Bridging selenocarbonyl ligands: An open and shut case.

Benjamin J. Frogley,^a Anthony F. Hill^{a,*} and Lachlan J. Watson^a

Novel bis(isoselenocarbonyl) complexes $[\text{W}_2\text{Pt}(\mu\text{-CSe})_2(\text{CO})_4(\text{L}_2)(\text{Tp}^*)_2]$ (L_2 = cyclo-octadiene, norbornadiene) upon heating eliminate the diene to provide $[\text{W}_2\text{Pt}(\mu\text{-CSe})_2(\text{CO})_4(\text{Tp}^*)_2]$, in which CSe ligands close to bridge W-Pt bonds in a $\sigma\text{-}\pi$ mode that may be re-opened by addition of new ligands (CNR: $\text{R} = \text{tBu}$, $\text{C}_6\text{H}_2\text{Me}_3$) to re-establish the isoselenocarbonyl coordination in $[\text{W}_2\text{Pt}(\mu\text{-CSe})_2(\text{CO})_4(\text{CNR})_2(\text{Tp}^*)_2]$.

In advance of their synthesis, King has computationally explored how complexes with two or even more thiocarbonyl (CS) ligands might bridge bi- or polymetallic complexes.¹ A recurring result of the computational studies is the preference for the heavier chalcocarbonyls, rather than CO, to assume bridging roles. That such detailed computational studies presage experimental observation of poly(chalcocarbonyl) complexes^{2,3} in part reflects the technical challenges in actually designing synthetic routes to such species, given that the ligands of interest (CS, CSe and CTe) are not independently stable or accessible species on which to draw.

We have begun to explore the possibility of preparing bridging selenocarbonyl complexes, inspired in part by serendipitous observations that CS and CSe ligands may be activated towards carbon-chalcogen bond cleavage to afford μ -carbido complexes.⁴ Whilst the first bridging selenocarbonyl complex arose unexpectedly from the cleavage of an alkynylselenolatocarbene ligand,^{5a} a range of μ -CSe complexes has since been accessed,⁵ in most cases *via* strategic reactions of the selenocarbonylates $[\text{M}(\text{CSe})(\text{CO})_2(\text{Tp}^*)]^-$ ($\text{M} = \text{Mo}, \text{W}$)^{5d,6} with electrophilic metal halide complexes. This approach parallels that developed by Angelici for the synthesis of μ -CS complexes $[\text{WAu}(\mu\text{-CS})(\text{CO})_2(\text{PPh}_3)(\text{Tp}^*)]$ and $[\text{MoW}(\mu\text{-CS})(\text{CO})_4(\text{Tp}^*)(\eta^5\text{-C}_7\text{H}_9)]$ (C_7H_9 = indenyl),⁷ and has allowed the identification of a range of possible CSe bridging modes (Chart 1). Herein we report an extension of this strategy directed towards the preparation of trimetallic platinum(II) derivatives which were found to exhibit unprecedented and *switchable* binding modes.

Chart 1. Four possible binuclear selenocarbonyl bonding modes with associated valence electron contribution to each metal centre in red.

Treatment of the selenocarbonylate $[\text{W}(\equiv\text{CSe})(\text{CO})_2(\text{Tp}^*)]\text{NEt}_4$ **1** with half an equivalent of $[\text{PtCl}_2(\text{L}_2)]$ in CH_2Cl_2 rapidly furnishes $[\text{W}_2\text{Pt}(\mu\text{-CSe})_2(\eta^4\text{-L}_2)(\text{CO})_4(\text{Tp}^*)_2]$ (L_2 = COD, cycloocta-1,5-diene **2**; L_2 = NBD, norbornadiene **3**) *via* salt elimination involving displacement of both chloride ligands on Pt by the nucleophilic Se of the selenocarbonyl complex (Scheme 1). These brick-red and brown complexes, respectively, feature a $\text{W}\equiv\text{C}-\text{Se}-\text{Pt}-\text{Se}-\text{C}\equiv\text{W}$ trimetallic 'chain' involving two isoselenocarbonyl linkages (Chart 1d) to a single central Pt(II) centre.

