Isoselenocarbonyls *via* acetylenic C–Se activation†

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The first examples of isoselenocarbonyl linked bimetallics arise from the chemoselective insertion of platinum(0) into the alkynyl–selenium bond of a molybdenum alkynylselenolatoalkyidyne complex.

The end-on coordination of a diatomic unit between two metals has held intrigue, dating from Prussian Blue to contemporary interest in the activation of diatomics (CO, O₂, N₂, NO, CN) in industrial and biological contexts alike. Herein, we wish to report the first examples of bimetallics spanned by the diatomic carbon monoselenide, *i.e.*, isoselenocarbonyls L_nMCSeM'L_n.

The alkynylselenolatoalkyidyne complex [Mo(≡CSeC≡CCMe₃)(CO)₂{HB(pzMe₂)₃}] (**1**, pz = pyrazol-1-yl, Scheme 1)[†]

Scheme 1 Possible pathways for the reactions of **1** with transition metal reagents “ML_n”. (R = CMe₃, L = HB(pzMe₂)₃).

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presents, in principle, a rich array of potential functionalities for interaction with transition metal reagents. As with the related propargylidynes [M(≡CC≡CCMe₃)(CO)₂(L)] (M = Mo, W; L = η-C₅H₅, HB(pz)₃, HB(pzMe₂)₃),² one might envisage coordination of either the (a) Mo≡C or (b) C≡C triple bonds, or simply (c) selenoether coordination. Alternatively, although oxidative addition of alkynyl selenoethers to transition metals has yet to be observed, this would appear feasible, raising the question in the case of **1** as to which Se–C bond might prove the more reactive. Insertion of a metal into the alkylidyne–selenium bond (d) would provide constituent μ-carbido and alkynylselenolato ligands. Templeton *et al.* have reported the synthesis of [(η-C₅H₅)(CO)₂Fe–C≡Mo(CO)₂{HB(pzMe₂)₃}] from [Mo(≡CCl)(CO)₂{HB(pzMe₂)₃}] and K[Fe(CO)₂(η-C₅H₅)],³ whilst we have previously described the first examples of alkynylselenolato complexes in which the ligand coordinates in either a *dihapto* (η²-C,C')⁴ or monodentate (σ-Se) mode.⁵ There are of course a vast number of metal alkynyl complexes, however the second constituent arising from the alternative cleavage (e), an isoselenocarbonyl linkage, is without precedent. Indeed, no bimetallic selenocarbonyl complexes have been reported. Angelici *et al.* have, however, described examples of (A) symmetrical bridging, (B) semi-bridging, (C) μ:σ-π-bridging (‘4-electron’) thio-carbonyls and (D) isothiocarbonyls (Scheme 2) from pre-formed mononuclear thio-carbonyl complexes,⁶ whilst Cummins *et al.* have structurally characterised an isothiocarbonyl complex obtained *via* the activation of CS₂ by a sterically enshrouded molybdenum triamide (E).⁷ Herein, we report the reaction of **1** with [Pt(η-C₂H₄)(PPh₃)₂] which ultimately provides the first examples of isoselenocarbonyl complexes.

Scheme 2 Bridging modes for thiocarbonyl ligands (Cp = η-C₅H₅, Tp = HB(pz)₃, Ind = η¹-C₉H₇). (A) Symmetrical;^{6a} (B) semi-bridging;^{6b} (C) μ:σ,π bridging;^{6c} (D)^{6d} and (E) isothiocarbonyls.⁷

The reaction of **1** with [Pt(η-C₂H₄)(PPh₃)₂] proceeds over seven days to ultimately provide a single compound. If the reaction is quenched after 2 h by which time all of **1** is consumed

