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 $Mo(NBu^t)(CHBu^t)[OCH(CF_3)_2]_2$, which are catalytically active in alkene metathesis reactions, is reported.

Carbene complexes of the type $M(NR)(CHBu^t)(OR')_2$ (M = W, 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 molybdenum[7] and appears to be limited to only one type of imido ligand NR (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]

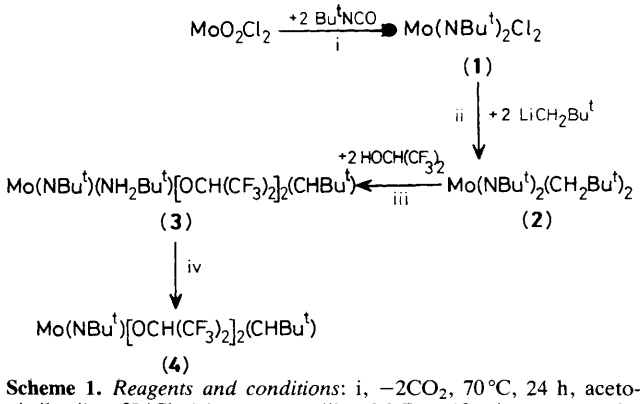
In the first step, MoO_2Cl_2 is treated under nitrogen with Bu^tNCO (2 equiv.) in acetonitrile (70 °C, 24 h) and yellow $Mo(NBu^t)_2Cl_2$† (**1**) is obtained in high yield (95%) (Scheme 1). This bisimido compound was reported previously;[10] however, it was incompletely characterised[10] and our new 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 $Mo(NBu^t)_2(CH_2Bu^t)_2$† (**2**) as a brown, very air-sensitive oil (yield 85%). This dineopentyl compound is analogous to the methyl[10] and mesityl[11] derivatives found in the literature. The addition of two equivs. of $(CF_3)_2CHOH$ to (**2**) in pentane then leads to the penta-co-ordinate neopentylidene complex $Mo(NBu^t)(CHBu^t)[OCH(CF_3)_2]_2(NH_2Bu^t)$ (**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 $Mo(NBu^t)(CHBu^t)[OCH(CF_3)_2]_2(MeCN)$, which loses acetonitrile *in vacuo* to give the desired tetra-co-ordinate carbene complex $Mo(NBu^t)(CHBu^t)[OCH(CF_3)_2]_2$ (**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 $Mo(NBu^t)(CHBu^t)[OCH(CF_3)_2]_2(L)$ [L = PMe_3 (**5**), C_5H_5N (**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 stoicheiometrically exchanged with the substituted fragment of this alkene; further carbene complexes such as $Mo(NBu^t)(CHPh)[OCH(CF_3)_2]_2$ (**7**) and $Mo(NBu^t)[C(CH_2)_3CH_2][OCH(CF_3)_2]_2$ (**8**)† could thus be synthesised by addition of, respectively, CH_2=CHPh and CH_2=$C(CH_2)_3CH_2$ 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 analogues[2] 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 $Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(CHBu^t)[OC(Me)(CF_3)_2]_2$.[2] Methylpent-3-eneoate converts compound (**8**) into



Scheme 1. *Reagents and conditions*: i, $-2CO_2$, 70 °C, 24 h, acetonitrile; ii, −2LiCl, 1 h, pentane; iii, $-MeBu^t$, 10 min, pentane; iv, NH_2Bu^t, acetonitrile, then vacuum.

† (**1**): satisfactory elemental analysis was obtained; i.r. (Nujol mull, ν in cm^{-1}): 1235, 1200 ($\nu_{Mo=N}$); 325, 290 (ν_{Mo-Cl}); ^1H n.m.r. (200 MHz, C_6D_6, δ): 1.44 ($NCMe_3$); $^{13}C\{^1H\}$ n.m.r. (50 MHz, C_6D_6, δ): 74.1 ($NCMe_3$), 30.1 ($NCMe_3$).

(**2**): i.r. (ν in cm^{-1}): 1230, 1208 ($\nu_{Mo=N}$); ^1H n.m.r. (200 MHz, C_6D_6, δ): 1.89 (s, 4H, CH_2CMe_3), 1.52 (s, 18H, $NCMe_3$), 1.31 (s, 18H, CH_2CMe_3); $^{13}C\{^1H\}$ n.m.r. (50 MHz, C_6D_6, δ): 74.8 (CH_2CMe_3), 67.4 ($NCMe_3$), 34.1 ($NCMe_3$), 32.7 (CH_2CMe_3).

(**3**): i.r. (ν in cm^{-1}): 3320, 3250 (ν_{N-H}); 1200 ($\nu_{Mo=N}$); 748, 689 (ν_{Mo-O}); ^1H n.m.r. (200 MHz, C_6D_6, δ): 12.68 (s, 1H, $CHCMe_3$), 4.55 [sept, $^3J_{HF}$ 7 Hz, 2H, $OCH(CF_3)_2$], 1.45 (s, 9H, $NCMe_3$), 1.27 (s, 9H, $CHCMe_3$), 0.83 (s, 9H, NH_2CMe_3).

