# Selenoketenyl and selenoalkyne complexes *via* the reactions of ketenyl complexes with Woollins' reagent

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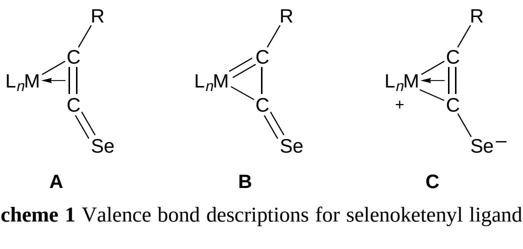
**The complexes [ML($\eta^2$-OCCR)(CO)(Tp)] [M = W, Mo; L = PMe$_2$Ph, PPh$_3$, P(OMe)$_3$; R = C$_6$H$_4$Me-4; Tp = hydrotris(pyrazol-1-yl)borate] react with 'Woollins' reagent' [4(PPh)$_5$/5Se$_8$] to provide the first examples of selenoketenyl complexes [ML($\eta^2$-SeCCR)(CO)(Tp)], alkylation of which provides selenoalkyne complexes; the crystal structures of [W($\eta^2$-SeCCR)(CO)(PMe$_2$Ph)(Tp)] and [W($\eta^2$-MeSeCCR)(CO)(PPh$_3$)(Tp)]I are also reported.**

The study of ligands featuring carbon–selenium multiple bonds is hampered by the shortage of suitable ligand precursors, with the majority of studies involving CSe$_2$ and CSSe as source molecules. Thioketenyl ligands have recently begun to attract attention[1–3] however no reports have appeared concerning the preparation of selenoketenyl complexes (Scheme 1). This report is concerned with (*i*) the development of synthetic routes to the first examples of selenoketenyl complexes; (*ii*) the structural characterisation of one such complex, [W($\eta^2$-SeCCR)(CO)(PMe$_2$Ph)(Tp)] **2b** [hereafter R = C$_6$H$_4$Me-4, Tp = hydrotris(pyrazol-1-yl)borate]; (*iii*) alkylation of selenoketenyl ligands to provide rare examples of mononuclear selenoalkyne complexes; (*iv*) structural characterisation of one example in the salt [W($\eta^2$-MeSeC≡CR)(CO)(PPh$_3$)(Tp)]I **4a**.

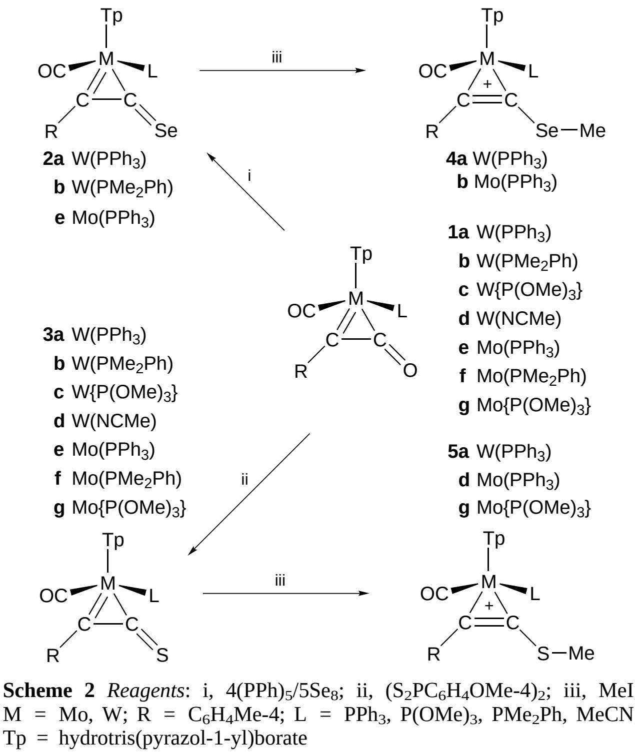
We have recently described two routes for the conversion of ketenyl complexes of tungsten to their sulfur congeners.[3] The first involves the initial conversion of a ketenyl ligand to a chloroalkyne and then treatment with sodium hydrosulfide. In our hands, this approach has so far failed in the case of sodium hydroselenide or lithium selenide, with intractible mixtures being obtained. The second approach involves the reaction of a ketenyl ligand with Lawesson's oxygen/sulfur transfer reagent and appeared attractive except that the selenium analogue has yet to be reported.[4,5] Woollins has prepared a range of organophosphorus selenides from the reaction of cyclopolyphosphines with selenium.[5] For brevity, we shall refer to as Woollins' reagent, the compound which is presumed to be 2,4-bis(phenyl)-1,3-diselena-2,4-diphosphetane-2,4-diselenide, obtained from (PPh)$_5$ and elemental selenium (P : Se ratio 1 : 2). Studies to date suggest a similar reactivity profile, at least in part, to that of Lawesson's reagent.[5] The ketenyl complex [W($\eta^2$-OCCR)(CO)(PPh$_3$)(Tp)] **1a**[6] reacts cleanly with Woollins' reagent to provide [W($\eta^2$-SeCCR)(CO)(PPh$_3$)(Tp)] **2a** in high yield as the only isolable species (Scheme 2). The formulation follows from spectroscopic data† which are comparable to those for the related thioketenyl complexes[3] and the complexes [ML($\eta^2$-SeCCR)(CO)(Tp)] [ML = WPMe$_2$Ph, MoPPh$_3$, MoP(OMe)$_3$] which may be obtained in a similar manner from Woollins' reagent and [ML($\eta^2$-OCCR)(CO)(Tp)] (Scheme 2). The series of complexes **1a**, **3a** and **2a** shows a steady increase in the IR frequency of the carbonyl-associated absorption [**1a**, 1883; **2a**, 1909; **3a**, 1919 cm$^{-1}$], suggesting that the $\pi$-acidity of chalcoketenyl ligands increases in the order O, S, Se.