(IR) an intermediate **2** predominates and at times between one and seven days (or if isolated **2** is redissolved), mixtures of **2**, a second intermediate **3** and the final product **4** are obtained which may be separated by cryostatic chromatography (silica gel, $-33\text{ }^{\circ}\text{C}$). Each complex was characterised on the basis of spectroscopic data and in the cases of **3** and **4** by crystallographic analyses. The solution instability of **2** prevented us from obtaining crystallographic grade crystals however its formulation rests firmly upon comparison of spectroscopic data with those for related complexes from the literature. Specifically, alkyne complexes of the form $[\text{Pt}(\text{RC}\equiv\text{CR})(\text{PPh}_3)_2]$ have been known for 50 years⁸ whilst, more recently, μ -alkylidyne complexes $[\text{WPt}(\mu\text{-CR})(\text{CO})_2(\text{PR}')_2\{\text{HB}(\text{pz})_3\}]$ were developed by Stone *et al.*⁹ including those bearing thiolato substituents ($\text{R} = \text{SMe}$).^{9c}

Fortunately, spectroscopic data[‡] for these two classes of compound are sufficiently distinctive that we are able to confidently infer that it is the $\text{C}\equiv\text{C}$ rather than $\text{Mo}\equiv\text{C}$ bond that coordinates to the zerovalent platinum centre, *i.e.*, **2** is a somewhat unconventional alkyne complex rather than the μ -alkylidyne isomer (Scheme 3).

Scheme 3 Coordination and oxidative addition of **1** to $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ [$\text{L} = \text{HB}(\text{pzMe}_2)_3$, $\text{R} = \text{CMe}_3$].

Both **4** and the intermediate **3** en route to it were identified as isomers that arise from the oxidative addition of the alkynyl-selenoether linkage to the electron-rich platinum centre. Alkynyl selenoether oxidative additions are unprecedented, however they might reasonably be expected to occur, given that aryl and vinyl selenides have been shown to add to zerovalent platinum substrates, albeit very recently.¹⁰ Furthermore, the insertion of platinum into the $\text{C}-\text{Se}$ bond of selenophenes has been demonstrated by Sweigart *et al.*¹¹

Phosphorus-31 NMR data (δ_{P} , $^2J_{\text{PP}}$ and $^1J_{\text{PtP}}$) clearly identify the stereochemistry for the two isomers as being kinetically formed *cis*-**3** and thermodynamically favoured *trans*-**4**. In *cis*-**3** the two

phosphorus nuclei are inequivalent ($\delta_{\text{P}} = 19.59, 14.23$), mutually coupled ($^2J_{\text{PP}} = 16.5$) and show different couplings to the ^{195}Pt nucleus ($^1J_{\text{PtP}} = 2411, 3071\text{ Hz}$, respectively). In contrast, the symmetrical *trans*-**4** isomer shows a single phosphorus environment ($\delta_{\text{P}} 21.1$) and coupling to ^{195}Pt ($^1J_{\text{PtP}} = 2695\text{ Hz}$). Spectroscopic data associated with the $-\text{C}\equiv\text{Mo}(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}$ groups in **3** and **4** are remarkably insensitive to the changes in geometry at platinum, *e.g.*, the alkylidyne resonance moves from 297.5 to 302.5 ppm whilst the IR and $^{13}\text{C}\{^1\text{H}\}$ data for the CO ligands are essentially invariant (*ca.* 5 cm^{-1} (THF) and 0.8 ppm respectively). The isomers *cis*-**3** and *trans*-**4** were both the subjects of crystallographic studies, the results of which are summarised in Fig. 1 and 2, respectively. The geometrical features of the

