

A Simple Route to Molybdenum–Carbene Catalysts for Alkene Metathesis

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A convenient method for the synthesis of high oxidation state tetra-co-ordinate molybdenum–carbene complexes such as $\text{Mo}(\text{NBu}^t)(\text{CHBu}^t)[\text{OCH}(\text{CF}_3)_2]_2$, which are catalytically active in alkene metathesis reactions, is reported.

Carbene complexes of the type $\text{M}(\text{NR})(\text{CHBu}^t)(\text{OR}')_2$ ($\text{M} = \text{W}, \text{Mo}$), which have recently been shown to act as catalysts for alkene metathesis reactions,^{1–6} function efficiently without the need for a Lewis acid cocatalyst. Ring opening polymerisation reactions of cyclic alkenes, in particular, have been developed by which polyacetylenes^{5,6} and monodispersed polymers or block copolymers of norbornene derivatives^{3,4} can be synthesised. However, the initial synthesis of such complexes^{1,2} is far from being straightforward, and the more convenient preparation of tungsten derivatives recently published cannot be extended to molybdenum⁷ and appears to be limited to only one type of imido ligand NR ($\text{R} = 2,6$ -diisopropylphenyl).

We report a simple method for the high yield synthesis of analogous molybdenum compounds containing the *t*-butylimido ligand. Examples of *t*-butylimido–neopentylidene molybdenum complexes have been described previously.^{8,9}

In the first step, MoO_2Cl_2 is treated under nitrogen with Bu^tNCO (2 equiv.) in acetonitrile (70 °C, 24 h) and yellow $\text{Mo}(\text{NBu}^t)_2\text{Cl}_2$ (1) is obtained in high yield (95%) (Scheme 1). This bisimido compound was reported previously;¹⁰ however, it was incompletely characterised¹⁰ and our new method of preparation appears to be much simpler. Complex

(1) can be recrystallised from methylene chloride/pentane to yield fine yellow needles.

Complex (1) reacts with neopentyl-lithium to yield $\text{Mo}(\text{NBu}^t)_2(\text{CH}_2\text{Bu}^t)_2$ (2) as a brown, very air-sensitive oil (yield 85%). This dineopentyl compound is analogous to the methyl¹⁰ and mesityl¹¹ derivatives found in the literature. The addition of two equivs. of $(\text{CF}_3)_2\text{CHOH}$ to (2) in pentane then leads to the penta-co-ordinate neopentylidene complex $\text{Mo}(\text{NBu}^t)(\text{CHBu}^t)[\text{OCH}(\text{CF}_3)_2]_2(\text{NH}_2\text{Bu}^t)$ (3)†, a brown, highly soluble oil, in 80% yield (Scheme 1).

Finally, dissolution of (3) in acetonitrile leads *in situ* to free *t*-butylamine and $\text{Mo}(\text{NBu}^t)(\text{CHBu}^t)[\text{OCH}(\text{CF}_3)_2]_2(\text{MeCN})$, which loses acetonitrile *in vacuo* to give the desired tetra-co-ordinate carbene complex $\text{Mo}(\text{NBu}^t)(\text{CHBu}^t)[\text{OCH}(\text{CF}_3)_2]_2$ (4)† as a brown oil. The co-ordinated *t*-butylamine molecule in (3) can, of course, also be easily replaced by stronger Lewis bases to yield further isolatable penta-co-ordinate adducts of the type $\text{Mo}(\text{NBu}^t)(\text{CHBu}^t)[\text{OCH}(\text{CF}_3)_2]_2(\text{L})$ [$\text{L} = \text{PMe}_3$ (5), $\text{C}_5\text{H}_5\text{N}$ (6)].† The molecular structures shown for compounds (4) and (3,5,6) are consistent with their i.r. and n.m.r. spectra.

When (4) is treated with a terminal alkene, its neopentylidene ligand is stoichiometrically exchanged with the substituted fragment of this alkene; further carbene complexes such as $\text{Mo}(\text{NBu}^t)(\text{CHPh})[\text{OCH}(\text{CF}_3)_2]_2$ (7) and $\text{Mo}(\text{NBu}^t)[\text{C}(\text{CH}_2)_3\text{CH}_2][\text{OCH}(\text{CF}_3)_2]_2$ (8)† could thus be synthesised by addition of, respectively, $\text{CH}_2=\text{CHPh}$ and $\text{CH}_2=\text{C}(\text{CH}_2)_3\text{CH}_2$ to (4), and isolated as brown powders (90% yield).

