Nucleophilic Displacement at Terminal Chloromethylidyne Ligands. New Synthetic Routes to Organothio-, Organoseleno-, and Organotelluro-methylidyne and Carbon Monosulphide, Monoselenide, and Monotelluride Complexes of Molybdenum: *X*-Ray Crystallographic Characterisation of η^1-*p*-Nitrophenylthiomethylidyne(dicarbonyl)-[hydrotris(3,5-dimethylpyrazol-1-yl)borato]molybdenum(IV)

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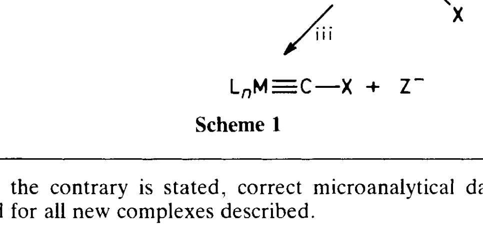
Nucleophilic displacement at the carbon atom of a terminal methylidyne ligand has been observed for the first time in the reaction of $[\mathrm{Mo}(\eta^1\text{-CCl})(\mathrm{CO})_2(\mathrm{L})]$ [L = hydrotris(3,5-dimethylpyrazol-1-yl)borato] with RE^- (E = S, Se) and E^{2-} (E = S, Se, Te); the products isolated include the organothiomethylidyne complex $[\mathrm{Mo}(\eta^1\text{-CSC}_6\mathrm{H}_4\mathrm{NO}_2\text{-}p)(\mathrm{CO})_2(\mathrm{L})]$ (which has been characterised by *X*-ray crystallographic methods), the first organoselenomethylidyne complex $[\mathrm{Mo}(\eta^1\text{-CSeC}_6\mathrm{H}_5)(\mathrm{CO})_2(\mathrm{L})]$, and the first Group 6B carbon monotelluride complex $[\mathrm{Mo(CTe)(CO)_2(L)}]^-$ which in turn has been converted into $[\mathrm{Mo}(\eta^1\text{-CTeMe})(\mathrm{CO})_2(\mathrm{L})]$, the first organotelluromethylidyne complex.

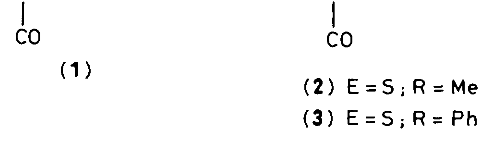
Nucleophilic addition to the metal–carbon triple bond of octahedral Group 6B methylidyne complexes generates carbene ligands (reaction i, Scheme 1).[1] In some cases the addition appears to be effectively reversible (reaction ii, Scheme 1)[2] and a theoretical study suggests that the forward process may be frontier- rather than charge-controlled.[3,4] Departure of the original methylidyne substituent with regeneration of the metal–carbon triple bond and formation of a new methylidyne ligand (reaction iii, Scheme 1) has been speculated upon[5] but has never been directly observed. We now report the first examples of this latter reaction and its exploitation as a synthetic route to some unusual new Group 6B complexes.

Terminal halogenomethylidyne complexes such as $[\mathrm{Mo}(\eta^1\text{-CCl})(\mathrm{CO})_2\{\mathrm{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3}\}]$ (**1**, $\mathrm{3,5\text{-}Me_2\text{-}C_3HN_2} \equiv$ 3,5-dimethylpyrazol-1-yl)[6] should be ideal candidates for methylidyne–methylidyne interconversions *via* nucleophilic displacement since (unlike previously studied examples[3,4]) the methylidyne carbon bears a good potential anionic leaving-group. This expectation is realised in practice. Complex (**1**) reacts readily with organothiolate and organoselenolate anions under phase-transfer conditions (50% aq. NaOH–$\mathrm{Bu^n_4NBr}$–$\mathrm{Et_2O}$) to yield the η^1-organothiomethylidyne complexes (**2**), (**3**), and (**4**) and the η^1-organoselenomethylidyne complex (**5**) (Scheme 2).† Yields are quantitative for (**3**) and (**5**) and *ca.* 70% for (**2**) and (**4**). Compound (**5**) is the first recorded example of an η^1-organoselenomethylidyne complex.