Fig. 1 Molecular structure of *cis*-**3** (60% displacement ellipsoids, hydrogen atoms omitted, phenyl and pyrazolyl groups simplified). Selected bond lengths ($\text{\AA}$) and angles ($^{\circ}$): $\text{Pt1}-\text{C19}$ 1.997(3), $\text{Pt1}-\text{P2}$ 2.2617(8), $\text{Pt1}-\text{P1}$ 2.3334(8), $\text{Pt1}-\text{Se1}$ 2.4889(3), $\text{Se1}-\text{C3}$ 1.836(3), $\text{Mo1}-\text{C3}$ 1.832(3), $\text{C19}-\text{Pt1}-\text{P2}$ 88.25(9), $\text{C19}-\text{Pt1}-\text{P1}$ 171.10(9), $\text{P2}-\text{Pt1}-\text{P1}$ 97.71(3), $\text{C19}-\text{Pt1}-\text{Se1}$ 88.79(9), $\text{P1}-\text{Pt1}-\text{Se1}$ 84.94(2), $\text{C3}-\text{Se1}-\text{Pt1}$ 105.36(10), $\text{Mo1}-\text{C3}-\text{Se1}$ 166.5(2).

Fig. 2 Molecular structure of *trans*-**4** (60% displacement ellipsoids, hydrogen atoms omitted, phenyl and pyrazolyl groups simplified). Selected bond lengths ($\text{\AA}$) and angles ($^{\circ}$): $\text{Pt1}-\text{Se1}$ 2.4914(4), $\text{Pt1}-\text{P1}$ 2.308(1), $\text{Pt1}-\text{P2}$ 2.3175(9), $\text{Pt1}-\text{C51}$ 1.992(4), $\text{Mo1}-\text{C1}$ 1.834(4), $\text{Se1}-\text{C1}$ 1.828(4), $\text{Se1}-\text{Pt1}-\text{P1}$ 96.03(2), $\text{Se1}-\text{Pt1}-\text{P2}$ 93.30(3), $\text{P1}-\text{Pt1}-\text{C51}$ 84.93(11), $\text{P2}-\text{Pt1}-\text{C51}$ 85.91(11), $\text{Pt1}-\text{Se1}-\text{C1}$ 104.86(12), $\text{Se1}-\text{C1}-\text{Mo1}$ 163.1(2).

$\text{C}\equiv\text{Mo}(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}$ groups in both **3** and **4** are unremarkable and conform to copious precedent for alkylidyne based on more conventional carbon substituents.¹² For **3**, a typically short $\text{Mo}\equiv\text{C}$ separation (1.832(3) Å) is observed and this is identical to that in **4** (1.834(4) Å), within precision limits, but longer than in $[\text{Mo}(\equiv\text{CSeC}\equiv\text{CSiMe}_3)(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}]$ (1.805(12) Å).¹ The $\text{Mo}-\text{C}-\text{Se}$ angle is less than 180° in both cases (**3**: $166.5(2)^\circ$; **4**: $163.1(2)^\circ$) presumably reflecting a response to non-bonding repulsive interactions between the bulky platinum group and the pyrazolyl chelates. For **3**, the alkynyl ligand on platinum nestles in the cleft provided by two pyrazolyl groups on molybdenum.

The bonding of the isoselenocarbonyl linkage may be considered from two perspectives (Scheme 4), as either a Lewis acid ($^{\text{II}}\text{Pt}^+$) adduct of an anionic selenocarbonyl complex (F) or as a Se-metallated selenolatocarbyne (G). Although the selenocarbonyl molybdate $[\text{Mo}(\text{CSe})(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}]^-$ has been claimed,¹³ only IR data were provided. Nevertheless, $^{13}\text{C}\{^1\text{H}\}$ NMR data for more fully characterised terminal selenocarbonyls generally span the range $\delta_{\text{Cse}} = 279\text{--}308$,¹⁴ whilst chalcogenolatoalkylidyne $[\text{M}(\equiv\text{CER})(\text{CO})_2(\text{L})]$ [$\text{M} = \text{Mo}, \text{W}$; $\text{E} = \text{S}, \text{Se}$; $\text{L} = \text{HB}(\text{pz})_3, \text{HB}(\text{pzMe}_2)_3$] have $\delta_{\text{M}\equiv\text{C}} = 261\text{--}271$.^{12a} The considerable shift to low frequency from 245 ppm in **1** to around 300 ppm in **3** and **4** would certainly appear to argue for a considerable degree of selenocarbonyl character. Structural data for terminal selenocarbonyls are somewhat limited^{15,16} to four examples based on ruthenium, osmium and chromium such that comparison of metal–carbon bond lengths has little value. However, in all cases the $\text{M}-\text{C}-\text{Se}$ angle falls within the narrow range $175\text{--}180^\circ$ whilst there is some variation in $\text{C}-\text{Se}$ bond length from 1.61–1.79 Å.¹⁶ Thus the $\text{C}-\text{Se}$ bond lengths in **3** and **4** are longer than the formal triple bonds in terminal selenocarbonyl complexes and double bonds in selenoketones but shorter than those found in mesomerically elongated selenoureas and selenoamides,^{12b} and that of $[\text{Mo}(\equiv\text{CSeC}\equiv\text{CSiMe}_3)(\text{CO})_2\{\text{HB}(\text{pzMe}_2)_3\}]$ (1.887(12) Å),¹ indicating at least a degree of $\text{C}-\text{Se}$ multiple bonding (F, Scheme 4).