The two ends of the 'chain' in both **2** and **3** are spectroscopically equivalent, giving rise to one set of ν_{CO} absorbances in the infrared spectra and one set of Tp^* signals in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra in their typical positions.⁸ The identity of the diene ligand on platinum has only a very minor influence on the carbyne carbon $^{13}\text{C}\{^1\text{H}\}$ NMR resonances ($\delta_{\text{C}} = 266.6$ and 268.8 , respectively) but a rather profound influence on the chemical shift of the selenium atoms in the ^{77}Se NMR spectra ($\delta_{\text{Se}} = 597$ and 660 ppm, respectively) (Table 1). This most likely reflects the smaller bite angle of the NBD *cf.* COD chelating diene impacting on the hybridisation at platinum. The crystallographically determined molecular structure of **3** (Figure 1) confirms the *cis*-bis(isoselenocarbonyl) geometry.

^a Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory, ACT 2601, Australia.

* Corresponding author. E-mail: a.hill@anu.edu.au

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Scheme 1. Platinum coordination to a tungsten selenocarbonyl complex. (i) $[\text{PtCl}_2(\text{L}_2)]$, L_2 = COD, NBD, (ii) CNR, $\text{R} = \text{tBu}$, $\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$, (iii) CH_2Cl_2 , (iv) $[\text{AuCl}(\text{SMe}_2)]$.

Table 1. Selected spectroscopic and structural data for **2–10**.

	δ_{C}^a ppm	δ_{Pt}^a ppm	δ_{Se}^a ppm	$r_{\text{W}=\text{C}}$ Å	$r_{\text{Se}-\text{Pt}}$ Å	$\angle_{\text{WCSe}}$ deg.	ν_{CO}^b cm^{-1}
1	311.3	-	542	1.872(11)	-	170.9(7)	1895, 1801
2	266.6	-3839	597	c	c	c	1964, 1876
3	268.8	-3724	660	1.813(8)	2.4239(9)	168.5(5)	1972, 1873
4	d	d	502	1.892(9)	2.4554(9)	177.8(5)	1972, 1895
5	289.0	d	d	1.828(6)	2.4584(7)	166.4(3)	1951, 1864 ^e
6	d	d	d	c	c	c	1954, 1864/
7	257.1	-3701	545	1.934(7)	2.4459(7)	148.8(4)	1988 1904
				1.914(7)	2.4544(7)	152.2(4)	
8	255.2	-3594	587	c	c	c	2010, 1932
9	247.3	-	673	c	-	c	1983, 1893
10	245.4	-	702	1.933(17)	-	145.8(10)	2008, 1926

^a Measured in CDCl_3 (ppm). ^b Measured in CH_2Cl_2 . ^c Data not acquired. ^d Insufficiently soluble for adequate data acquisition. ^e $\nu_{\text{CN}} = 2205$, 2193 cm^{-1} . ^f $\nu_{\text{CN}} = 2184 \text{ cm}^{-1}$.

Figure 1. Molecular structure of **3** in a crystal of $3 \cdot (\text{CH}_2\text{Cl}_2)_2$ (50% displacement ellipsoids, pyrazolyl and NBD groups simplified, hydrogen atoms and solvent omitted for clarity, only one-half of the C_2 -symmetric molecule is unique). Selected distances [Å] and angles [°]: W1–C1 1.813(8), C1–Se1 1.867(8), Se1–Pt 2.4239(9), W1–C1–Se1 168.5(5), C1–Se1–Pt 102.5(2), Se1–Pt1–Se1 85.01(4).