Productive metathesis of the terminal alkene is not observed in these reactions, but the tetra-co-ordinate complexes (4), (7), and (8) behave like their analogues² as effective catalysts for the metathesis of internal alkenes. For instance, solutions of (4) in chlorobenzene catalyse the metathesis of 100 equivs. of pent-2-ene to the equilibrium mixture of but-2-enes and hex-3-enes at an initial rate of 4 mol Mo min^{–1} at room temperature. This rate remains, however, significantly lower than that obtained with the most active homologous complex $\text{Mo}(N-2,6\text{-Pr}_2\text{C}_6\text{H}_3)(\text{CHBu}^t)[\text{OC}(\text{Me})(\text{CF}_3)_2]_2$.² Methylpent-3-eneoate converts compound (8) into

† (1): satisfactory elemental analysis was obtained; i.r. (Nujol mull, ν in cm^{-1}): 1235, 1200 ($\nu_{\text{Mo=N}}$); 325, 290 ($\nu_{\text{Mo-Cl}}$); ^1H n.m.r. (200 MHz, C_6D_6 , δ): 1.44 (NCMe₃); $^{13}\text{C}\{^1\text{H}\}$ n.m.r. (50 MHz, C_6D_6 , δ): 74.1 (NCMe₃), 30.1 (NCMe₃).

(2): i.r. (ν in cm^{-1}): 1230, 1208 ($\nu_{\text{Mo=N}}$); ^1H n.m.r. (200 MHz, C_6D_6 , δ): 1.89 (s, 4H, CH_2CMe_3), 1.52 (s, 18H, NCMe₃), 1.31 (s, 18H, CH_2CMe_3); $^{13}\text{C}\{^1\text{H}\}$ n.m.r. (50 MHz, C_6D_6 , δ): 74.8 (CH_2CMe_3), 67.4 (NCMe₃), 34.1 (NCMe₃), 32.7 (CH_2CMe_3).

(3): i.r. (ν in cm^{-1}): 3320, 3250 ($\nu_{\text{N-H}}$); 1200 ($\nu_{\text{Mo=N}}$); 748, 689 ($\nu_{\text{Mo-O}}$); ^1H n.m.r. (200 MHz, C_6D_6 , δ): 12.68 (s, 1H, CHCMe_3), 4.55 [sept, $^3J_{\text{HF}}$ 7 Hz, 2H, $\text{OCH}(\text{CF}_3)_2$], 1.45 (s, 9H, NCMe₃), 1.27 (s, 9H, CHCMe_3), 0.83 (s, 9H, NH_2CMe_3).

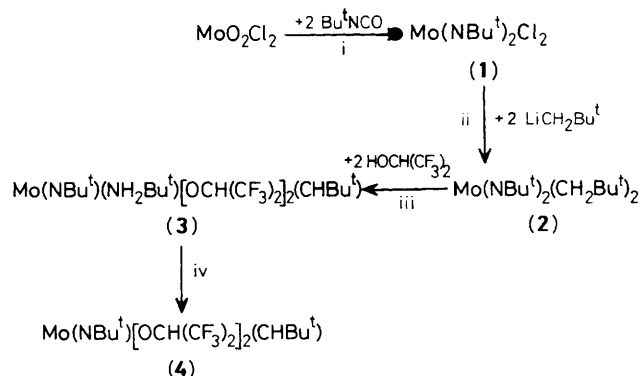
(4): i.r. (ν in cm^{-1}): 1210 ($\nu_{\text{Mo=N}}$); 743, 690 ($\nu_{\text{Mo-O}}$); ^1H n.m.r. (200 MHz, C_6D_6 , δ): 12.73 (s, 1H, CHCMe_3), 4.61 [sept, $^3J_{\text{HF}}$ 7 Hz, 2H, $\text{OCH}(\text{CF}_3)_2$], 1.49 (s, 9H, NCMe₃), 1.31 (s, 9H, CHCMe_3); $^{13}\text{C}\{^1\text{H}\}$ n.m.r. (50 MHz, C_6D_6 , δ): 301.6 (CHCMe_3), 121.5, 121.1 [q, $^1J_{\text{CF}}$ 290 Hz, $\text{OCH}(\text{CF}_3)_2$], 73.7 (NCMe₃), 71.5 [sept, $^2J_{\text{CF}}$ 32 Hz, $\text{OCH}(\text{CF}_3)_2$], 40.2 (CHCMe_3), 32.6 (NCMe₃), 30.5 (CHCMe_3); 'Off resonance': 301.6 (d, $^1J_{\text{CH}}$ 119 Hz).

(5), (6): ^1H n.m.r. (200 MHz, C_6D_6 , δ): (5): 12.62 (d, $^3J_{\text{PH}}$ 6 Hz, 1H, CHCMe_3), 4.70 [sept, 2H, $\text{OCH}(\text{CF}_3)_2$], 1.21 (s, 9H, NCMe₃), 1.10 (s, 9H, CHCMe_3), 0.97 (s, 9H, PMe_3); (6): 13.16 (s, 1H, CHCMe_3), 8.75 (d, 2H, *ortho*-NC₅H₅), 6.73 (dd, 2H, *meta*-NC₅H₅), 6.40 (t, 1H, *para*-NC₅H₅), 4.65 [sept, 2H, $\text{OCH}(\text{CF}_3)_2$], 1.19 (s, 9H, NCMe₃), 1.18 (s, 9H, CHCMe_3).