Scheme 4 Isoselenocarbonyl canonical forms.

To conclude, the first isoselenocarbonyls have been isolated and structurally characterised. We have previously demonstrated the lability of alkynyl–selenoether linkages in combination with transition metals leading to selenolatovinylidene formation.¹⁷ The present illustration of this fragility suggests that facile $\text{C}-\text{Se}$ oxidative addition of alkynyl selenoethers may provide a further synthetic approach to poly-yn-diyl bridged bimetallics¹⁸ through the use of poly-ynyl selenoethers, a possibility we are currently exploring.

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Notes and references

‡ *Selected data.* **2**: A solution of **1**¹ (0.150 g, 0.241 mmol) and $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ (0.180 g, 0.241 mmol) in THF (20 mL) was stirred at room temperature for 2 h after which time IR spectroscopy indicated complete consumption of **1**. The solvent was removed quickly *in vacuo* to provide **2** as an orange solid in spectroscopically quantitative yield. IR (KBr): $\nu = 2524\text{w}(\text{BH}), 1978\text{s}, 1959\text{sh}, 1894\text{s}, 1874\text{sh}(\text{CO}), 1722\text{w}(\text{C}\equiv\text{C}), 1542\text{w}(\text{CN})\text{ cm}^{-1}$. IR (THF): $\nu = 1980, 1897(\text{CO})\text{ cm}^{-1}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C , 121.4 MHz): $\delta = 26.2, 25.4(\text{d} \times 2, {}^2J_{\text{PP}} = 20\text{ Hz})$. MS (ESI^+): m/z (%) 1365(<5) [$\text{M} + \text{Na}^+$], 1062(5) [$\text{M} - 2\text{CO} - \text{PPh}_3 + \text{K}^+$], 841(100) [$\text{M} - 2\text{PPh}_3 + \text{Na}^+$]. *Synthesis of cis-3*: Compound **2** as prepared above was redissolved in THF (20 mL) and the solution stirred for a further 3 days at which time the solvent was removed and the residue chromatographed (silica gel, -33°C). Elution with CH_2Cl_2 –hexane (1 : 1) afforded initially **3** (0.085 g, 26%) and secondly **4** (0.178 g, 58%). *Synthesis of trans-4*: A solution of **1** (0.150 g, 0.241 mmol) and $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ (0.180 g, 0.241 mmol) in THF (20 mL) was stirred at room temperature for 7 days. The solvent was removed to give a crude yield of 0.320 g (98%). Chromatography of the golden residue (silica gel, -33°C , CH_2Cl_2 –hexane 1 : 2 eluant) afforded a major gold band which was crystallised from CH_2Cl_2 –EtOH(aq) to afford **4** as a pure yellow solvated solid. Yield 0.298 g (91%). *Data for cis-3*: IR (KBr): $\nu = 2524\text{w}(\text{BH}), 1957\text{s}, 1867\text{s}, (\text{CO}), 1542\text{w}(\text{CN})\text{ cm}^{-1}$. IR (THF): $\nu = 1957, 1875(\text{CO})\text{ cm}^{-1}$. ^1H NMR (CD_2Cl_2 , 25°C , 300.1 MHz): $\delta = 7.50, 7.41, 7.29, 7.16(\text{m} \times 4, 30\text{ H}, \text{C}_6\text{H}_5), 5.79, 5.72(\text{s} \times 2, 2\text{ H}, \text{C}_3\text{N}_2\text{H}), 2.74, 2.35, 2.33, 2.29(\text{s} \times 4, 6:3:6:3\text{ H}, \text{pzCH}_3), 0.30(\text{s}, 9\text{ H}, \text{'Bu})$. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C , 75.4 MHz): $\delta = 297.2(\text{Mo}\equiv\text{C}), 228.9(\text{MoCO}), 152.2, 151.5, 145.2, 144.3[2:1:1:2, \text{C}^{3,5}(\text{pz})], 135.3, 134.9, 128.2, 127.9[\text{d} \times 4, \text{C}^{2,6,3,5}(\text{C}_6\text{H}_5)], 132.4, 130.8[\text{d} \times 2, \text{C}^1(\text{C}_6\text{H}_5)], 130.6, 130.3[\text{C}^4(\text{C}_6\text{H}_5)], 122.5(\text{d}, \text{PtC}\equiv\text{C}), 83.0(\text{d}, \text{PtC}\equiv\text{C}), 106.1, 105.9[2:1, \text{C}^4(\text{pz})], 30.7(\text{'Bu}-\text{CH}_3), 29.0, [\text{C}(\text{CH}_3)_3], 16.6, 14.7, 12.7, 12.6(2:1:2:1, \text{pzCH}_3)$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C , 121.4 MHz): $\delta = 19.59(\text{d}, {}^2J_{\text{PP}} = 16.5, {}^1J_{\text{PPt}} = 2411), 14.23(\text{d}, {}^2J_{\text{PP}} = 16.5, {}^1J_{\text{PPt}} = 3071\text{ Hz})$. MS (ESI^+): m/z (%) 1365(46) [$\text{M} + \text{Na}^+$], 1341(<1) [M^+], 1062(27) [$\text{M} - 2\text{CO} - \text{PPh}_3 + \text{K}^+$], 841(100) [$\text{M} - 2\text{PPh}_3 + \text{Na}^+$]. Elemental analysis (%) for $\text{C}_{60}\text{H}_{61}\text{BMoN}_4\text{O}_2\text{P}_2\text{PtSe}$. Calcd. C, 53.74; H, 4.59; N, 6.27%. Found: C, 53.86; H, 4.68; N, 6.47%. Crystals for diffractometry grown slowly from a mixture of CH_2Cl_2 and aqueous ethanol. *Crystal data for 3*: $(\text{CH}_2\text{Cl}_2)_{1.55}(\text{EtOH})_2(\text{H}_2\text{O})_{1.5}$; $\text{C}_{60}\text{H}_{61}\text{BMoN}_4\text{O}_2\text{P}_2\text{PtSe}(\text{CH}_2\text{Cl}_2)_{1.55}(\text{C}_2\text{H}_5\text{OH})_2(\text{H}_2\text{O})_{1.5}$, $M_w = 1591.68$, $T = 110(2)\text{ K}$, triclinic, $P\bar{1}$ (No. 2), $a = 11.6097(1)$, $b = 14.8220(2)$, $c = 21.5820(3)\text{ Å}$, $\alpha = 80.746(1)^\circ$, $\beta = 82.351(1)^\circ$, $\gamma = 81.470(1)^\circ$, $V = 3602.15(8)\text{ Å}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.467\text{ Mg m}^{-3}$, $\mu(\text{Mo}-\text{K}\alpha) = 2.828\text{ mm}^{-1}$, $F(000) = 1600$, $2\theta_{\text{max}} = 60^\circ$, 86507 