Selenoaroyl complexes of molybdenum

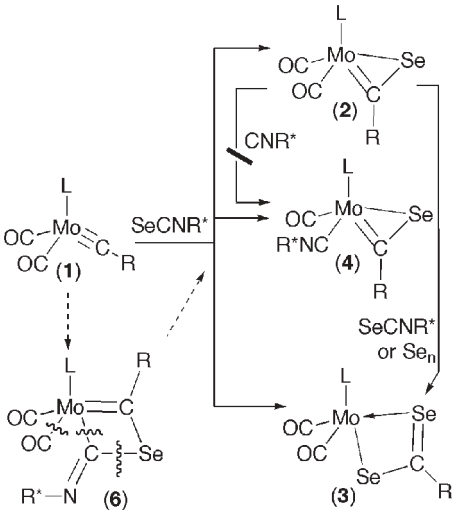
Lorraine M. Caldwell, Anthony F. Hill* and Anthony C. Willis

Received (in Cambridge, UK) 11th November 2004, Accepted 23rd February 2005
First published as an Advance Article on the web 5th April 2005
DOI: 10.1039/b417508e

The reaction of mesityl isoselenocyanate with molybdenum alkylidynes provides the first structurally characterised examples of mononuclear selenoaroyl complexes, which may also be obtained directly from elemental selenium in the presence of a catalytic amount of mesityl isocyanide.

The majority of acyl and aroyl complexes arise from migratory insertion processes involving carbonyl and σ-organyl ligands, a factor that explains the comparative lack of studies involving analogues based on the heavier chalcogens $L_nMC(=A)R$ (A = S, Se, Te). The requisite chalcocarbonyl/σ-organyl precursors are rare for A = S[1] and unknown for A = Se and Te. To date the only complete set of chalcoaroyl complexes $[Os(\eta^2\text{-}ACC_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ arose not from migratory insertion processes but rather *via* addition of elemental chalcogens to the alkylidyne complex $[Os(\equiv CC_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$ or NaAH to the chlorobenzylidene complex $[Os(=CClC_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$.[2] Whilst the isolation of this series established the viability of chalcoaroyl ligands, the methodology employed has not met with wider success *e.g.*, the addition of elemental sulfur or selenium to group 6 alkylidynes provides dichalcocarboxylato complexes.[3] The addition of selenium[4] or tellurium[5] to bridging alkylidyne complexes has however provided binuclear selenoaroyl and telluroaroyl complexes and we have shown that methylthiirane serves as a *single* sulfur atom transfer reagent allowing access to thioaroyl complexes of molybdenum and tungsten.[6] The synthetic challenge would therefore appear to lie in identifying a suitable protocol to allow the transfer of a single selenium atom to an alkylidyne complex. Herein we wish to report the synthesis of the first group 6 selenoaroyl complexes (Scheme 1). Our strategy follows from the previous demonstration that the heteroallenes CS_2 and MeNCS react with $[Ru(\equiv CPh)Cl(CO)(PPh_3)_2]$ to provide thioaroyl derivatives $[Ru(\eta^2\text{-}SCPh)Cl(CA)(PPh_3)_2]$ (A = O, S).[7] We therefore suspected that aryl isoselenocyanates might serve as single atom selenium transfer agents.

Treating the complex $[Mo(\equiv CR)(CO)_2\{HB(pz)_3\}]$ (**1**)[6b] with SeCNR* (hexane reflux, 4 h; hereafter R = C_4H_3S-2, R* = $C_6H_2Me_3$-2,4,6, pz = pyrazol-1-yl) leads to a mixture of compounds (**2**)–(**4**) that may be separated by cryostatic chromatography (−20 °C, silica gel, Scheme 1). The major product is the desired selenoaroyl complex $[Mo(\eta^2\text{-}SeCR)(CO)_2\{HB(pz)_3\}]$ (**2**) for which direct comparison of spectroscopic data† with those for the thioaroyl analogue $[Mo(\eta^2\text{-}SCR)(CO)_2\{HB(pz)_3\}]$ (**5**)[6b] is possible. Thus the infrared spectrum of **2** reveals an intensity profile for the ν_{CO} absorptions† similar to that of **5**, (1980, 1897 cm^{-1}) but moved marginally to higher frequency. The $^{13}C\{^1H\}$ NMR spectrum of **2** includes a resonance at δ = 264.5 attributable to the selenoaroyl carbon, to higher field of that for **1** (δ_C 276.8) but comparable to that for molybdenum thioaroyls (δ_C 260–280). The ^1H and $^{13}C\{^1H\}$ NMR spectra for **2** indicate only one pyrazolyl environment on the NMR timescales.



