Novel carbon-centred reactivity of $[(H)C(PPh_2Se)_2]^-$ in the formation of structurally diverse Sn(IV), Te(IV) and Hg(II) complexes of the triseleno ligand $[(Se)C(PPh_2Se)_2]^{2-}$†

Jari Konu and Tristram Chivers*

Received (in Berkeley, CA, USA) 13th November 2009, Accepted 15th January 2010
First published as an Advance Article on the web 27th January 2010
DOI: 10.1039/b923910c

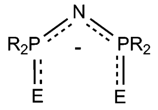
Metathetical reactions between TMEDA·Li[(H)C(PPh$_2$Se)$_2$] and MCl$_2$ (M = Hg, Sn, Te) in a 2 : 1 molar ratio afforded the homoleptic complexes, {M[(H)C(PPh$_2$Se)$_2$]$_2$}, as intermediates which undergo a surprising selenium/hydrogen exchange at the carbon centre to yield the dianionic triseleno ligand in {M$_n$[(Se)C(PPh$_2$Se)$_2$]$_2$} (*n* = 1, M = Sn, Te; *n* = 2, M = Hg).

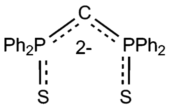
Dichalcogenoimidodiphosphinate monoanions, $[N(PR_2E)_2]^-$ (**1**) (R = ^{i}Pr, ^{t}Bu, Ph; E = S, Se, Te), are versatile acyclic ligands that have attracted considerable interest over the decades.[1,2] In the past 5 years, investigations of the coordination chemistry of the isoelectronic PCP-bridged dianion $[C(PPh_2S)_2]^{2-}$ (**2**)[3] have led to the creation of novel M═C double bonds with main group[4] and transition metals,[3,5] as well as with lanthanides[6] and actinides.[7] In addition, the mild oxidation of Li$_2$**2** with C_2Cl_6[3] or I_2[8] produces unusual carbenoid species stabilised by the incorporation of lithium halides and, in the absence of LiI, the unsaturated $C_2P_2S_2$ ring **3** as a result of a sulfur-transfer process.[8]

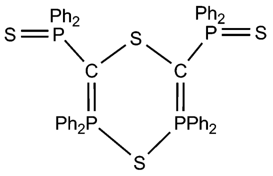
Our recent development of synthetic routes to the monoanions $[(H)C(PR_2Se)_2]^-$ (**4**, R = Ph, ^{i}Pr)[9] has provided an opportunity to compare the behaviour of these dichalcogeno PCP-bridged ligands with that of the isoelectronic PNP-bridged species **1**. An initial indication that different chemistry may occur was provided by the observation of carbon-centred reactivity upon one-electron oxidation of **4** in contrast to the formation of dimers or cyclic cations with chalcogen–chalcogen bonds from the oxidation of **1**.[10,11]

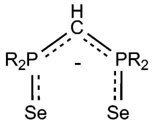
In this communication we report that reactions of the monoanion $[(H)C(PR_2Se)_2]^-$ (**4**, R = Ph) with group 12, 14 or 16 dihalides, involve an unexpected carbon-centred reactivity that produces the novel triseleno dianion, $[(Se)C(PPh_2Se)_2]^{2-}$, in the homoleptic metal complexes {M$_n$[(Se)C(PPh$_2$Se)$_2$]$_2$} [*n* = 1, M = Sn (**6**), Te (**7**); *n* = 2, M = Hg (**8**)] which exhibit intriguingly different structural features (Scheme 1).

In the initial study of the coordination chemistry of **4** (R = Ph) the metathetical reactions between Li**4** and MCl$_2$ (M = Zn, Hg) were shown to proceed in a predictable manner to give homoleptic group 12 complexes, {M[(H)C(PPh$_2$Se)$_2$]$_2$} (**5a**, M = Zn; **5b**, M = Hg) (Scheme 1), with distorted tetrahedral metal centres.[9,12] Complexes **5a** and **5b** were comprehensively characterized in solution by multinuclear NMR spectra.[9]