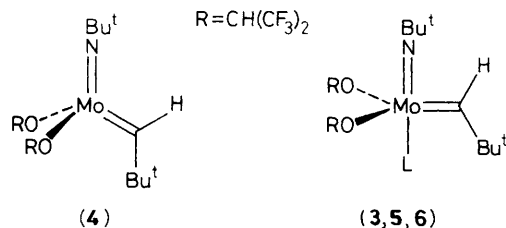
(7), (8): ^1H n.m.r. (200 MHz, δ): (7) (C_6D_6): 13.19 (s, 1H, CHPh), 7.66 (d, 2H, *ortho*-Ph), 7.40–7.10 (m, 2H, *meta*-Ph), 7.0 (t, 1H, *para*-Ph), 4.02 [sept, $^3J_{\text{HF}}$ 7 Hz, 2H, $\text{OCH}(\text{CF}_3)_2$], 1.56 (s, 9H, NCMe₃); (8) (CD_2Cl_2): 4.49 (br., 2H, $=\text{CCH}_2$), 4.07 [sept, $^3J_{\text{HF}}$ 7 Hz, 2H, $\text{OCH}(\text{CF}_3)_2$], 3.75 (br., 2H, $=\text{CC}'\text{H}'_2$), 2.12 (br., 2H, $=\text{CCH}_2\text{CH}_2$), 1.52 (br., 2H, $=\text{CCH}_2\text{C}'\text{H}'_2$), 1.45 (s, 9H, NCMe₃).

(9): ^1H n.m.r. (200 MHz, C_6D_6 , δ): 12.10 (t, 1H, $\text{CHCH}_2\text{CO}_2\text{Me}$), 4.31 (d, 2H, $\text{CHCH}_2\text{CO}_2\text{Me}$), 3.77 (s, 3H, $\text{CHCH}_2\text{CO}_2\text{Me}$), 1.44 (s, 9H, NCMe₃).

(10): ^1H n.m.r. (200 MHz, C_6D_6 , δ): 5.45, 4.98 [sept, $^3J_{\text{HF}}$ 7 Hz, 1H, $\text{OCH}(\text{CF}_3)_2$], 3.47 (d, 2H, $\text{CH}_2\text{H}_3\text{CMe}_3$), 2.55 (d, 2H, $\text{CH}_2\text{H}_3\text{CMe}_3$), 1.30 (s, 9H, NCMe₃), 1.13 (s, 18H, CH_2CMe_3).



Scheme 1. Reagents and conditions: i, $-\text{2CO}_2$, 70 °C, 24 h, acetonitrile; ii, $-\text{2LiCl}$, 1 h, pentane; iii, $-\text{MeBu}^t$, 10 min, pentane; iv, NH_2Bu^t , acetonitrile, then vacuum.



mainly $\text{Mo}(\text{NBu}^t)(\text{CHCH}_2\text{CO}_2\text{Me})[\text{OCH}(\text{CF}_3)_2]_2$ (**9**), one of the two catalytic propagating carbene species expected in this case (as shown by *in situ* ^1H n.m.r. spectroscopy),[†] but does not undergo further metathesis under these conditions. The corresponding propagating carbene complexes expected for the metathesis of norbornene or pent-2-ene in the presence of (**4**) or (**8**) were observed similarly.

Unfortunately, reaction of (**2**) with many other alcohols does not lead to carbene complexes of type (**3**). Poorly acidic alcohols like MeOH, Bu^tCH₂OH, or Bu^tOH do not react at all, whereas various phenol derivatives yield mainly dineopentyl precursors of (**3**) such as $\text{Mo}(\text{NBu}^t)(\text{NHBu}^t)(\text{OAr})(\text{CH}_2\text{Bu}^t)_2$ or $\text{Mo}(\text{NBu}^t)(\text{OAr}')_2(\text{CH}_2\text{Bu}^t)_2$.¹² An analogue of the latter, $\text{Mo}(\text{NBu}^t)[\text{OCH}(\text{CF}_3)_2]_2(\text{CH}_2\text{Bu}^t)_2$, (**10**), is indeed detected *in situ* by n.m.r. spectroscopy[†] during the reaction of (**2**) with $(\text{CF}_3)_2\text{CHOH}$ to yield (**3**). Specific electronic and steric constraints seem thus to be required for the third step of Scheme 1 to occur, particularly in the probable hexa-co-ordinate intermediates such as $\text{Mo}(\text{NBu}^t)(\text{CH}_2\text{Bu}^t)_2[\text{OCH}(\text{CF}_3)_2]_2(\text{NH}_2\text{Bu}^t)$. However, extension

of this method to complexes containing other imido ligands, in particular those with stronger electron withdrawing substituents, now seems feasible and we can anticipate¹³ an increase in the catalytic activity of such complexes.

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