High Oxidation State Alkyl and Carbene Complexes of Molybdenum Containing the t-Butylimido Ligand

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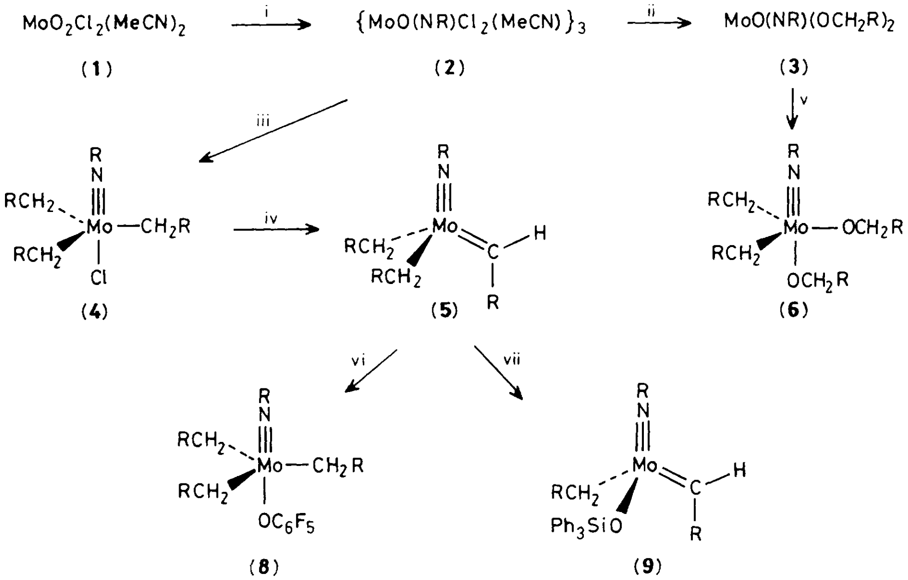
Alkylation reactions of imido-oxo complexes of molybdenum(VI) lead to the formation of various imido-alkyl and imido-carbene compounds.

High oxidation state alkyl and carbene chemistry of molybdenum[1] has been almost totally neglected when compared with that of tungsten. This is somewhat surprising since molybdenum to carbon bonds may be involved in several important catalytic oxidation processes (*e.g.* conversion of propene into acrolein or acrylonitrile[2]) as well as in olefin[1b,3] metathesis. The presence of oxo and/or imido ligands on Mo is also of considerable interest both as possible reactive[4] and stabilising or activating[5] units. In recent years a number of interesting imido complexes of Mo with ancillary ligands such as dithiocarbamate,[4a] phosphine, and cyclopentadienyl[6] groups have thus been synthesised. We present now the convenient synthesis of new oxo-imido and imido complexes of molybdenum(VI), including several containing molybdenum to carbon single and double bonds (Scheme 1).

Compound (**1**)[7] when treated with RNCO (1 equiv.; R = Bu^t) yields CO_2 and $\{MoO(NR)Cl_2(MeCN)\}_n$ (**2**) as an orange powder in quantitative yield. We suggest an oxo-bridged structure for (**2**) ($\nu_{Mo-O-Mo}$ 720 cm^{-1}), probably trimeric as found for $\{W(\mu\text{-}O)(NPh)Me_2\,(PMe_3)\}_3$,[8] although a dimeric form cannot be excluded. Complex (**2**) reacts with 2 equiv. of $Li(OCH_2R)$ to give LiCl and the yellow-green crystalline product $MoO(NR)(OCH_2R)_2$ (**3**). The ν_{Mo-O} frequency at 850 cm^{-1} shows (**3**) to be possibly monomeric {*cf.* $W(NR)_2(OR)_2$[9]}, although bridging may occur *via* the imido ligands [see $\{Mo(NR)_2Me_2\}_2$[1c]].



Scheme 1.† (R = Bu^t). *Reagents* (25 °C): i, RNCO (1 equiv.), MeCN, 48 h (*ca.* 100%); ii, $Li(OCH_2R)$ (2 equiv.), Et_2O, 1 h (80%); iii, $(RCH_2)_2Mg$·dioxane (1.1 equiv.), Et_2O, 1 h (35%); iv, $(RCH_2)Li$ (1 equiv.), C_6H_6, 10 min (75%); v, $(RCH_2)_2Mg$·dioxane (1 equiv.), Et_2O, 2 h (75%); vi, C_6F_5OH (1 equiv.), pentane, 10 min; vii, Ph_3SiOH (1 equiv.), pentane, 1 h.