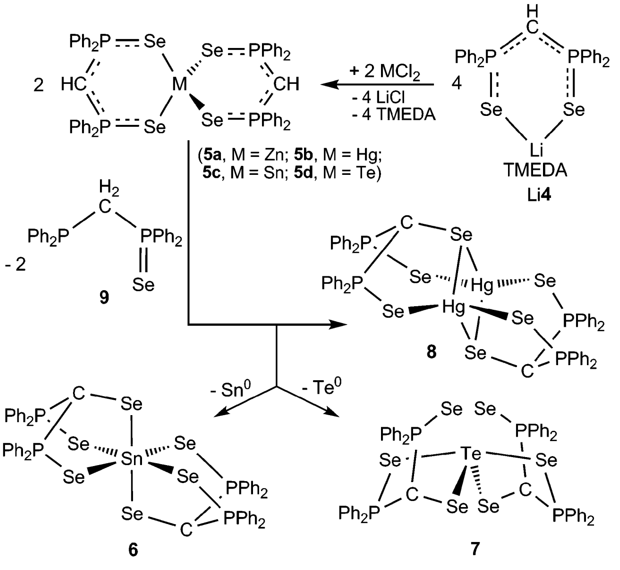

1


2


3


4

The reaction between Li**4** (R = Ph) and SnCl$_2$ at −80 °C produced an orange-yellow solution and a small amount of red powder upon warming to room temperature. The multinuclear NMR spectra (^{1}H, ^{31}P{^{1}H}, ^{77}Se) of the solution† were consistent with the formation of the expected homoleptic Sn(II) complex, {Sn[(H)C(PPh$_2$Se)$_2$]$_2$} (**5c**), on the basis of comparison with the spectra of **5a** and **5b**.[9,13] After a prolonged reaction time or upon moderate heating (55 °C), the singlet for **5c** in the ^{31}P{^{1}H} NMR spectrum of the reaction mixture was gradually replaced by two mutually coupled doublets at δ 31.2 [$^1J(^{31}P,^{77}Se)$ = 752 Hz] and −25.3



Scheme 1 Formation of the triseleno dianion, $[(Se)C(PPh_2Se)_2]^{2-}$.

University of Calgary, Department of Chemistry,
2500 University Drive N.W., T2N 1N4, Calgary, AB, Canada.
E-mail: chivers@ucalgary.ca; Fax: +1-403-289-9488;
Tel: +1-403-220-5741

† Electronic supplementary information (ESI) available: Experimental and crystallographic data in pdf-format. CCDC 754680–754682 contain crystallographic data for compounds **6**, **7** and **8**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b923910c

[$^2J(^{31}P,^{31}P)$ = 82.8 Hz] indicating the formation of the neutral *monoseleno* compound, [$(H_2)C(PPh_2)(PPh_2Se)$] (**9**, Scheme 1),[14] while more red powder was formed. The $^{31}P\{^1H\}$ NMR spectrum of the red powder in CD_2Cl_2 displayed a singlet at 61.6 ppm with ^{77}Se satellites [$^1J(^{31}P,^{77}Se)$ = 536 Hz and $^2J(^{31}P,^{31}P)$ = 33.2 Hz]. The ^1H NMR spectrum, however, exhibited only the typical pattern for phenyl groups, and no signal for the PC(H)P hydrogen was detected.‡

After recrystallisation from a toluene–THF mixture this red product was identified as $\{Sn[(Se)C(PPh_2Se)_2]_2\cdot(C_7H_8)_2\}$ (**6**$\cdot(C_7H_8)_2$)‡ by X-ray crystallography. The structural determination revealed the formation of the novel triseleno dianion, $[(Se)C(PPh_2Se)_2]^{2-}$, two of which are coordinated to a tin(IV) centre in a slightly distorted octahedral environment (Fig. 1): the Sn–Se(C) contacts are *ca.* 0.17 Å shorter than the Sn–Se(P) bonds. The formation of **6** formally involves a remarkable selenium/hydrogen exchange[15] (deprotonation–selenation sequence) at the carbon centre of the ligand **4** (R = Ph) with the formation of the monoselenide **9** (*vide supra*) and the triseleno dianion, $[(Se)C(PPh_2Se)_2]^{2-}$. The 2^- charge for this new ligand indicates a redox process at the metal centre [Sn(II) → Sn(IV) + Sn(0)] as depicted in Scheme 1. The markedly non-planar carbon centres in **6** ($\sum \angle C(1)$ 341°) exhibit P–C bond lengths of 1.749(6) Å, consistent with the distance typically observed for a three-coordinate carbon atom in a PCP unit, *cf.* for example *ca.* 1.72 Å in Li**4**, **5a** and **5b**[9] *vs.* 1.84 Å for the four-coordinate carbon atom in $[(H_2)C(PPh_2Se)_2]$[16] or 1.63 Å for the two-coordinate (double bonded) carbon in $[C(PPh_3)_2]$.[17]