The $\text{W}=\text{C}$ (1.813(8) Å) and $\text{C}-\text{Se}$ (1.867(8) Å) distances are consistent with triple and single bonds, respectively, and are in good agreement with the small number of other reported isoselenocarbonyl complexes.⁵ The selenium–platinum distance in **3** (2.4239(9) Å) is somewhat (*ca* 75 e.s.d.) shorter than the corresponding distances in *cis* and *trans* isomers of $[(\text{Tp}^*)(\text{CO})_2\text{Mo}=\text{CSePt}(\text{PPh}_3)_2\text{Br}]$ (2.4889(3) and 2.4914(4) Å, respectively)^{5a} and the (alkynylselenolato)platinum complexes *trans*- $[\text{Pt}(\text{SeC}\equiv\text{C}-n\text{-C}_5\text{H}_{11})_2\text{L}_2]$ ($\text{L}_2 = (\text{PPh}_3)_2$ 2.4902(9); $\text{L}_2 = 1,1'$ -bis(diphenylphosphino)ferrocene, 2.4639(5), 2.4608(6) Å),⁹ presumably reflecting the reduced steric congestion at Pt afforded by the diene *cf.* the bulkier phosphine ligands. The diene ligands in **2** and **3** are moderately labile and may be displaced by heating either **2** (5 hrs) or **4** (1.5 hrs) in toluene under reflux to provide the same complex $[\text{W}_2\text{Pt}(\mu_2\text{-CSe})_2(\text{CO})_4(\text{Tp}^*)_2]$ (**4**) as a purple solid (Scheme 1). Alternative synthetic approaches to **4** were also explored but with limited success. Reaction of **1** with Zeise's salt, $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ (CH_2Cl_2 , RT, 2.5 h), did indeed furnish a small amount of **4** inseparably admixed with a second unidentified product, whilst $[\text{PtCl}_2(\text{NCMe})_2]$ under the same conditions provided a complex mixture of unidentified products devoid of **4**.

The spectroscopic data for **4** were consistent with loss of the diolefin ligand on Pt but failed to unequivocally establish the

CSe coordination mode(s), which however followed from X-ray crystallographic analysis (Figure 2).

Figure 2. Molecular structure of **4** in a crystal of $4 \cdot 2\text{CH}_2\text{Cl}_2$ showing 50% thermal probability ellipsoids. Only one-half of the molecule is crystallographically unique. Pyrazolyl groups are simplified, hydrogen atoms and solvent are not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.892(9), C1–Se1 1.820(9), W1–Se1 3.0576(4), W1–Pt1 3.0576(4), C1–Pt1 2.058(8), Se1–Pt1 2.4554(9), W1–C1–Se1 177.8(5), W1–C1–Pt1 101.4(4), C1–Se1–Pt1 55.2(2). Inset = view along Se1–Se2 vector.

The centrosymmetric molecular structure of **4** features a co-planar $\text{W}_2\text{C}_2\text{Se}_2\text{Pt}$ core in which the CSe ligands bridge the rather long Pt–W bonds (3.0576(4) Å, typically 2.70–2.85 Å for W–Pt single bonds) in a σ - π manner (Chart 1c) but with only negligible deformation of the essentially linear W–C–Se spines (177.8(5)°). Compared to the isoselenocarbonyl complex **3**, the W–C distance in **4** (1.892(9) Å) is somewhat elongated (*ca* 0.1 Å) by the interaction with platinum. The data for **4** are comparable to the (only) three other examples of σ - π bridging heavier chalcocarbonyls in $[\text{W}(\mu\text{-CS})(\text{CO})_4(\eta^5\text{-C}_9\text{H}_7)(\text{Tp})]$ (C_9H_7 = indenyl, Tp = hydrotris(pyrazolyl)borate) (W–C 1.895(5) Å; W–C–S 170.8(3)°),^{7a} and the complexes $[\text{WCu}(\mu\text{-CE})(\text{CO})_2(\text{Tp}^*)(\text{PR}_3)]$ (E = Se, R = Ph, W–C 1.895(14) Å, W–C–Se 177.0(7)°),^{5d} E = Te, R = cyclohexyl, W–C 1.876(5) Å, W–C–Te 175.4(2)°).¹⁰

The complex **4** does not react with excess cycloocta-1,5-diene or norbornadiene to return the diene complexes **2** or **3**, but does react with more strongly coordinating ligands, *e.g.*, isonitriles (CNR) to reveal the platinum(II) centre by opening the isoselenocarbonyl linkages to provide *trans*- $[\text{W}_2\text{Pt}(\mu_2\text{-CSe})_2(\text{CNR})_2(\text{CO})_4(\text{Tp}^*)_2]$ (R = *t*Bu **5**, R = $\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ **6**), as orange solids (Scheme 1). The same species can also be prepared directly from **2** or **3** by addition of the same reagents. In the absence of a *cis*-enforcing chelating diene ligand, the especially bulky 'W(CO)₂(Tp*)' groups assume a mutually *trans* disposition.