Scheme 1 Synthesis of selenoaroyl complexes. R = C_4H_3S-2, R* = $C_6H_2Me_3$-2,4,6; L = $HB(pz)_3$.

The molecular geometry of **2** in a crystal of **2.CH_2Cl_2** (Fig. 1) confirms the gross formulation and reveals a ground-state geometry in which the plane of the selenoaroyl ligand approximately (though not crystallographically) bisects the N–Mo–N and

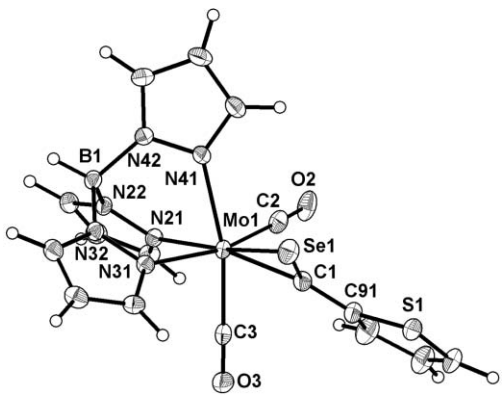


Fig. 1 Molecular geometry of **2** in a crystal of **2.CH_2Cl_2** (30% displacement ellipsoids, one of two disordered thienyl orientations depicted). Selected bond lengths (Å) and angles (°): Mo1–Se1 2.6897(4), Mo1–N21 2.199(2), Mo1–N31 2.229(2), Mo1–N41 2.227(2), Mo1–C1 1.995(3), Se1–C1 1.849(3), Se1–Mo1–C1 43.42(8), Mo1–Se1–C1 47.85(9), Se1–C1–C91 122.8(9) Mo1–C1–C91 148.4(9).

*a.hill@anu.edu.au

C–Mo–C angles. The geometry of the $HB(pz)_3Mo(CO)_2$ unit is generally unremarkable and interest focuses on the metallaselenirene ring, for which no structural precedent exists. The Mo1–C1 bond length of 1.995(3) Å clearly indicates multiple bonding character, falling within the range found for molybdenum alkylidenes. Multiple bonding can also be invoked for the C1–Se1 separation [1.849(3) Å] although precedent is somewhat more limited; C–Se bond lengths for π-C,Se seleno-aldehyde, -ketone and -ketene complexes fall within the range 1.805–1.960 Å,[8] whilst the selenoketenyl complex $[W(Se{=}CCC_6H_4Me)(CO)(PMe_2Ph)\{HB(pz)_3\}]$ has an exocyclic C=Se bond length of 1.835 Å.[9] Complexes of carbon monoselenide presumably represent the limit of C–Se multiple bonding, *e.g.*, $[MCl_2(CO)(CSe)(PPh_3)_2]$ (M = Ru 1.666; M = Os 1.608 Å).[10]