The oxo ligand in (**2**) and (**3**) is surprisingly reactive. If alkylation of (**2**) is carried out with $(RCH_2)_2Mg$ (1.1 equiv.), $Mo(NR)(CH_2R)_3Cl$ (**4**) is obtained as colourless crystals. Spectroscopic data indicate (**4**) to be isostructural with $MoO(CH_2R)_3Cl$[1b] and $W(NR')(CH_2R)_3Cl$[10,11] (R' = Me or Ph) previously described. Treatment of (**4**) with 1 equiv. of RCH_2Li yields $Mo(NR)(CHR)(CH_2R)_2$ (**5**), the first simple alkylidene complex of molybdenum in a high oxidation state. Complex (**5**) is obtained as a brown oil (at 25 °C) after purification by short-path distillation (40 °C; 10^{-4} mm Hg) and is characterised in particular by the carbene n.m.r. signals at δ 9.22 (^1H) and 249.5 (^{13}C). The observation by ^1H n.m.r. spectroscopy of two equivalent neopentyl ligands possessing two diastereotopic methylenic protons allows us to ascribe to (**5**) the structure shown in Scheme 1. A single isomer is indicated, although the n.m.r. spectra would also be consistent with the presence of two isomers equilibrating rapidly by rotation of the carbene ligand about the molybdenum–carbon double bond. Such a rotation process is slow however for analogous tungsten carbene compounds which have recently been described.[12] Alkylation of (**3**) with $(RCH_2)_2Mg$ (1 equiv.) yields $Mo(NR)(CH_2R)_2(OCH_2R)_2$ (**6**) as brown crystals which can be purified by recrystallisation from pentane or sublimation (70 °C; 10^{-4} mm Hg). ^1H and ^{13}C N.m.r. data clearly indicate the structure shown in Scheme 1. Using 1.5 equiv. of $(RCH_2)_2Mg$ leads to formation of $Mo(NR)(CH_2R)_3(OCH_2R)$, an alkoxylated derivative of (**4**), as well as variable yields of an unusual carbene complex (**7**) of formula $Mo_2O(NR)_2(CHR)(CH_2R)_4$. This latter yellow crystalline complex shows in particular n.m.r. signals of the carbene ligand at δ 11.71 (^1H) and 269.2 (^{13}C), as well as two non-equivalent NR ligands and two types of $-CH_2R$ groups of relative ratio 3:1. The i.r. spectrum shows the probable presence of an Mo–O–Mo linkage, and although certain dimeric structures can be proposed for (**7**), details must await an *X*-ray determination.

These carbene complexes undergo some interesting reactions. For example, C_6F_5OH reacts rapidly with (**5**) to yield $Mo(NR)(CH_2R)_3(OC_6F_5)$ (**8**) resulting from addition of $C_6F_5O{-}H$ across the metal–carbon double bond. By contrast Ph_3SiOH reacts to form the new carbene complex $Mo(NR)(CHR)(CH_2R)(OSiPh_3)$ (**9**), in which a neopentyl group in (**5**) is replaced by a siloxo ligand. Like their tungsten analogues,[12] certain of these complexes metathesise olefins

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† *Spectroscopic data:* ^1H (200 MHz) and ^{13}C (50 MHz) n.m.r. δ, C_6D_6, *J* in Hz; i.r. in Nujol mull, ν in cm^{-1}; eq. = equatorial, ax. = axial.

(**2**) $\{MoO(NCMe_3)Cl_2(MeCN)\}_n$: ^1H n.m.r. 2.3 (s, 3H, *Me*CN), 1.6 (s, 9H, $NC\mathit{Me}_3$); i.r. 720 ($\nu_{Mo-O-Mo}$), 330 (ν_{Mo-Cl}), 2280, 2305 ($\nu_{C\equiv N}$).

(**3**) $MoO(NCMe_3)(OCH_2CMe_3)_2$: ^1H n.m.r. 4.90 (s, 4H, $OC\mathit{H}_2CMe_3$), 1.50 (s, 9H, $NC\mathit{Me}_3$), 1.20 (s, 18H, $OCH_2C\mathit{Me}_3$); i.r. 850 ($\nu_{Mo=O}$), 670 (ν_{Mo-O}).

(**4**) $Mo(NCMe_3)(CH_2CMe_3)_3Cl$: ^1H n.m.r. 2.97 (s, 6H, $C\mathit{H}_2CMe_3$), 1.41 (s, 9H, $NC\mathit{Me}_3$), 1.28 (s, 27H, $CH_2C\mathit{Me}_3$); $^{13}C\{^1H\}$ n.m.r. 77.8 ($\mathit{C}H_2CMe_3$), 34.0 ($CH_2C\mathit{Me}_3$), 28.0 ($NC\mathit{Me}_3$); i.r. 260 (ν_{Mo-Cl}).