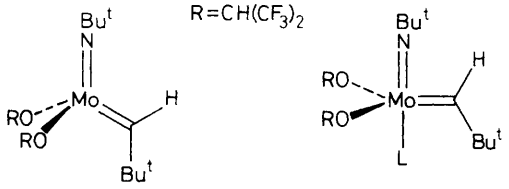
(**4**): i.r. (ν in cm^{-1}): 1210 ($\nu_{Mo=N}$); 743, 690 (ν_{Mo-O}); ^1H n.m.r. (200 MHz, C_6D_6, δ): 12.73 (s, 1H, $CHCMe_3$), 4.61 [sept, $^3J_{HF}$ 7 Hz, 2H, $OCH(CF_3)_2$], 1.49 (s, 9H, $NCMe_3$), 1.31 (s, 9H, $CHCMe_3$); $^{13}C\{^1H\}$ n.m.r. (50 MHz, C_6D_6, δ): 301.6 ($CHCMe_3$), 121.5, 121.1 [q, $^1J_{CF}$ 290 Hz, $OCH(CF_3)_2$], 73.7 ($NCMe_3$), 71.5 [sept, $^2J_{CF}$ 32 Hz, $OCH(CF_3)_2$], 40.2 ($CHCMe_3$), 32.6 ($NCMe_3$), 30.5 ($CHCMe_3$); 'Off resonance': 301.6 (d, $^1J_{CH}$ 119 Hz).

(**5**), (**6**): ^1H n.m.r. (200 MHz, C_6D_6, δ): (**5**): 12.62 (d, $^3J_{PH}$ 6 Hz, 1H, $CHCMe_3$), 4.70 [sept, 2H, $OCH(CF_3)_2$], 1.21 (s, 9H, $NCMe_3$), 1.10 (s, 9H, $CHCMe_3$), 0.97 (s, 9H, PMe_3); (**6**): 13.16 (s, 1H, $CHCMe_3$), 8.75 (d, 2H, *ortho*-NC_5H_5), 6.73 (dd, 2H, *meta*-NC_5H_5), 6.40 (t, 1H, *para*-NC_5H_5), 4.65 [sept, 2H, $OCH(CF_3)_2$], 1.19 (s, 9H, $NCMe_3$), 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, $^3J_{HF}$ 7 Hz, 2H, $OCH(CF_3)_2$], 1.56 (s, 9H, $NCMe_3$); (**8**) (CD_2Cl_2): 4.49 (br., 2H, =CCH_2), 4.07 [sept, $^3J_{HF}$ 7 Hz, 2H, $OCH(CF_3)_2$], 3.75 (br., 2H, =$CC'H'_2$), 2.12 (br., 2H, =CCH_2CH_2), 1.52 (br., 2H, =$CCH_2C'H'_2$), 1.45 (s, 9H, $NCMe_3$).

(**9**): ^1H n.m.r. (200 MHz, C_6D_6, δ): 12.10 (t, 1H, $CHCH_2CO_2Me$), 4.31 (d, 2H, $CHCH_2CO_2Me$), 3.77 (s, 3H, $CHCH_2CO_2Me$), 1.44 (s, 9H, $NCMe_3$).

(**10**): ^1H n.m.r. (200 MHz, C_6D_6, δ): 5.45, 4.98 [sept, $^3J_{HF}$ 7 Hz, 1H, $OCH(CF_3)_2$], 3.47 (d, 2H, $CH_AH_BCMe_3$), 2.55 (d, 2H, $CH_AH_BCMe_3$), 1.30 (s, 9H, $NCMe_3$), 1.13 (s, 18H, CH_2CMe_3).



(4) (3,5,6)

mainly Mo(NBu^t)(CHCH$_2$CO$_2$Me)[OCH(CF$_3$)$_2$]$_2$ (**9**), one of the two catalytic propagating carbene species expected in this case (as shown by *in situ* ^{1}H 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^{t}CH$_2$OH, or Bu^{t}OH do not react at all, whereas various phenol derivatives yield mainly dineopentyl precursors of (**3**) such as Mo(NBu^t)(NHBu^t)(OAr)(CH$_2$Bu^t)$_2$ or Mo(NBu^t)(OAr')$_2$(CH$_2$Bu^t)$_2$.[12] An analogue of the latter, Mo(NBu^t)[OCH(CF$_3$)$_2$]$_2$(CH$_2$Bu^t)$_2$, (**10**), is indeed detected *in situ* by n.m.r. spectroscopy† during the reaction of (**2**) with (CF$_3$)$_2$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 Mo(NBu^t)(CH$_2$Bu^t)$_2$-[OCH(CF$_3$)$_2$]$_2$(NH$_2$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 anticipate[13] an increase in the catalytic activity of such complexes.

Received, 7th March 1989; Com. 9/01007F

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