**Scheme 1** Valence bond descriptions for selenoketenyl ligands

One example, **2b**, of this new class of compound was characterised by X-ray crystallography (Fig. 1).‡ The overall structure is remarkably similar to that of [W($\eta^2$-OCCR)(CO)(PPh$_3$)(Tp)].[6] The bonding of the selenoketenyl ligand is dihapto through C(1) and C(36), the C=C=Se grouping lying in the equatorial coordination plane which also contains the carbonyl ligand. The W–N distances are unremarkable and in the range 2.188(9)–2.251(8) Å, the shortest of these being that *trans* to the phosphine, whilst the N–W–N angles are similar [79.8(3)–82.2(3)°]. The binding of the selenoketenyl ligand is best described by three resonance forms **A**–**C** (Scheme 1). There is clearly multiple bonding between W and C(1) [2.003(11) Å], W and C(36) [2.078(10) Å] and C(1) and C(36) [1.328(13) Å]. Furthermore, whilst there is little appropriate crystallographic precedent,[7] the C(36)–Se(37) separation [1.834(11) Å] clearly indicates a degree of partial double bond character.

Consistent with their alternative formulation as chalcogenoxyalkyne complexes (**C**, Scheme 1), the new complexes **2** and the related thioketenyl complexes [ML($\eta^2$-SCCR)(CO)(Tp)][3] are readily alkylated at the chalcogen to provide complexes of selenolato and thiolato alkynes (Scheme 2). Thus the new complexes **4** and **5** were readily obtained from the reaction of



**Scheme 2** *Reagents*: i, 4(PPh)$_5$/5Se$_8$; ii, (S$_2$PC$_6$H$_4$OMe-4)$_2$; iii, MeI; M = Mo, W; R = C$_6$H$_4$Me-4; L = PPh$_3$, P(OMe)$_3$, PMe$_2$Ph, MeCN; Tp = hydrotris(pyrazol-1-yl)borate

