Thioacyl complexes of molybdenum and tungsten

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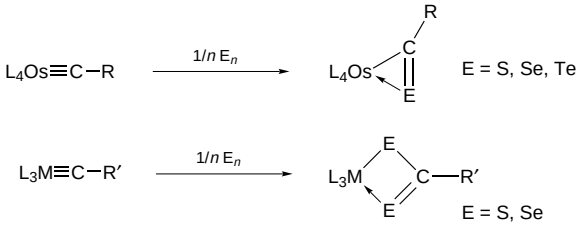
The reactions of a range of alkylidyne complexes of molybdenum and tungsten [M(≡CR)L_n] with 2-methylthiirane provide the first thioacyl complexes [M(η²-SCR)L_n] of these elements, which serve as precursors for complexes bearing dithiocarboxylate, thioselenocarboxylate, thiolatocarbene and α-thioalkyl ligands and thioacyl-bridged binuclear complexes.

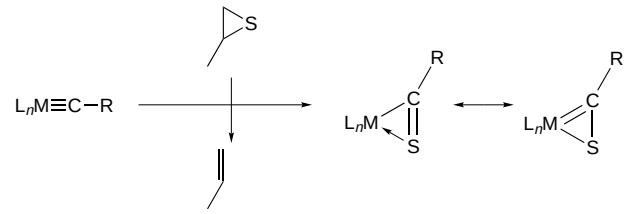
The addition of chalcogens to the metal–carbon multiple bonds of alkylidyne complexes takes one of two courses depending on the metal centre (Scheme 1):[1] Roper and coworkers originally showed that elemental chalcogens add once to group 8 toluidyne complexes to provide chalcotoluoyl ligands.[2] Alkylidyne complexes of molybdenum and tungsten, however, add sulfur or selenium twice to provide dichalcocarboxylate complexes,[3] which Kreißl subsequently obtained from the reaction of these precursors with cyclohexene sulfide.[4] Whilst no intermediate thio- or seleno-acyl complexes have been observed or isolated from these reactions, even for sterically congested systems,[5] Kreißl has shown that [W(η²-$S_2CC_6H_4$Me)-$(CO)_2$(η-C_5H_5)] reacts with PMe_3 to provide the adduct [W{η²-SC(PMe_3)C_6H_4Me}$(CO)_2$(η-C_5H_5)].[6] We have recently shown that thiobenzoyl complexes of ruthenium are obtained from the reaction of [Ru(≡CPh)Cl$(CO)(PPh_3)_2$] with CS_2 or isothiocyanates,[7] a result which further prompted our curiosity as to why these ligands appear to be disfavoured for group 6 metals. We report herein that thioacyl complexes of molybdenum and tungsten are indeed accessible and that they are useful precursors to a wide range of mono- and di-nuclear complexes.

Under careful control of reagent stoichiometry and reaction conditions, we find that the alkylidyne complexes shown in Scheme 2 react cleanly with 2-methylthiirane to provide the corresponding thioacyl complexes. The formulation follows from spectroscopic data† and their subsequent reactions with sulfur or excess propylene sulfide to provide the appropriate dithiocarboxylate complex. Most notable amongst these data are the ^{13}C NMR chemical shifts for the thioacyl carbon which typically appear in the range δ 260–280, this being to slightly higher field of those previously observed for group 8 metals (δ *ca*. 310).[2,7] Scheme 2 also indicates some instances where this reaction fails: notably alkylidyne complexes of chromium, sterically congested benzylidyne complexes and aminomethylidyne complexes. This last result is perhaps surprising given that thiocarboxamide complexes have been prepared by alternative strategies and are stable and robust species.[8] The M–C multiple bond of aminomethylidyne complexes is, however, well known to be comparatively unreactive.[1] Finally for completeness, it should be noted that ruthenium benzylidynes also react with 2-methylthiirane to provide thiobenzoyl complexes, although this approach offers no advantage over the use of elemental sulfur.