The second product of the reaction is the diselenocarboxylato complex $[Mo(\kappa^2\text{-}Se_2CR)(CO)_2\{HB(pz)_3\}]$ (**3**), spectroscopic data for which† may be compared with the complexes $[Mo(\eta^2\text{-}Se_2CCH_2CMe_3)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ and $[W(\eta^2\text{-}Se_2CC_6C_4Me)(CO)_2(\eta\text{-}C_5H_5)]$.[3] Complex **3** was also structurally characterised in a study that confirmed the molecular geometry, however the precision of the model was compromised by unresolved systematic errors in the diffraction data precluding detailed discussion. Notably, it could be shown that heating **2** with either elemental selenium or alternatively with further SeCNR* led to clean conversion to **3**. The final product is a second example of a selenoaroyl complex $[Mo(\eta^2\text{-}SeCR)(CO)(CNR^*)\{HB(pz)_3\}]$ (**4**),† akin to **2** but in which one carbonyl ligand is replaced by an isonitrile. The formulation followed from spectroscopic data and was confirmed by a crystallographic study (Fig. 2). If the selenoaroyl group is considered as a single ligand, the coordination at molybdenum approximates to octahedral geometry, with the plane of the selenoaroyl ligand lying in essentially the same position as for **2**. The geometrical parameters within the metallaselenirene are remarkably close to those for **2**. There is a very modest shortening of the Mo–C1 bond (7σ) and lengthening of the C1–Se1 bond (6σ) relative to those in **2**, however there is a

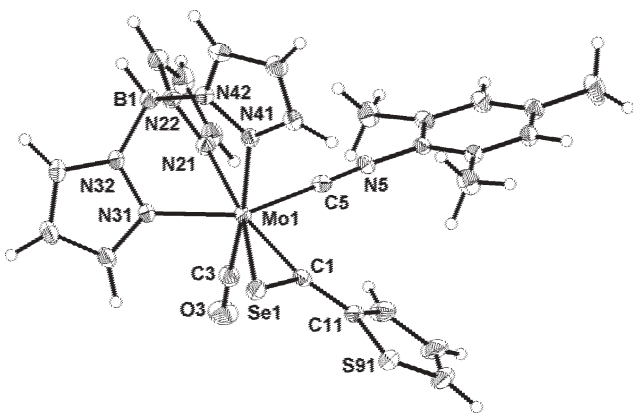


Fig. 2 Molecular geometry of **4** in a crystal of **4.CH_2Cl_2** (30% displacement ellipsoids, one of two disordered thienyl orientations depicted). Selected bond lengths (Å) and angles (°): Mo1–Se1 2.6605(5), Mo1–N21 2.218(3), Mo1–N31 2.221(3), Mo1–N41 2.238(3), Mo1–C1 1.975(3), Mo1–C5 2.066(4), Se1–C1 1.866(3), N5–C5 1.162(4), C1–C11 1.437(6), Se1–Mo1–C1 44.48(10), Mo1–Se1–C1 47.89(11), C5–N5–C51 175.0(3), Se1–C1–Mo1 87.63(14), Se1–C1–C11 122.9(3), Mo1–C1–C11 149.3(4).

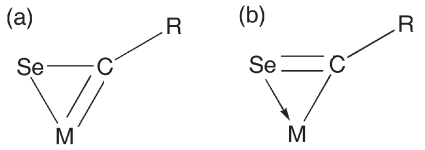


Fig. 3 (a) Metallaselenirene and (b) η^2-selenoaroyl canonical forms.

dramatic shortening of the Mol–Se1 bond (*ca.* 60σ). Geometric parameters for both **2** and **4** would appear to point towards contributions from both the metallaselenirene and η^2-selenoaroyl canonical forms depicted in Fig. 3, and similar arguments may apply to Jones' iridaphosphirene.[11]

The formation of **4** is mechanistically significant in that isolated **2** does not react with CNR* under the conditions of the synthesis of **2**, **3** and **4**, *i.e.*, **2** is not an intermediate in the formation of **4**. In the reaction of $[Ru(\equiv CPh)Cl(CO)(PPh_3)_2]$ with CS_2, we have suggested a metallacyclobuten-thione as a plausible intermediate to account for the generation of both thiocarbonyl and thioacyl ligands.[7] In the present case, an analogous metallacyclobuten-imine (Scheme 1, **6**) could serve as a common intermediate from which isonitrile extrusion (to provide **2**) competes with CO dissociation followed by metallacycle collapse with retention of the isonitrile within the coordination sphere, thereby providing **4**.

