int} = 0.0163$), corrected semiempirically for absorption. Structure solution was from Patterson and difference syntheses, refinement by full-matrix least-squares analysis on F^2 for all independent reflections.[14] A riding model was used for isotropic H atoms, except that the α-CH_2 atoms were refined freely; other atoms were anisotropic. wR (all data) = $\{\Sigma[w(F_o^2\text{-}F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.0678$, conventional R [on F values of 4625 reflections with $F_o^2 > 2\sigma(F_o^2)$] = 0.0237, goodness of fit S = 1.044 on F^2 values for 288 parameters.

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

‡ Satisfactory elemental analyses have been obtained. Selected spectroscopic data for **1**: ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 4.32 (sept., 2H, $^3J_{HH}$ 6.8 Hz, $CHMe_2$), 3.41 (s, 6H, $MeOCH_2$), 3.18 (s, 4H, $MeOCH_2$), 1.42 (d, 12H, $^3J_{HH}$ 6.8 Hz, $CHMe_2$), 1.27 (s, 9H, $NCMe_3$). For **3a**: ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 3.74 (sept., 2H, $^3J_{HH}$ 6.9 Hz, $CHMe_2$), 3.06 (d, 2H, $^2J_{HH}$ 12.8 Hz, CH_2CMe_3), 1.29 (d, 12H, $^3J_{HH}$ 6.9 Hz, $CHMe_2$), 1.25 (s, 9H, $NCMe_3$), 0.94 (d, 2H, $^2J_{HH}$ 12.8 Hz, CH_2CMe_3). ^{13}C NMR (C_6D_6, 100.6 MHz, 298 K): δ 77.85 (t, CH_2CMe_3), 70.74 (s, $NCMe_3$), 33.59 (q, CH_2CMe_3), 33.37 (s, CH_2CMe_3), 32.00 (q, $NCMe_3$), 28.13 (d, $CHMe_2$), 23.51 (q, $CHMe_2$). For **3b**: ^1H NMR (C_6D_6, 400 MHz, 298 K): δ 3.74 (sept., 2H, $^3J_{HH}$ 6.9 Hz, $CHMe_2$), 3.01 (d, 2H, $^2J_{HH}$ 12.8 Hz, CH_2CMe_2Ph), 1.52 (s, 6H, CH_2CMe_2Ph), 1.50 (s, 6H, CH_2CMe_2Ph), 1.29 (d, 12H, $^3J_{HH}$ 6.8 Hz, $CHMe_2$), 1.09 (s, 9H, $NCMe_3$), 0.98 (d, 2H, $^2J_{HH}$ 12.8 Hz, CH_2CMe_2Ph). For **4**: ^1H NMR (C_7D_8, 300 MHz, 293 K): δ 13.79 (s, 1H, $CHCMe_2Ph$), 4.07 (sept., 2H, $^3J_{HH}$ 6.7 Hz, $CHMe_2$), 2.41 (d, 1H, $^2J_{HH}$ 12.2 Hz, $NH_AH_BCMe_3$), 2.36 (d, 1H, $^2J_{HH}$ 12.2 Hz, $NH_AH_BCMe_3$), 2.00 (s, 6H, $CHCMe_2Ph$), 1.43 (d, 6H, $^3J_{HH}$ 6.7 Hz, $CHMe_2$), 1.25 (d, 6H, $^3J_{HH}$ 6.7 Hz, $CHMe_2$), 1.20 (s, 6H, $CHCMe_2Ph$), 0.49 (s, 9H, NH_2CMe_3).

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