The infrared spectra of **5** and **6** each contain a single major isonitrile-based absorbance (CH_2Cl_2 : **5** 2205; **6** 2184 cm^{-1}) consistent with the *trans* geometry at platinum, although for **5** a shoulder is also observed at 2193 cm^{-1} which we attribute to a second conformer with respect to hindered rotation of the bulky $\text{SeC}\equiv\text{W}(\text{CO})_2(\text{Tp}^*)$ units, which is not differentiated on NMR timescales. The carbyne carbon for **5** resonates at $\delta_{\text{C}} = 289.0$, shifted *ca* 20 ppm down-field from the precursors (the poor solubility of **6** prevented the carbyne resonance from being confidently identified). The crystal structure of **5** was determined, confirming the *trans* geometry at platinum which

lies on a crystallographic inversion centre ($0, \frac{1}{2}, 0$; Figure 3). Despite the structural reorganization, the distances and angles associated with the $W\equiv C-Se-Pt$ isoselenocarbonyl linkages in *trans*-**5** are within precision limits essentially identical to those of the precursor *cis*-**3**.

Figure 3. Molecular structure of **5** in a crystal (50% displacement ellipsoids, one-half of the centrosymmetric molecule is crystallographically unique, pyrazolyl groups simplified and hydrogen atoms omitted for clarity). Selected distances [Å] and angles [°]: W1–C1 1.828(6), C1–Se1 1.849(6), Se1–Pt1 2.4584(7), Pt1–C4 1.949(6), C4–N7 1.158(7), W1–C1–Se1 166.4(3), C1–Se1–Pt1 105.60(17), Se1–Pt1–C4 93.92(17), Pt1–C4–N7 177.2(6).

The tungsten–carbon multiple bonds within the isoselenocarbonyl linkage in **2** and **3** are susceptible towards further reaction and treatment with two equivalents of $[AuCl(SMe_2)]$ (a reagent with demonstrated proclivity for delivering ‘AuCl’ to carbynes¹¹) results in coordination of ‘AuCl’ across both of the $W\equiv C$ bonds, furnishing the pentametallic complexes $[W_2PtAu_2(\mu_3-CSe)_2Cl_2(L_2)(CO)_4(Tp^*)_2]$ ($L_2 = COD$ **7**; $L_2 = NBD$ **8**, Scheme 2), respectively. In the $^{13}C\{^1H\}$ NMR spectra, gold(I) coordination has a modest influence on the resonances of the carbyne carbon nuclei (**7** 257.1; **8** 255.2 ppm), with small up-field shifts of *ca* 10 ppm from the respective precursors. The ^{195}Pt and ^{77}Se NMR spectra manifest similar up-field shifts, of *ca* 150 and 50 ppm, respectively.

The molecular structure of **7** (Figure 4) reveals a number of interesting features. The tungsten–carbon distance is elongated *ca* 0.1 Å upon gold(I) coordination, reflecting a reduction in multiple bond character as expected, however what distinguishes **7** from conventional dimetallacyclopropenes¹¹ is the presence of two comparatively long Pt–Au metallophilic interactions directed towards opposite sides of the molecule. The Pt–Au separations (3.2493(5), 3.1940(5) Å) suggest that fairly weak gold–platinum interactions operate, being markedly longer than reported intramolecular $d^{8...d^{10}}$ Pt–Au distances (2.86–2.95 Å) supported by polydentate supporting ligands,¹² although this is highly ligand-dependent and in other systems the distances can range from 2.6–3.3 Å.¹³ Nonetheless, the Pt–Au distance remains shorter than the sum of the Pt and Au van der Waals radii (*ca* 3.41 Å) and implies that there is some, albeit small, interaction present between the two metals.