The reaction of **1** with elemental selenium very slowly provides a mixture of **2** and **3**. In contrast, both the base-catalysed (DBU) reaction of CNR* with selenium to provide SeCNR*, and the reaction of this with **1** are comparatively rapid. It therefore seemed plausible that CNR* might serve the purpose of activating elemental selenium in a pseudo-catalytic manner. This is indeed the case; the reaction of **1** with selenium in the presence of DBU and CNR* (5 mol%) quickly provides **2**, **3** and **4**. The eventual accumulation of **4** prevents the CNR* from being a true catalyst. Nevertheless, the use of mesityl isonitrile to activate otherwise inert elemental selenium in heterogeneous reactions could have considerable potential for systems where the isonitrile is less likely to appear in the final product.

Lorraine M. Caldwell, Anthony F. Hill* and Anthony C. Willis
Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra ACT, Australia.
E-mail: a.hill@anu.edu.au; Fax: (+61) 2 61253216;
Tel: (+61) 2 61258577

Notes and references

† Selected data, **2**: IR (CH_2Cl_2) 1988, 1909 cm^{-1}. NMR (CD_2Cl_2). δ_H 4.67 (br, 1H, HB), 6.26, 7.47, 7.81 [s(br) × 3, 9H, H(pz)], 7.30, [m, 1H, $H^4(C_4H_3S)$], 7.86, 7.89 [m × 2, 2H, $H^{3,5}(C_4H_3S)$]. δ_C 264.5 (SeC), 230.4 (CO), 145.0, 136.9, 106.4 (pz), 154.9 [$C^1(C_4H_3S)$], 135.9 [$C^{3,5}(C_4H_3S)$], 129.5 [$C^4(C_4H_3S)$]. Anal (Calcd.) C, 35.84 (35.65); H, 2.20 (2.43); N, 15.24 (15.59)%. *Crystal data for* **2.CH_2Cl_2**: $C_{16}H_{13}BMoN_6O_2SSe.CH_2Cl_2$, M = 624.03, monoclinic, $P2_1/n$, a = 13.6357(2), b = 8.4301(1), c = 21.0335(3) Å, β = 107.25(5)°, V = 2309.05(5) Å^3, Z = 4, D_c = 1.795 g cm^{-3}, μ(Mo–Kα) = 24.93 cm^{-1}, T = 200 K, black needle, 5300 independent measured reflections ($2\theta_{max}$ = 55°), F refinement, R = 0.026, wR = 0.028 for 3672 independent absorption corrected reflections [$I > 3\sigma(I)$], 296 parameters. CCDC 253399. **3**: IR (CH_2Cl_2) 1939, 1860 cm^{-1}. NMR (CD_2Cl_2). δ_H 6.29 [t, 3H, H^4(pz)], 7.13 [m, 1H, $H^4(C_4H_3S)$], 7.75, 8.19 [d × 2, 6H, $H^{3,5}$(pz)], 7.79, 7.85 [m × 2, 2H, $H^{3,5}(C_4H_3S)$]. δ_C 251.6 (Se_2C), 209.0 (CO), 145.9, 136.3, 106.4 (pz), 156.5 [$C^1(C_4H_3S)$], 132.4, 123.9, [$C^{3,5}(C_4H_3S)$], 130.1 [$C^4(C_4H_3S)$]. Anal (Calcd.) C, 30.79 (31.09); H, 2.12 (2.12); N, 13.32 (13.50)%. **4**: IR (CH_2Cl_2) 2099, 1885 cm^{-1}. NMR (CD_2Cl_2). δ_H 1.93 [s, 6H, 2 × CH_3], 2.22 [s, 3H, CH_3], 6.22, 6.27,