The metathetical reaction of Li**4** with TMTU·$TeCl_2$ (TMTU = tetramethylthiourea) produced a deep red solution, but no clear evidence for the presence of the homoleptic Te(II) complex, $\{Te[(H)C(PPh_2Se)_2]_2\}$ (**5d**),[18] was obtained by NMR spectroscopy.† Instead, the $^{31}P\{^1H\}$ NMR spectra indicated a continuous depletion of Li**4** together with the formation of the monoselenide **9**. In addition, two broad singlets were apparent in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture at *ca.* δ 64 and 53 in an approximate 1 : 1 ratio. After work-up, a brownish-red powder was isolated for which the $^{31}P\{^1H\}$ NMR spectrum in d_8-THF at −10 °C displayed two mutually coupled doublets at 64.3 and 53.3 ppm with $^2J(^{31}P,^{31}P)$ = 39.0 Hz. Both signals also showed ^{77}Se satellites with $^1J(^{31}P,^{77}Se)$ = 500 and 679 Hz, respectively, indicating two unequivalent PSe units one of which is only weakly coordinated, *cf.* $^1J(^{31}P,^{77}Se)$ = *ca.* 530 Hz in **5a**, **5b** and **6** *vs.* 752 Hz for the terminal P═Se unit in **9**.[9,14] Similarly to **6**, the ^1H NMR spectrum of this product exhibited only the typical signal pattern for phenyl groups and no signal for the PC(H)P hydrogen.‡ Furthermore, the $^{77}Se\{^1H\}$ NMR spectrum showed two doublets at 223 and −195 ppm, with values of $^1J(^{31}P,^{77}Se)$ matching those resolved in the $^{31}P\{^1H\}$ NMR spectrum, and a singlet at −314 ppm in an approximate 1 : 1 : 1 ratio. Taken together, the NMR data suggested that a transformation of the ligand **4** (R = Ph) similar to that observed in the formation of the tin(IV) complex **6** had occurred.

The crystal structure of the toluene solvate, $\{Te[(Se)C(PPh_2Se)_2]_2\cdot(C_7H_8)\}$ (**7**$\cdot(C_7H_8)$, Fig. 2),‡ confirmed the presence of two triseleno dianions coordinated to a tellurium(IV) centre. In contrast to **6**, however, the dianionic ligand is connected to Te by the carbon-bound selenium and one of the PSe units while the second PSe unit shows only a weak Se···Te interaction of 3.374(1)–3.463(1) Å (*cf.* sum of van der Waals' radii for Se and Te is 4.20 Å[19]) presumably as a result of the stereochemically active lone pair on the tellurium(IV) centre which adopts a see-saw geometry. The inequality of the PSe units results in a slight disparity of *ca.* 0.09 and 0.02 Å in the P–Se and P–C bond lengths, respectively.[20] The remaining bond parameters and the non-planarity of the carbon centres are comparable to those in **6**.