Scheme 1

Hydrotris(pyrazol-1-yl)borate tungsten complexes related to (**2**)—(**4**) have also been prepared [but in much lower overall yield from $\mathrm{M(CO)_6}$] by two entirely different routes: reaction of the anionic thiocarbonyl complex $[\mathrm{W(CO)_2(CS)}\{\mathrm{HB(C_3H_3N_2)_3}\}]^-$ (**6**, $\mathrm{C_3H_3N_2} \equiv$ pyrazol-1-yl) with reactive organic halides and reaction of $[\mathrm{WI(CS)(CO)_2}\{\mathrm{HB(C_3H_3N_2)_3}\}]$ (**7**) with organolithium compounds.[7] In order to establish beyond doubt that the organothiolate and



$$\underset{\mathrm{CO}}{\overset{\mathrm{CO}}{\mathrm{LMo}}}{\equiv}\mathrm{C{-}Cl} \xrightarrow{\mathrm{RE}^-} \underset{\mathrm{CO}}{\overset{\mathrm{CO}}{\mathrm{LMo}}}{\equiv}\mathrm{C{-}ER} + \mathrm{Cl}^-$$

(**1**)

(**2**) E = S ; R = Me
(**3**) E = S ; R = Ph
(**4**) E = S ; R = $\mathrm{C_6H_4NO_2}$-*p*
(**5**) E = Se; R = Ph

Scheme 2. L = $\mathrm{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3}$.

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† Unless the contrary is stated, correct microanalytical data were obtained for all new complexes described.

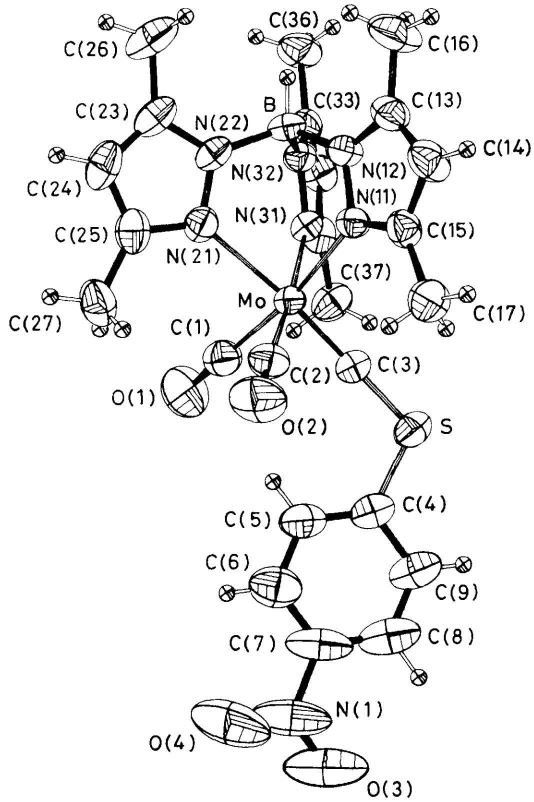
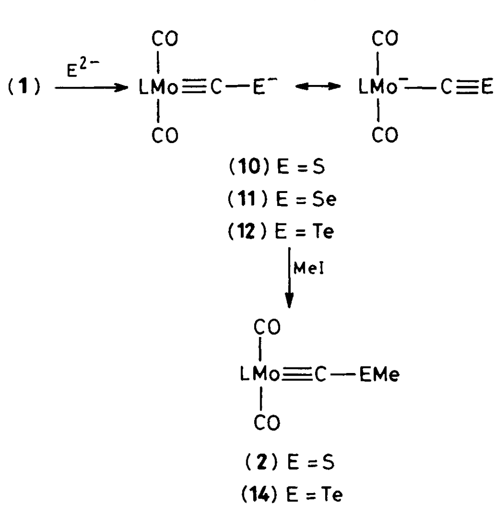


Figure 1. Molecular structure of (**4**). Important dimensions: Mo–C(3), 1.801(4); C(3)–S, 1.712(4); S–C(4), 1.768(5); Mo–C(1), 1.997(5); Mo–C(2), 1.987(5); C(1)–O(1), 1.148(6); C(2)–O(2), 1.153(6); Mo–N(11), 2.214(3); Mo–N(21), 2.290(4); Mo–N(31), 2.218(3) Å. Bond angles: Mo–C(3)–S, 179.5(2); C(3)–S–C(4), 106.9(2)°.

organoselenolate anions simply replace the halogen group in (**1**) we determined the crystal structure of (**4**) by *X*-ray methods.‡

Crystal data: $C_{24}H_{26}BMoN_7O_4S$, M_r = 615.33, orthorhombic, space group $P2_12_12_1$, a = 10.688(3), b = 12.731(2), c = 20.200(5) Å, U = 2748.6 Å^3, Z = 4, D_c = 1.49 g cm^{-3}, 3410 observed reflections, R = 0.033.