Figure 4. Molecular structure of **7** in a crystal of $7 \cdot (CH_2Cl_2)_4$ (50% displacement ellipsoids, pyrazolyl and COD groups simplified and solvent molecules omitted for clarity). Selected distances [Å] and angles [°]: W1–C1 1.934(7), C1–Se1 1.838(8), Se1–Pt1 2.4459(7), Pt1–Se2 2.4544(7), Se2–C2 1.840(8), C2–W2 1.914(7), W1–Au1 2.8193(4), C1–Au1 2.019(7), Au1–Cl1 2.3020(19), C2–Au2 2.041(7), W2–Au2 2.8231(4), Au2–Cl2 2.2979(19), Pt1–Au1 3.2493(5), Pt1–Au2 3.1940(5), W1–C1–Se1 148.8(4), C1–Se1–Pt1 97.6(2), Se1–Pt1–Se2 92.76(3), Pt1–Se2–C2 98.7(2), Se2–C2–W2 152.2(4). Inset = alternative view of core.

The preceding reactions of the tungsten selenocarbonyl $[1]NEt_4$ were conducted in dichloromethane as this was found to be one of the few solvents capable of dissolving the especially insoluble salt as well as the platinum reagents employed. Despite the short reaction times, however, a small amount of a new brown compound was also formed and could frequently be isolated from the ethanol filtrates (in which **2** and **3** are insoluble). This was found to be the result of a slow, but not insignificant, reaction between $[1]^-$ and the dichloromethane solvent. Stirring $[1]NEt_4$ in CH_2Cl_2 for five hours under ambient conditions results in nearly quantitative conversion to $[W(\equiv CSeCH_2Cl)(CO)_2(Tp^*)]$ (**9**) by nucleophilic substitution of a chloride of CH_2Cl_2 by the selenium of $[1]^-$ (Scheme 2). Only the free selenocarbonylate $[1]^-$ reacts with dichloromethane; once formed, the platinum complexes **2–6** are stable in air- and moisture-free CH_2Cl_2 solutions for at least 24 hours. The aurated complexes **7** and **8** decompose within hours into intractable mixtures but by a different process involving the elimination of gold (mirror).^{11g}

In the 1H NMR spectrum of **9** the methylene protons resonate at $\delta_H = 5.04$ and exhibit selenium satellites ($^2J_{HSe} = 14$ Hz; ^{77}Se $I = \frac{1}{2}$, 7.6% abundance). The carbyne carbon nuclei resonate at $\delta_C = 247.3$ ($^1J_{CW} = 219$ Hz) in the $^{13}C\{^1H\}$ NMR spectrum and the selenium resonance appears as a triplet at $\delta_{Se} = 673$ ($^2J_{SeH} = 13$ Hz) in the ^{77}Se NMR spectrum due to coupling to the methylene protons. As with **2** and more conventional carbynes,¹¹ **9** is also susceptible towards gold(I) coordination at the $W\equiv C$ multiple bond such that treatment with $[AuCl(SMe_2)]$ gives the bimetallic derivative $[WAu(\mu-CSeCH_2Cl)Cl(CO)_2(Tp^*)]$ (**10**) (Scheme 2, Figure 5). Gold(I) coordination has scant influence on the chemical shifts of the methylene protons ($\delta_H = 5.23$, $^2J_{SeH} = 13$ Hz) and carbyne carbon ($\delta_C = 245.4$, $^1J_{WC} = 156$ Hz) in the 1H and $^{13}C\{^1H\}$ NMR spectra, respectively, but does reduce the magnitude of the $^1J_{WC}$ coupling for the carbyne carbon reflecting the increased coordination (*s*-character) at carbon.

Figure 5. Molecular structure of **10** in a crystal of **10**·CH₂Cl₂ showing 50% thermal probability ellipsoids. Pyrazolyl groups are simplified and solvent are not shown for clarity. Selected distances [Å] and angles [°]: W1–C1 1.933(17), W1–Au1 2.7737(7), C1–Au1 2.029(18), Au1–Cl1 2.283(5), C1–Se1 1.843(18), Se1–C4 1.92(2), W1–C1–Se1 145.8(10), C1–Se1–C4 99.5(9). Inset = alternative view of core.