In the light of the unexpected formation of the triseleno dianion $[(Se)C(PPh_2Se)_2]^{2-}$ and the concomitant redox process

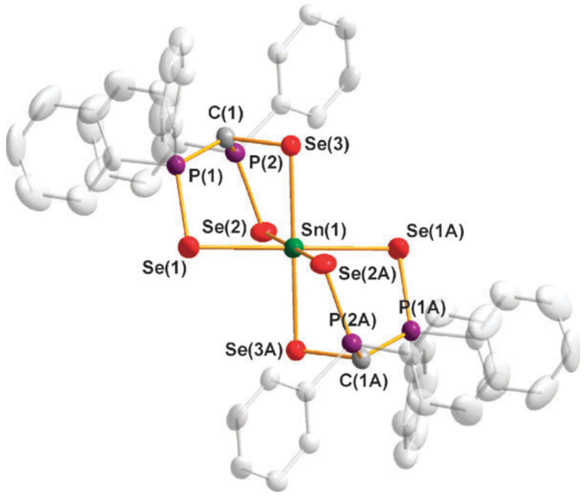


Fig. 1 Crystal structure of **6** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and toluene solvates have been omitted for clarity. Relevant bond parameters (in Å and °): Sn(1)–Se(1) 2.812(1), Sn(1)–Se(2) 2.810(1), Sn(1)–Se(3) 2.637(1), P(1)–Se(1) 2.181(2), P(2)–Se(2) 2.187(2), C(1)–P(1) 1.749(6), C(1)–P(2) 1.749(5), C(1)–Se(3) 1.929(6), P(1)–C(1)–P(2) 123.1(3), P(1)–C(1)–Se(3) 108.3(4), P(2)–C(1)–Se(3) 109.4(3). Symmetry operation A: −*x*, 1 − *y*, −*z*.†

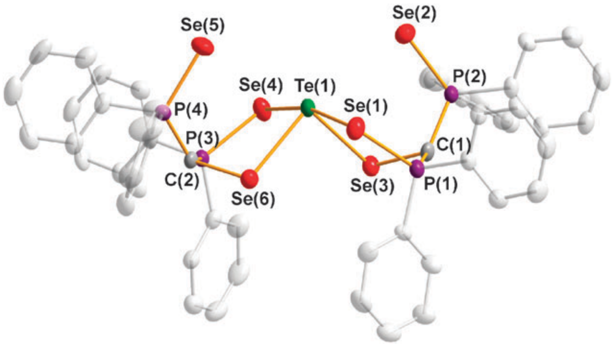


Fig. 2 Crystal structure of **7** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and toluene solvate have been omitted for clarity. Only one of the two independent molecules is shown. Pertinent bond parameters (in Å and °): Te(1)–Se(1) 2.744(1), Te(1)–Se(2) 3.463(1), Te(1)–Se(3) 2.637(1), P(1)–Se(1) 2.226(2), P(2)–Se(2) 2.133(2), C(1)–P(1) 1.744(6), C(1)–P(2) 1.760(6), C(1)–Se(3) 1.890(5), P(1)–C(1)–P(2) 123.7(3), P(1)–C(1)–Se(3) 107.7(3), P(2)–C(1)–Se(3) 110.4(3).†

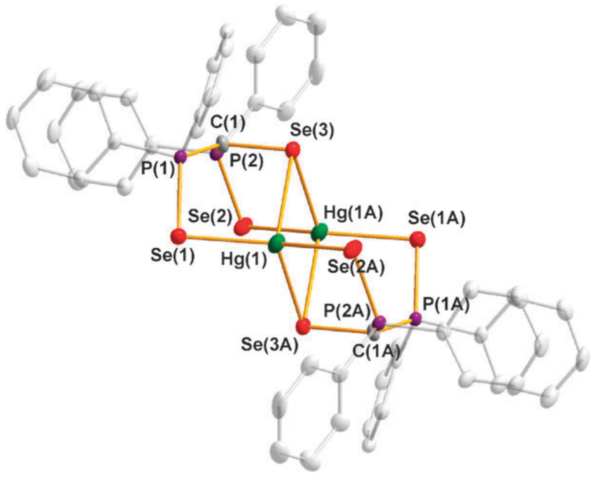


Fig. 3 Crystal structure of **8** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms and THF solvates have been omitted for clarity. Relevant bond parameters (in Å and °): Hg(1)–Se(1) 2.5682(2), Hg(1)–Se(3) 2.8458(9), Hg(1)–Se(3A) 2.7271(6), Hg(1A)–Se(2) 2.5781(7), P(1)–Se(1) 2.217(1), P(2)–Se(2) 2.208(1), C(1)–P(1) 1.729(3), C(1)–P(2) 1.722(3), C(1)–Se(3) 1.936(3), P(1)–C(1)–P(2) 130.1(2), P(1)–C(1)–Se(3) 110.6(2), P(2)–C(1)–Se(3) 112.0(2). Symmetry operation A: 1 − *x*, 1 − *y*, −*z*.†