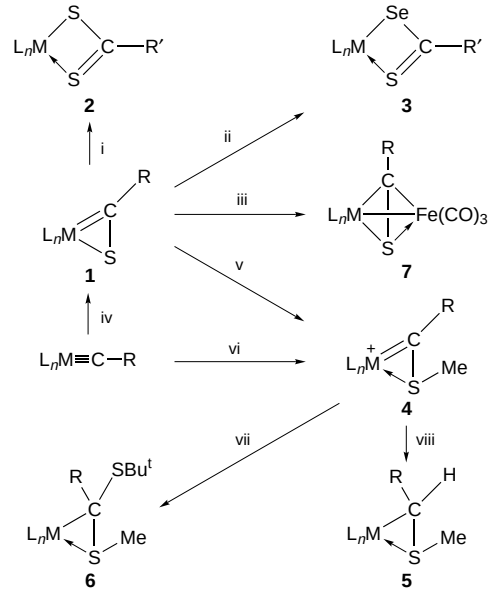
All of the thioacyl complexes obtained are somewhat thermally and photolytically sensitive both as solids and in solution. Nevertheless, these compounds serve as useful precursors for a number of transformations, some of which are summarised in Scheme 3. These include (*i*) the synthesis of mixed thioselenocarboxylate ligands (to our knowledge previously unknown), *e.g.* [Mo(η²-SSeCC_6H_4OMe-4)$(CO)_2$-{HB($pz)_3$}] **3** (pz = pyrazol-1-yl); (*ii*) alkylation at sulfur to provide bidentate thiolatocarbene complexes, *e.g.* [Mo(η²-MeSCC_6H_4OMe)$(CO)_2${HB($pz)_3$}]BF_4 **4**‡ which may be converted to bidentate α-thiolatoalkyl or α,α-bis(thiolato)alkyl



Scheme 1 Chalcogen addition to alkylidynes of group 6 and 8 metals. R = C_6H_4Me-4; R′ = C_6H_4Me-4, CH_2Bu^t; L_4Os = OsCl$(CO)(PPh_3)_2$;[2] L_3M = Mo{$P(OMe)_3$}$_2$(η-C_5H_5), W$(CO)_2$(η-C_5H_5).[3]



Scheme 2 R = Ph, C_6H_4Me-4, C_6H_4OMe-4, 2-C_4H_3S; L_nM = MoBr-(bipy)$(CO)_2$, Mo$(CO)_2${HB($pz)_3$}, WBr(bipy)$(CO)_2$, W$(CO)_2${HB($pz)_3$}, RuCl$(CO)(PPh_3)_2$ (not all combinations). Reaction fails for: R = $C_6H_2Me_3$-2,4,6, NPr^i_2; L_nM = CrBr(bipy)$(CO)_2$, MoBr$(CO)_2$(tmeda), MoBr(pico-line)$_2(CO)_2$].



Scheme 3 R = C_6H_4OMe-4; ML_n = Mo$(CO)_2${HB($pz)_3$}. *Reagents and conditions* (25 °C): i, S_8 or C_3H_6S, CH_2Cl_2; ii, Li[Et_3BH] : Se_8 = 8 : 1, thf; iii, [$Fe_2(CO)_9$] thf; iv, SC_3H_6, CH_2Cl_2; v, [Me_3O]BF_4 CH_2Cl_2; vi, [$MeSSMe_2$]BF_4, CH_2Cl_2; vii, $HSBu^t$, DBU, CH_2Cl_2; viii, Li[$BHEt_3$], thf.

complexes with Li[BHEt$_3$] or *tert*-butylthiolate, respectively,§ *e.g.* the complexes [Mo{η^2-MeSCHC$_6$H$_4$OMe-4}(CO)$_2$-{HB(pz)$_3$}] **5** and [Mo{η^2-MeSC(SBu^t)C$_6$H$_4$OMe-4}(CO)$_2$-{HB(pz)$_3$}] **6**; (*iii*) bridge-assisted metal–metal bond formation providing the bimetallic complex [MoFe(μ-SCC$_6$H$_4$OMe-4)(CO)$_5${HB(pz)$_3$}] **7**.[11]

The results above show that the previous unavailability of thioacyl complexes of group 6 metals has been due to a lack of suitable synthetic strategy rather than any intrinsic instability in the 'metallathiirene' unit. Furthermore, preliminary studies of the reactivity of these ligands, once constructed, clearly indicate considerable synthetic utility, a feature we are investigating further.