In conclusion, the presence of 4-valence electron $\mu\text{:}\sigma\text{-}\pi$ bridging carbonyl ligands provides a means of masking metal centres that would otherwise be coordinatively unsaturated. Addition of extraneous ligands is normally accommodated by the carbonyl ligand converting to a terminal coordination mode as exemplified by the rich ligand-addition chemistry of complexes such as $[\text{Mo}_2(\mu\text{:}\sigma\text{-}\pi\text{-CO})_4(\eta\text{-C}_5\text{H}_5)_2]$.¹⁵ In contrast, it has been shown here that the heavier selenocarbonyl ligand may also facilitate ligand addition, but *via* an alternative change in coordination mode that leaves the *metal-chalcogen* bond intact with adoption of the isoselenocarbonyl mode (Scheme 3). Although it might anticipated that thiocarbonyl and tellurocarbonyl ligands might also behave similarly, this has yet to be established.

Scheme 2. Opening of $\mu\text{:}\sigma\text{-}\pi$ Carbonyl (A = O) or Selenocarbonyl (A = Se) Bridges.

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Notes and references

- (a) H. Gong, Q. Luo, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer, III, *Inorg. Chem.*, 2015, **54**, 132-142. (b) Z. Zhang, Q.-S. Li, R. B. King and H. F. Schaefer, III, *Eur. J. Inorg. Chem.*, 2012, 1104-1113. (c) Z. Zhang, Q.-S. Li, Y. Xie and R. B. King, *Polyhedron*, 2012, **31**, 1-11. (d) Z. Zhang, Q.-S. Li, Y. Xie and R. B. King, *Inorg. Chim. Acta*, 2011, **375**, 193-204. (e) Z. Zhang, Q.-S. Li, Y. Xie and R. B. King, *J. Organomet. Chem.*, 2011, **696**, 2958-2965. (f) Z. Zhang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer, III, *Eur. J. Inorg. Chem.*, 2010, 4175-4186. (g) Z. Zhang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer, III, *J. Phys. Chem., A*, 2010, **114**, 2365-2375. (h) Z. Zhang, Q.-S. Li, Y. Xie, R. B. King and H. F. Schaefer, III, *New J. Chem.*, 2010, **34**, 92-102.
- (a) M. G. Choi, L. M. Daniels and R. J. Angelici, *J. Organomet. Chem.*, 1990, **383**, 321-337. (b) R. J. Angelici and J. W. Dunker, *Inorg. Chem.*, 1985, **24**, 2209-2215. (c) J. W. Dunker, J. S. Finer, J. Clardy and R. J. Angelici, *J. Organomet. Chem.*, 1976, **114**, C49-C52.
- (a) A. E. Fenster and I. S. Butler, *Inorg. Chem.*, 1974, **13**, 915-920. (b) T. J. Collins and W. R. Roper, *J. Organomet. Chem.*, 1977, **139**, C9-C12. (8) G. R. Clark, K. Marsden, C. E. F. Rickard, W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 1988, **338**, 393-410. (d) A. F. Hill and J. D. E. T. Wilton-Ely, *Organometallics*, 1996, **15**, 3791-3797.
- (a) R. D. Young, A. F. Hill, G. E. Cavigliasso and R. Stranger, *Angew. Chem. Int. Ed.*, 2013, **52**, 3699 – 3702. (b) I. A. Cade, A. F. Hill and C. M. A. McQueen, *Organometallics*, 2009, **28**, 6639 – 6641. (c) H. J. Barnett, L. K. Burt and A. F. Hill, *Dalton Trans.*, 2018, **47**, 9570 – 9574. (d) S. I. Kallaene, T. Braun, M. Teltewskoi, B. Braun, R. Herrmann and R. Laubenstein *Chem. Commun.*, 2015, **51**, 14613 – 14616.
- (a) L. M. Caldwell, A. F. Hill, J. Wagler and A. C. Willis, *Dalton Trans.*, 2008, 3538-3541. (b) I. A. Cade, A. F. Hill and C. M. A. McQueen, *Dalton Trans.*, 2019, **48**, 2000-2012. (c) A. F. Hill and C. M. A. McQueen, *Organometallics*, 2012, **31**, 2482-2485. (d) B. J. Frogley, A. F. Hill and L. J. Watson, *Dalton Trans.*, 2019, **48**, 12598-12606. (e) S. Takemoto, J. Ohata, K. Umetani, M. Yamaguchi and H. Matsuzaka, *J. Am. Chem. Soc.*, 2014, **136**, 15889-15892.