at the metal centre (Sn, Te) in the formation of **6** and **7** (Scheme 1), we sought to determine if the selenium/hydrogen exchange between the ligands in homoleptic complexes of the type **5** is dependent on the redox capability of the central atom. Consequently, we investigated the thermolysis of the Hg(II) complex, {Hg[(H)C(PPh$_2$Se)$_2$]$_2$} (**5b**),[9] for which oxidation of the metal centre [to Hg(IV)] is unlikely to occur.

A solution (THF or toluene) of **5b** at 65 °C† was monitored by ^{31}P{^{1}H} NMR spectroscopy. After 2 h, the resonances for **9**[14] became evident and a yellow precipitate started to appear. After *ca.* 48 h, **5b** had been completely consumed and a *very insoluble* yellow powder was obtained that exhibited a weak, broad singlet at 52.5 ppm in the ^{31}P{^{1}H) NMR spectrum measured in d$_6$-DMSO at 70 °C. Consistently with **6** and **7**, no signal for the PC(H)P hydrogen was observed in the ^{1}H NMR spectrum.

Crystals of {Hg[(Se)C(PPh$_2$Se)$_2$]·(THF)}$_2$ (**8**·(THF)$_2$) were obtained from an undisturbed THF solution of **5b** at 100 °C in a sealed glass tube after 24 h.† The structure determination revealed a complex comprised of two [(Se)C(PPh$_2$Se)$_2$]$^{2-}$ dianions and *two* Hg(II) centres (Fig. 3). The overall geometry in the dimer **8** resembles that of the tin complex **6** with the six-coordinate Sn(IV) centre replaced by two four-coordinate Hg(II) atoms. Consequently, one of the Se atoms in each of the [(Se)C(PPh$_2$Se)$_2$]$^{2-}$ ligands is three-coordinate. The distance between the two mercury centres in **8** (3.1046(7) Å) is at the sum of van der Waals' radii (3.10 Å[19]).

In summary, we have discovered a new aspect of carbon-centred reactivity for dichalcogeno PCP-bridged ligands that involves the formation of the novel tridentate seleno-ligand [(Se)C(PPh$_2$Se)$_2$]$^{2-}$ from the homoleptic complexes {M[(H)C(PPh$_2$Se)$_2$]$_2$} (M = Hg, Sn, Te). While the mechanism of this intriguing selenium/hydrogen exchange process (deprotonation-selenation sequence) remains to be elucidated, the divergent coordination modes observed in the three complexes **6**, **7** and **8** portends a rich coordination chemistry for this new class of ligand.

Financial support from NSERC (Canada) is gratefully acknowledged.

Notes and references

‡ The ^{1}H NMR spectrum of **6** and **7** also showed a singlet at 2.33 and 2.31 ppm, respectively, arising from the toluene CH$_3$ group indicating a trapped solvent in the bulk product.

1 For recent reviews on metal complexes of sulfur and selenium-centered ligands, see: I. Haiduc, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier Ltd., Amsterdam, 2003, pp. 323–347; C. Silvestru and J. E. Drake, *Coord. Chem. Rev.*, 2001, **223**, 117.

2 For reviews on the chemistry of tellurium-centered ligands, see: T. Chivers, J. Konu, J. S. Ritch, M. C. Copsey, D. J. Eisler and H. M. Tuononen, *J. Organomet. Chem.*, 2007, **692**, 2658; J. S. Ritch, T. Chivers, M. Afzaal and P. O'Brien, *Chem. Soc. Rev.*, 2007, **36**, 1622.

3 T. Cantat, N. Mézailles, L. Ricard, Y. Jean and P. Le Floch, *Angew. Chem., Int. Ed.*, 2004, **43**, 6382; T. Cantat, L. Ricard, Y. Jean, P. Le Floch and N. Mézailles, *Organometallics*, 2006, **25**, 4965.