Data collection and structure solution were carried out as described previously.[6] A view of the molecule of (**4**) is shown in Figure 1 and important parameters are given in the caption. The analysis confirmed the presence of the *p*-nitrophenylthiomethylidyne ligand in (**4**). The bond lengths and angles within the $[\mathrm{Mo{\equiv}C{-}S{-}C_6H_4NO_2}\text{-}p]$ moiety of (**4**) are almost identical to those found in the tungsten phenylthiomethylidyne complex $[W(\eta^1\text{-}CSPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (**8**).[8] However, the Mo–C (methylidyne) distance in (**4**) [Mo–C(3), 1.801(4) Å] is significantly shorter than the corresponding distance in the η^1-chloromethylidyne complex (**1**) (1.894 Å).[6]



Scheme 3. L = $HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3$.

$[W(CO)_2(CS)\{HB(C_3H_3N_2)_3\}]^-$
(**6**)

$[WI(CS)(CO)_2\{HB(C_3H_3N_2)_3\}]$
(**7**)

$[W(\eta^1\text{-}CSPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$
(**8**)

$[Mo(\eta^1\text{-}CPh)(CO)_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$
(**9**)

$[Mo(CO)_3\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]^-$
(**13**)

Complex (**1**) is substantially decomposed by PhLi in Et_2O at room temperature but a low yield (*ca.* 18%) of the new phenylmethylidyne complex $[Mo(\eta^1\text{-}CPh)(CO)_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$ (**9**) was isolated from the reaction mixture.§ No reaction could be detected between (**1**) and phenoxide, cyanide, thiocyanate, or dithiocarbamate anions. Complex (**1**) is similarly unreactive towards MeMgI and PhC≡CLi. However, (**1**) reacts readily with Li_2S[10] or Li_2SE[11] in tetrahydrofuran or with Na_2Te[12] in aqueous methanol to give the new anionic chalcogenocarbonyl complexes (**10**), (**11**), and (**12**) which were isolated in *ca.* 60% yield as their moderately air-stable tetraethylammonium salts (Scheme 3). Together with $[Mo(CO)_3\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]^-$ (**13**),[13] complexes (**10**)—(**12**) constitute the first complete homologous series of Group 6B chalcogenocarbonyl complexes. In addition, complex (**12**) is only the second reported complex containing the otherwise unknown carbon monotelluride ligand.[14] Complex (**12**) is less stable than its sulphur and selenium congeners and the analytical data were slightly outside the permitted limits. It has been characterised spectroscopically¶ and by conversion into a stable derivative. The electron-rich thiocarbonyl complex (**10**) reacts with MeI in MeCN to yield the known (see above) methylthiomethylidyne complex (**2**). Tellurocarbonyl complex (**12**) behaves similarly to produce $[Mo(\eta^1\text{-}CTeMe)(CO)_2\{HB(3,5\text{-}Me_2\text{-}$

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ Completely satisfactory microanalytical data could not be obtained for (**9**) which was characterised by spectroscopic methods: ν(CO) (cyclohexane) 1991 s and 1909 vs cm^{-1}; ^{13}C n.m.r. ($CDCl_3$, Me_4Si) δ 288.07 (methylidyne carbon[9]) and 225.86 (CO) p.p.m.; mass spectrum, parent ion M^+ at m/z 540, prominent daughter ions at m/z 512 (M^+ – CO) and 484 (M^+ – 2CO).

¶ I.r. (KBr) (**10**) ν(CO) 1886 and 1794 vs cm^{-1}, ν(CS) 1139 vs cm^{-1}; (**11**) ν(CO) 1913 and 1824 vs cm^{-1}; ν(CSe) 1005 s cm^{-1}; (**12**) ν(CO) 1924 and 1840 vs cm^{-1}; ν(CTe) 951 s cm^{-1}.

$C_3HN_2)_3\}]$ (**14**), the first example of an organotelluromethylidyne complex, in *ca.* 20% yield. Correct microanalytical data were obtained for (**14**) and its spectroscopic properties are very similar to those of (**2**).**

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** Selected spectroscopic data for (**14**) [with corresponding values for (**2**) in parentheses]: i.r. ν(CO) 1992 and 1911 s (1987 and 1904 s) cm^{-1}; ^{13}C n.m.r. ($CDCl_3$, Me_4Si) δ 266.22 (267.62) (methylidyne carbon) and 226.62 (226.76) (CO) p.p.m.