6.32 [3 × s(br), 3H, H^4(pz)], 6.80 [s, 2H, (C_6H_2)], 7.13 [dd, 1H, $H^4(C_4H_3S)$], 7.34, 7.83, 7.95 (3 × s(br), 3H), 7.67 (m(br), 3H), 7.79 (s(br), 2H), [6H, $H^{3,5}$(pz), 2H, $H^{3,5}(C_4H_3S)$]. δ_C 267.6 (SeC), 239.5 (CO), 186.3 (CN), 155.6 [$C^1(C_4H_3S)$], 146.6, 145.0, 143.1, 136.3, 135.7, 106.1, 106.0 (pz), 138.6 [$C^4(C_6H_2)$], 134.0 [$C^{2,6}(C_6H_2)$], 133.9, 133.7 [$C^{3,5}(C_4H_3S)$], 128.8 [$C^{3,5}(C_6H_2)$], 128.6 [$C^4(C_4H_3S)$], 125.8 [$C^1(C_6H_2)$], 21.1 (CH_3), 18.4 (2 × CH_3). Anal (Calcd. For **4**.0.5 CH_2Cl_2) C, 43.63 (43.83); H, 3.51 (3.61); N, 13.89 (14.03)%. *Crystal data for* **4.CH_2Cl_2**: $C_{25}H_{24}BMoN_7OSSe.CH_2Cl_2$, M = 741.22, triclinic, $P\bar{1}$ (No. 2), a = 8.8257(1), b = 12.2737(2), c = 14.3685(3) Å, α = 82.1624(7), β = 84.5846(7), γ = 84.6839(11)°, V = 1530.00(4) Å^3, Z = 2, D_c = 1.609 g cm^{-3}, μ(Mo–Kα) = 18.94 cm^{-1}, T = 200 K, black rod, 7007 independent measured reflections ($2\theta_{max}$ = 54°), F refinement, R = 0.031, wR = 0.034 for 4192 independent absorption corrected reflections [$I > 3\sigma(I)$], 378 parameters. CCDC 253400. See http://www.rsc.org/suppdata/cc/b4/b417508e/ for crystallographic data in CIF or other electronic format.

1 (*a*) G. R. Clark, T. J. Collins, K. Marsden and W. R. Roper, *J. Organomet. Chem.*, 1978, **157**, C23; (*b*) G. R. Clark, T. J. Collins, K. Marsden and W. R. Roper, *J. Organomet. Chem.*, 1983, **259**, 215; (*c*) C. E. F. Rickard, W. R. Roper, D. M. Salter and L. J. Wright, *Organometallics*, 1992, **11**, 3931.

2 G. R. Clark, K. Marsden, W. R. Roper and L. J. Wright, *J. Am. Chem. Soc.*, 1980, **102**, 6570.

3 D. S. Gill, M. Green, K. Marsden, I. Moore, A. G. Orpen, F. G. A. Stone, I. D. Williams and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1984, 1343.

4 (*a*) P. G. Byrne, M. E. Garcia, J. C. Jeffery, P. Sherwood and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1987, 1215; (*b*) A. F. Hill, B. A. Nasir and F. G. A. Stone, *Polyhedron*, 1989, **8**, 179; (*c*) S. Anderson, D. J. Cook and A. F. Hill, *Organometallics*, 2001, **20**, 2468.

5 A. J. Hulkes, A. F. Hill, B. A. Nasir, A. J. P. White and D. J. Williams, *Organometallics*, 2004, **23**, 679.

6 (*a*) D. J. Cook and A. F. Hill, *Chem. Commun.*, 1997, 955; (*b*) D. J. Cook and A. F. Hill, *Organometallics*, 2003, **22**, 3502.

7 R. B. Bedford, A. F. Hill, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 95.

8 H. Fischer, R. Stumpf and G. Roth, *Adv. Organomet. Chem.*, 1998, **43**, 125.

9 I. D. Baxter, A. F. Hill, J. M. Malget, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1997, 2049.

10 G. R. Clark, K. Marsden, C. E. F. Rickard, W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 1988, **338**, 393.

11 M. Brym, C. Jones and M. Waugh, *Dalton Trans.*, 2003, 2889.