(**5**) $Mo(NCMe_3)(CHCMe_3)(CH_2CMe_3)_2$: ^1H n.m.r. 9.22 (s, 1H, $C\mathit{H}CMe_3$), 1.72 [d, 2H, $^2J(H_AH_B)$ 11, $C\mathit{H}_AH_BCMe_3$], 1.56 (s, 9H, $NC\mathit{Me}_3$), 1.39 (s, 9H, $CHC\mathit{Me}_3$), 1.32 [d, 2H, $^2J(H_AH_B)$ 11, $CH_A\mathit{H}_BCMe_3$], 1.26 (s, 18H, $CH_2C\mathit{Me}_3$); ^{13}C n.m.r. 249.3 [d, *J*(CH) 106, $\mathit{C}HCMe_3$], 73.9 (*t*, $\mathit{C}H_2CMe_3$), 70.7 (s, $N\mathit{C}Me_3$), 43.3 (s, $CH\mathit{C}Me_3$), 34.6 (q, $CH_2C\mathit{Me}_3$), 32.6 and 32.5 (q, $NC\mathit{Me}_3$ and $CHC\mathit{Me}_3$).

(**6**) $Mo(NCMe_3)(CH_2CMe_3)_2(OCH_2CMe_3)_2$: ^1H n.m.r. 4.49 (s, 2H, $OC\mathit{H}_2CMe_3$ ax.), 4.33 (s, 2H, $OC\mathit{H}_2CMe_3$ eq.), 2.88 [d, 2H, $^2J(H_AH_X)$ 7, $C\mathit{H}_AH_XCMe_3$], 2.18 [d, 2H, $^2J(H_AH_X)$ 7, $CH_A\mathit{H}_XCMe_3$], 1.55 (s, 9H, $NC\mathit{Me}_3$), 1.38 (s, 9H, $OCH_2C\mathit{Me}_3$ ax.), 1.36 (s, 18H, $CH_2C\mathit{Me}_3$), 1.06 (s, 9H, $OCH_2C\mathit{Me}_3$ eq.); $^{13}C\{^1H\}$ n.m.r. 94.5 ($O\mathit{C}H_2CMe_3$ ax.), 81.3 ($O\mathit{C}H_2CMe_3$ eq.), 74.2 ($\mathit{C}H_2CMe_3$), 35.8 ($N\mathit{C}Me_3$), 35.2 ($OCH_2\mathit{C}Me_3$ ax.), 34.3 ($CH_2C\mathit{Me}_3$, 32.6 ($OCH_2\mathit{C}Me_3$ eq.), 31.0 ($NC\mathit{Me}_3$), 28.0 ($OCH_2C\mathit{Me}_3$ ax.), 26.7 ($OCH_2C\mathit{Me}_3$ eq.).

(**7**) $Mo_2O(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)_4$: ^1H n.m.r. 11.71 (s, 1H, $C\mathit{H}CMe_3$), 2.65 [d, 1H, $^2J(H_AH_B)$ 9, $C\mathit{H}_AH_BCMe_3$], 2.57 (d, 3H, ^2J ($H_{A'}H_{B'}$), 7, $C\mathit{H}_{A'}H_{B'}CMe_3$], 2.46 [d, 3H, ^2J ($H_{A'}H_{B'}$) 7, $CH_{A'}\mathit{H}_{B'}CMe_3$), 2.17 [d, 1H, $^2J(H_AH_B)$ 9, $CH_A\mathit{H}_BCMe_3$], 1.67 (s, 9H, $NC\mathit{Me}_3$), 1.60 (s, 9H, $NC\mathit{Me}_3$), 1.53 (s, 9H, $CHC\mathit{Me}_3$), 1.46 (s, 9H, $CH_2C\mathit{Me}_3$), 1.29 (s, 27H, $CH_2C\mathit{Me}_3$); ^{13}C $\{^1H\}$ n.m.r. 269.2 ($\mathit{C}HCMe_3$), 73.7 ($\mathit{C'}H_2CMe_3$), 57.0 ($\mathit{C}H_2CMe_3$), 34.5 ($C'H_2C\mathit{Me}_3$), 33.1 ($C\mathit{Me}_3$), 29.0 ($C\mathit{Me}_3$); i.r. 770, 720 ($\nu_{Mo-O-Mo}$).

(**8**) $Mo(NCMe_3)(CH_2CMe_3)_3(OC_6F_5)$: ^1H n.m.r. 2.62 (s, 6H, $C\mathit{H}_2CMe_3$), 1.50 (s, 9H, $NC\mathit{Me}_3$), 1.17 (s, 27H, $CH_2C\mathit{Me}_3$).

(**9**) $Mo(NCMe_3)(CHCMe_3)(CH_2CMe_3)(OSiPh_3)$: ^1H n.m.r. 11.46 (s, 1H, $C\mathit{H}CMe_3$), 7.9, 7.3 (m, 15H, $OSi\mathit{Ph}_3$), 2.42 [d, 2H, $^2J(H_AH_B)$ 11, $C\mathit{H}_AH_BCMe_3$], 2.30 [d, 2H, $^2J(H_AH_B)$ 11, $CH_A\mathit{H}_BCMe_3$], 1.36 (s, 9H, $NC\mathit{Me}_3$), 1.32 (s, 9H, $CHC\mathit{Me}_3$), 1.26 (s, 9H, $CH_2C\mathit{Me}_3$).

without a Lewis acid cocatalyst. These results will be the subject of a separate publication.

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