4 C. Foo, K.-C. Lau, Y.-F. Yang and C.-W. So, *Chem. Commun.*, 2009, 6816.

5 T. Cantat, M. Demange, N. Mezailles, L. Ricard, Y. Jean and P. Le Floch, *Organometallics*, 2005, **24**, 4838; T. Cantat, L. Ricard, N. Mezailles and P. Le Floch, *Organometallics*, 2006, **25**, 6030.

6 T. Cantat, F. Jaroschik, F. Nief, L. Ricard, N. Mezailles and P. Le Floch, *Chem. Commun.*, 2005, 5178.

7 T. Cantat, T. Arliguie, A. Noel, P. Thuery, M. Ephritikhine, P. Le Floch and N. Mezailles, *J. Am. Chem. Soc.*, 2009, **131**, 963.

8 J. Konu and T. Chivers, *Chem. Commun.*, 2008, 4995.

9 J. Konu, H. M. Tuononen and T. Chivers, *Inorg. Chem.*, 2009, **48**, 11788.

10 T. Chivers, D. J. Eisler, J. S. Ritch and H. M. Tuononen, *Angew. Chem., Int. Ed.*, 2005, **44**, 4953; T. Chivers, D. J. Eisler, J. S. Ritch and H. M. Tuononen, *Chem.–Eur. J.*, 2007, **13**, 4643; S. D. Robertson, T. Chivers and H. M. Tuononen, *Inorg. Chem.*, 2008, **47**, 10634; S. D. Robertson, T. Chivers and H. M. Tuononen, *Inorg. Chem.*, 2009, **48**, 6755.

11 J. Konu, T. Chivers and H. M. Tuononen, *Chem. Commun.*, 2006, 1634; J. Konu, T. Chivers and H. M. Tuononen, *Inorg. Chem.*, 2006, **45**, 10678.

12 The only other structurally characterized complex of the anion **4**, {Cp*Rh[(H)C(PPh$_2$Se)$_2$]ClO$_4$}, exhibits a transannular Rh–C contact: M. Valderrama, R. Contreras and M. Bascunan, *Polyhedron*, 1994, **13**, 1101.

13 For the Sn(II) complex of the isoelectronic [N(PPh$_2$Se)]$^-$ anion, see: V. García-Montalvo, J. Novosad, P. Kilian, J. D. Woollins, A. M. Z. Slawin, P. G. Y. García, M. López-Cardoso, G. Espinosa-Pérez and R. Cea-Olivares, *J. Chem. Soc., Dalton Trans.*, 1997, 1025.

14 S. O. Grim and E. D. Walton, *Inorg. Chem.*, 1980, **19**, 1982.

15 A trinuclear complex containing the neutral ligand [(Se)C(PPh$_2$O)$_2$] has been isolated in unspecified yield from the reaction of [(H$_2$)C(PPh$_2$Se)$_2$] with CuCl$_2$·2H$_2$O; D. Cauzzi, C. Graiff, M. Lanfranchi, G. Predieri and A. Tiripicchio, *J. Chem. Soc., Chem. Commun.*, 1995, 2443.

16 P. J. Carroll and D. D. Titus, *J. Chem. Soc., Dalton Trans.*, 1977, 824.

17 A. T. Vincent and P. J. Wheatley, *J. Chem. Soc., Dalton Trans.*, 1972, 617.

18 For the Te(II) complex of the isoelectronic [N(PPh$_2$Se)]$^-$ anion, see: D. J. Birdsall, J. Novosad, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 2000, 425.

19 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, N.Y., 3rd edn, 1960.

20 P–Se distances in TeX$_2$ (X = Br, I) complexes of the neutral ligand [(H$_2$)C(PPh$_2$Se)$_2$] are in the range 2.14–2.16 Å; W. Levason, G. Reid, M. Victor and W. Zhang, *Polyhedron*, 2009, **28**, 4010; C. G. Hrib, P. G. Jones, W.-W. du Mont, V. Lippolis and F. Devillanova, *Eur. J. Inorg. Chem.*, 2006, 1294.