- (a) T. Desmond, F. J. Lalor, G. Ferguson and M. Parvez, *J. Chem. Soc., Chem. Commun.*, 1983, 457– 458. (b) R. L. Cordiner, A. F. Hill and J. Wagler, *Organometallics*, 2008, **27**, 5177 – 5179
- (a) R. A. Doyle, L. M. Daniels, R. J. Angelici and F. G. A. Stone, *J. Am. Chem. Soc.*, 1989, **111**, 4995-4997. (b) H. P. Kim, S. Kim, R. A. Jacobson and R. J. Angelici, *J. Am. Chem. Soc.*, 1986, **108**, 5154-5158.
- L. M. Caldwell, *Adv. Organomet. Chem.*, 2008, **56**, 1-94.
- S. Schäfer, C. Moser, J. J. Tirrée, M. Nieger and R. Pietschnig, *Inorg. Chem.*, 2005, **44**, 2798-2802.
- B. J. Frogley, A. F. Hill, C. S. Onn and L. J. Watson, *Angew. Chem. Int. Ed.*, 2019, DOI: 10.1002/anie.201909333.
- (a) G. A. Carriedo, J. C. Jeffery and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1597-1603. (b) G. A. Carriedo, V. Riera, G. Sánchez and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1988, 1957-1962. (c) C. E. Strasser, S. Cronje and H. G. Raubenheimer, *New J. Chem.*, 2010, **34**, 458-469. (d) A. L. Colebatch and A. F. Hill, *Dalton Trans.*, 2017, **46**, 4355-4365. (e) B. J. Frogley, A. F. Hill and C. S. Onn, *Dalton Trans.*, 2019, **48**, 11715-11723. (f) B. J. Frogley and A. F. Hill, *Angew. Chem. Int. Ed.*, 2019, **58**, 8044-8048. (g) A. R. Delaney, B. J. Frogley and A. F. Hill, *Dalton Trans.*, 2019, **48**, 13674-13684.
- (a) H.-K. Yip, H.-M. Lin, Y. Wang and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1993, 2939-2944. (b) G.-Q. Yin, Q.-H. Wei, L.-Y. Zhang and Z.-N. Chen, *Organometallics*, 2006, **25**, 580-587. (c) T. R. Cook, A. J. Esswein and D. G. Nocera, *J. Am. Chem. Soc.*, 2007, **129**, 10094-10095. (d) L.-J. Xu, X.-C. Zeng, J.-Y. Wang, L.-Y. Zhang, Y. Chi and Z.-N. Chen, *ACS Appl. Mater. Interfaces*, 2016, **8**, 20251-20257. (e) L.-Y. Zhang, L.-J. Xu, J.-Y. Wang, X.-C. Zeng and Z.-N. Chen, *Dalton Trans.*, 2017, **46**, 865-874. (f) F. Juliá, P. G. Jones and P. González-Herrero, *Inorg. Chem.*, 2012, **51**, 5037-5049.
- (a) S. A. Batten, J. C. Jeffery, P. L. Jones, D. F. Mullica, M. D. Rudd, E. L. Sappenfield, F. G. A. Stone and A. Wolf, *Inorg. Chem.*, 1997, **36**, 2570-2577. (b) R. Gericke, M. A. Bennett, S. H. Privér and S. K. Bhargava, *Organometallics*, 2017, **36**, 3178-3188.
- (a) A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441-451. (b) E. Clementi, D. L. Raimondi and W. P. Reinhardt, *J. Chem. Phys.*, 1967, **47**, 1300-1307.
- M. D. Curtis, L. Messerle, N. A. Fotinos and R. F. Gerlach, *ACS Symposium Series*, 1981, **155**(React. Met.-Met. Bonds), 221-257.

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The novel platinum bis(isoselenocarbonyl) complex $[\text{Pt}\{\text{SeCW}(\text{CO})_2(\text{Tp}^*)\}_2]$ is capable of opening both $\mu:\sigma\text{-}\mu\text{-CSe}$ bridges to allow addition of nucleophilic (CNR: R = $t\text{Bu}$, $\text{C}_6\text{H}_2\text{Me}_3$) reagents to platinum by varying the selenocarbonyl bridging mode.

Table of Contents Graphic

Alternative Table of Contents Graphic - Editor please advise.