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Footnotes

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† *Selected data* for representative new complexes {25 °C, IR [ν(CO), CH_2Cl_2], NMR ($CDCl_3$), satisfactory microanalytical and FABMS data}. **1**: [Mo(≡CC$_6$H$_4$OMe-4)(CO)$_2${HB(pz)$_3$}] (1.00 g, 1.90 mmol) and 2-methylthiirane sulfide (0.14 cm^3, 1.9 mmol) were stirred in CH_2Cl_2 (20 cm^3) in the dark for 12 h. The solvent was removed and the residue chromatographed (alumina, 10 °C, Et_2O). The blue–purple eluate was concentrated and then diluted with hexane and cooled (−20 °C). Yield 1.01 g (97%). IR: 1976, 1891 cm^{-1}. NMR: ^{1}H, δ 3.94 (CH_3), 6.24, 7.39, 7.74 (pz); 7.08, 8.04 [$(AB)_2$, C_6H_4]. ^{13}C{^{1}H}: 278.0 (CS), 233.6 (CO), 162.5–124.8 (C_6H_4 and pz), 55.6 (CH_3). **2**: yield 80%. IR: 1951, 1867 cm^{-1}. NMR: ^{1}H, δ 3.88 (CH_3), 6.25 [t, 3 H, H^4(pz)], 6.91, 8.00 [$(AB)_2$, C_6H_4], 7.68, 8.16 [H^{3,5}(pz)]. ^{13}C{^{1}H}: 250.4(S_2C); 222.3 (CO), 163.6–105.9 (C_6H_4 and pz), 55.6 (CH_3). **3** Yield 87%. IR: 1943, 1861 cm^{-1}. NMR: ^{1}H, δ 3.87 (CH_3), 6.25 [t, H^4(pz)], 6.89, 7.99 [$(AB)_2$, C_6H_4], 7.69, 8.20 [H^{3,5}(pz)]. ^{13}C{^{1}H}: 249.7 [CSeS, *J*(SeC) 23 Hz], 223.5 (CO), 163.7–113.9 (C_6H_4 and pz) 55.5 (CH_3). **4** Yield 94%. IR: 2053, 1986 cm^{-1}. NMR: insufficiently soluble. FABMS: *m/z* 533 [M]$^+$, 505 [M − CO]$^+$, 477 [M − 2CO]$^+$, 343 [M − 2CO, Me, C*C*$_6$H$_4$OMe]$^+$. **5**: Yield 76%. IR: 1949, 1812 cm^{-1}. NMR: ^{1}H, δ 2.10 (SCH_3), 3.86 (OCH_3), 5.79 (MoCH), 6.18 [br s, 3 H, H^4(pz)], 6.98, 7.47 [$(AB)_2$, C_6H_4, *J*(AB) 8.1 Hz], 7.59–8.10 [m, 6 H, H^{3,5}(pz)]. ^{13}C{^{1}H}, δ 234.8, 229.7 (CO), 158.8–105.7 (C_6H_4 and pz), 72.4 (MoCS), 55.3 (OCH_3), 19.9 (SCH_3). **6** Yield 80%. IR: 1950, 1820 cm^{-1}. NMR: ^{1}H, δ 1.11 [s, 9 H, C(CH_3)$_3$]; 2.68 (s, 3 H, SCH_3); 3.70 (s, 3 H, OCH_3); 6.03–7.95 [13 H, H(pz), C_6H_4] ^{13}C{^{1}H}, δ 237.9, 233.6 (CO), 157.9–104.9 (pz and C_6H_4), 55.2 (OCH_3), 51.1 ($SCMe_3$), 31.2 (CCH_3], 23.7 (SCH_3). **7** (R = C_6H_4Me-4). Yield 44%. IR: 2051, 1982, 1843 cm^{-1} NMR: ^{1}H, δ 2.41 (CH_3); 6.10, 6.25, 6.33 [H^4(pz)]; 7.19–7.86 [C_6H_4 and H^{3,5}(pz)]. ^{13}C{^{1}H}, δ 231.8, 226.8, 209.9, 209.7, 208.0 (CO), 144.7–135.7 (C_6H_4 and pz), 21.3 (CH_3).

‡ The related salt [W(η^2-HCSMe)(CO)$_2${HB(pz)$_3$}]BF_4 has been described, and results from the protonation (HBF_4) of [W(≡CSMe)(CO)$_2${HB(pz)$_3$}] see ref. 9.

§ For related examples of the reactions of dihapto-thiocarbene complexes with nucleophiles see ref. 10.

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