collected reflections, 20996 unique reflections, 793 parameters, $S = 1.048$, $R_1 = 0.0365$ (17466 reflections with $I > 2\sigma(I)$), $wR_2(F^2, \text{all data}) = 0.0943$, CCDC 659480. *Data for trans-4*: IR (KBr): $\nu = 1947\text{s}, 1864\text{s}(\text{CO})\text{ cm}^{-1}$. IR (THF): $\nu = 1952\text{s}, 1868\text{s}(\text{CO})\text{ cm}^{-1}$. ^1H NMR (CD_2Cl_2 , 25°C , 300.1 MHz): $\delta = 7.77, 7.35, 7.22(\text{m} \times 3, 30\text{ H}, \text{C}_6\text{H}_5), 5.66, 5.65(\text{s} \times 2, 1:2\text{ H}, \text{C}_3\text{N}_2\text{H}), 2.39, 2.28, 2.26(\text{s} \times 3, 6:9:3\text{ H}, \text{pzCH}_3), 0.36(\text{s}, 9\text{ H}, \text{'Bu})$. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C , 75.4 MHz): $\delta = 302.5(\text{Mo}\equiv\text{C}), 229.7(\text{MoCO}), 152.2, 151.7, 145.0, 144.2[2:1:1:2, \text{C}^{3,5}(\text{pz})], 135.6, 127.9[\text{vt} \times 2, \text{C}^{2,6/3,5}(\text{C}_6\text{H}_5)], 131.6[\text{vt}, {}^1J_{\text{PC}} = 29, \text{C}^1(\text{C}_6\text{H}_5)], 130.4[\text{C}^4(\text{C}_6\text{H}_5)], 120.2(\text{t, br, PtC}\equiv\text{C}), 74.5(\text{t}, {}^2J_{\text{PC}} = 16, \text{PtC}\equiv\text{C}), 106.1, 105.9[2:1, \text{C}^4(\text{pz})], 30.8(\text{'Bu}-\text{CH}_3), 29.2, [\text{'Bu}-\text{C}(\text{CH}_3)_3], 16.9, 14.6, 12.8, 12.6(2:1:2:1, \text{pzCH}_3)$. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25°C , 121.4 MHz): $\delta = 21.1$ (${}^1J_{\text{PPt}} = 2695\text{ Hz}$). MS (ESI^+): m/z (%) 1363(<1) [$\text{M} + \text{Na}^+$], 1342(<1) [M^+], 800(100) [$\text{Pt}(\text{PPh}_3)_2(\text{C}\equiv\text{C}'\text{Bu})^+$], 718(50) [$\text{Pt}(\text{PPh}_3)_2$]. Elemental analysis (%) for $\text{C}_{60}\text{H}_{61}\text{BMoN}_4\text{O}_2\text{P}_2\text{PtSe}$: Calcd. C, 53.74; H, 4.59; N, 6.27%. Found: C, 53.71; H, 4.77; N, 5.99%. *Crystal data for 4*: $\text{C}_{60}\text{H}_{61}\text{BMoN}_4\text{O}_2\text{P}_2\text{PtSe}$, $M_w = 1340.93$, $T = 200(2)\text{ K}$, monoclinic, $\text{C}2/c$, $a = 25.2562(5)$, $b = 12.3965(2)$, $c = 37.3364(7)\text{ Å}$, $\beta = 98.6699(8)^\circ$, $V = 11556.0(4)\text{ Å}^3$, $Z = 8$, $\rho_{\text{calcd}} = 1.541\text{ Mg m}^{-3}$, $\mu(\text{Mo}-\text{K}\alpha) = 3.368\text{ mm}^{-1}$, $F(000) = 5344$, $2\theta_{\text{max}} = 55.2^\circ$, 88179 collected reflections, 13327 unique reflections, 695 parameters, $S = 1.098$, $R_1 = 0.0229$ (7481 reflections with $I > 3\sigma(I)$), $wR_2(F, \text{all data}) = 0.0368$, CCDC 659481.

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