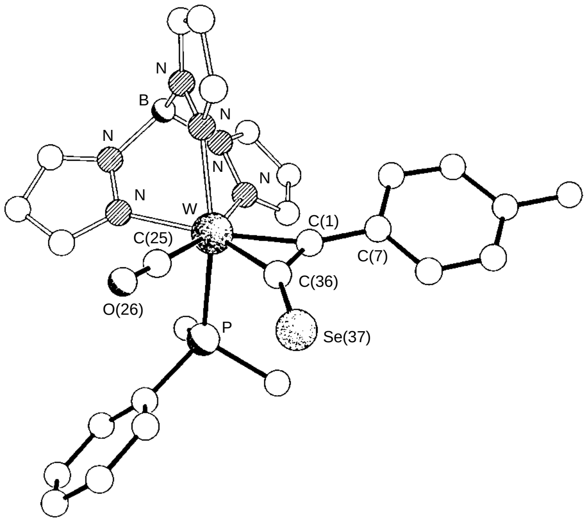


**Fig. 1** Molecular geometry of **2b** (hydrogen atoms omitted)

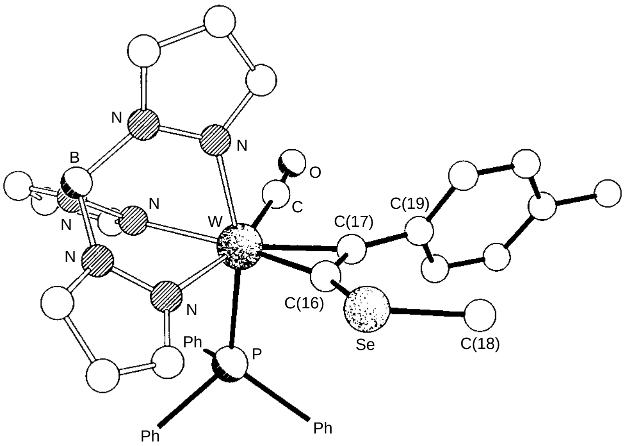


**Fig. 2** Molecular geometry of **4a** (phenyl groups, hydrogen atoms and iodide counter-anion omitted)

selected examples of **2** or **3** with iodomethane. The salts **4**† provide rare examples of mononuclear selenoalkyne complexes.[8] Notably, alkylation of **2** is considerably more rapid than for **3** and the ketenyl complexes **1** fail to react with alkyl halides.

The tungsten salt $[W(\eta^2\text{-MeSeCCR})(CO)(PPh_3)(Tp)]I$ **4a**, has been structurally characterised.‡ The molecular geometry of the cation (Fig. 2) is topologically similar to that of **2b** with the notable exception that the alkyne orientation now places the tolyl group *syn* to the carbonyl ligand *cf.* the *anti* arrangement of these groups in **2b**. Within the Tp scorpionate, the W–N bond *trans* to the carbonyl [2.172(13) Å] is somewhat shorter that the other two W–N distances [2.216(13), 2.218(12) Å]. The dimensions associated with the selenoalkyne coordination are somewhat similar to those of **2b**. Once again there is multiple bonding between W and C(17) [2.05(2) Å], and between W and C(16) [2.02(2) Å], however there is a notable loss of double bond character between C(16) and C(17) [1.39(2) Å] *cf.* **2b**. The C(16)–Se separation [1.81(2) Å] suggests that the partial double bond character observed in **2b** is retained upon alkylation, this being shorter than for the Se–C(18) separation [1.97(2) Å] which is typical for a Se–C($sp^3$) bond. The modest perturbation of these dimensions on alkylation lends further support to the significant contribution of resonance form **C** to the bonding description of **2b**.

The successful deployment of Woollins' reagent for the oxygen/selenium transfer conversion of coordinated organometallic ligands bodes well for the elaboration of further unsaturated organoselenium ligands, an avenue we are currently investigating. Ketenyl complexes are typically formed from the often reversible coupling of alkylidyne and carbonyl ligands. It remains to be seen if thioketenyl and selenoketenyl ligands may decouple to serve as precursors for chalcocarbonyl co-ligated alkylidyne complexes, $L_nM(\equiv CR)(CA)$ (A = S, Se).

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## Footnotes and References

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† *Data for selected complexes* (satisfactory microanalytical data obtained for all complexes): **2b**: yield 90%. IR ($CH_2Cl_2$) 1906 $cm^{-1}$ [$\nu$(CO)]. NMR ($CDCl_3$, 25 °C). $^1H$: $\delta$ 1.35, 1.60 [d × 2, 6 H, ($PMe_2$), $^2J$(PH) 8.6 Hz], 2.30 (s, 3 H, CMe), 5.96, 6.17, 6.25 [app. t × 3, 3 H, $H^4$(pz), $^3J$(HH) 2 Hz], 6.76–7.91 [m, 15 H, $C_6H_4$, Ph and $H^{3,5}$(pz)]. $^{13}C\{^1H\}$: $\delta$ 237.6 [W*C*Se], 231.6 [WCO], 222.4 [W=CCSe], 146.6, 145.7, 142.4 [$C^3$(pz)], 136.4, 135.6, 135.5 [$C^5$(pz)], 130.0–128.0 (Ph and $C_6H_4$), 106.7, 106.2, 106.0 [$C^4$(pz)], 21.5 (C*Me*), 15.6, 14.1 [d × 2, ($PMe_2$), $^1J$(PC) 24 Hz]. $^{31}P\{^1H\}$: $\delta$ −5.1 [$^1J$(WP) 328.9 Hz]. FABMS: *m/z* (%) 757(14) $[M]^+$, 728(45) $[M - CO]^+$, 592(82) $[M - CO - PMe_2Ph]^+$. **4a**: Yield 90%. The complex exists in solution as two isomers related by alkyne rotation: major isomer: IR ($CH_2Cl_2$): 1949 $cm^{-1}$ [$\nu$(CO)]. NMR ($CDCl_3$, 25 °C). $^1H$: $\delta$ 1.96 (s, 3 H, C*Me*), 2.40 (s, 3 H, SeMe), 5.93–7.35 [m, 22 H, $C_6H_4$, $C_6H_5$ and $H^5$(pz)], 7.79, 8.04, 8.09 [$H^3$(pz), $^3J$(HH) 2 Hz]. $^{13}C\{^1H\}$: $\delta$ 232.2 [WCO, $^1J$(WC) 140 Hz], 220.6 (W=*C*R), 147.4–128.3 [$C_6H_4$, Ph and $C^{3,5}$(pz)], 107.9, 107.6, 107.4 [$C^4$(pz)], 21.6(C*Me*), 10.7 (Se*Me*). $^{31}P\{^1H\}$: $\delta$ 32.8 [$^1J$(WP) 309 Hz]. FABMS: *m/z* (%) 897(80) $[M]^+$, 852(6) $[M - CO]^+$.

‡ *Crystal data*: **2b**: $C_{27}H_{28}BN_6OPSeW\cdot CHCl_3$, $M$ = 876.51, orthorhombic, space group *Pbca*, $a$ = 14.691(3), $b$ = 15.940(4), $c$ = 28.162(7) Å, $U$ = 6595(3) Å$^3$, $Z$ = 8, $D_c$ = 1.766 g $cm^{-3}$, $\mu$(Mo-K$\alpha$) = 4.93 $mm^{-1}$, $F$(000) = 3408. A dark green needle of dimensions 0.53 × 0.22 × 0.10 mm was used. **4a**: $C_{38}H_{35}BIN_6OPSeW\cdot 2CH_2Cl_2$, $M$ = 1193.06, triclinic, space group $P\bar{1}$, $a$ = 9.642(3), $b$ = 13.010(3), $c$ = 19.500(5) Å, $\alpha$ = 70.54(1), $\beta$ = 86.76(2), $\gamma$ = 86.67(2)°, $U$ = 2299(1) Å$^3$, $Z$ = 2, $D_c$ = 1.724 g $cm^{-3}$, $\mu$(Mo-K$\alpha$) = 4.28 $mm^{-1}$, $F$(000) = 1156. A blue block of dimensions 0.33 × 0.27 × 0.17 mm was used. For **2b** and **4a**, 5809 and 7980 independent reflections were measured, respectively, on a Siemens P4/PC diffractometer (graphite-monochromated Mo-K$\alpha$ radiation, 293(2) K) using $\omega$ scans. The structures were solved by direct methods and all the non-hydrogen atoms were refined anisotropically using full-matrix least squares based on $F^2$ and absorption-corrected data to give for **2b**, $R_1$ = 0.058, and $wR_2$ = 0.093 [3179 observed reflections, $|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 50°$, 368 parameters] and for **4a** $R_1$ = 0.075, and $wR_2$ = 0.144 [4865 observed reflections, $|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 50°$, 514 parameters]. CCDC 182/594.

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