

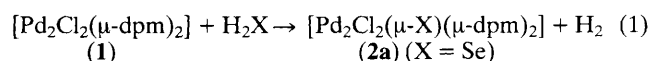
## Use of Hydrogen Selenide for Synthesis of Binuclear Palladium Complexes containing Bridging Selenide, and their Conversion into Novel Dimetallic Selenoxides

Gabor Besenyi, Chung-Li Lee, and Brian R. James\*

Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

The complexes  $[\text{Pd}_2\text{Cl}_2\{\mu\text{-PPh}_2\text{CH(R)PPh}_2\}_2]$ , where R = H or Me, react with  $\text{H}_2\text{Se}$  or elemental Se to yield the bridging-selenide derivatives  $[\text{Pd}_2\text{Cl}_2(\mu\text{-Se})\{\mu\text{-PPh}_2\text{CH(R)PPh}_2\}_2]$ ; these, on treatment with  $\text{Bu}^t\text{OOH}$ , yield the corresponding  $\mu\text{-SeO}$  (dimetallic selenoxide) species.

We have reported recently<sup>1</sup> on reaction (1) [X = S, dpm = bis(diphenylphosphino)methane], which allows for the quantitative recovery of  $\text{H}_2$  from  $\text{H}_2\text{S}$ , and it was of considerable interest to see if such chemistry existed for the X = Se and O systems.



A corresponding reaction does occur with  $\text{H}_2\text{Se}$ , although accompanying replacement of the terminal chloride ligands by  $\text{SeH}^-$  is also observed, which is presumably related to the higher acidity of  $\text{H}_2\text{Se}$  compared to that of  $\text{H}_2\text{S}$ ; the reaction<sup>†</sup>

gives a mixture of the A-frame complexes (2a),  $[\text{Pd}_2\text{Cl}(\text{SeH})(\mu\text{-Se})(\mu\text{-dpm})_2]$  (2b), and  $[\text{Pd}_2(\text{SeH})_2(\mu\text{-Se})(\mu\text{-dpm})_2]$  (2c). Complex (2a) can be made independently by treatment of (1) with elemental, amorphous selenium.<sup>‡</sup> The <sup>1</sup>H n.m.r. spectra of (2a–c) (Table 1) reveal the inequivalence of the methylene protons and the virtual coupling to the remote phosphorus nuclei, exactly analogous to the data reported<sup>3</sup> for  $[\text{Pd}_2\text{Cl}_2(\mu\text{-S})(\mu\text{-dpm})_2]$ ; the resonance for coordinated  $\text{SeH}^-$  in (2b) and (2c) is seen, respectively, at  $\delta -3.52$  (t,  $J_{\text{HP}} 13.00$  Hz) and  $\delta -3.56$  (qn,  $J_{\text{HP}} 6.39$  Hz), differences in splitting resulting from coupling to two and four P atoms, respectively. The recently isolated *anti*-isomer of

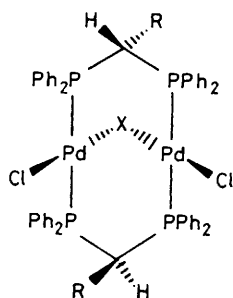
<sup>†</sup>  $\text{H}_2\text{Se}$ , generated *in situ* from  $\text{Al}_2\text{Se}_3$ , was transferred *via* Schlenk-tube techniques to cooled  $\text{CH}_2\text{Cl}_2$  solutions of (1) [or (2a)]; after *ca.* 1 h at 20 °C, addition of MeOH to a concentrated solution precipitated a mixture of (2a), (2b), and (2c).

<sup>‡</sup> Complex (1) was stirred with freshly prepared red selenium<sup>2</sup> [Se : (1) = 3] in  $\text{CH}_2\text{Cl}_2$  for 1.5 h under  $\text{N}_2$ ; removal of excess of Se by filtration, and concentration to a small volume, followed by addition of MeOH, yielded the pure, brown, crystalline product in 50% yield (C, H, and Se elemental analyses are satisfactory).

**Table 1.** N.m.r. spectral data<sup>a</sup> for the dinuclear palladium complexes.

Compound	<sup>1</sup> H, δ <sub>H</sub> splitting pattern ( <i>J</i> <sub>HH</sub> , <i>J</i> <sub>HP</sub> , Hz)	<sup>31</sup> P{ <sup>1</sup> H}, δ <sub>P</sub> p.p.m.
(2a)	CH <sub>2</sub> : 4.91 d.qn. (13.05, 5.76), 3.63 d.qn. (13.05, 3.51)	4.0 s
(2b) <sup>b</sup>	CH <sub>2</sub> : 4.98 d.qn. (13.07, 6.15), 3.80 d.qn. (13.07, 3.44)	AA'BB' <sup>c</sup>
(2c) <sup>d</sup>	CH <sub>2</sub> : 5.03 d.qn. (13.31, 5.76), 4.00 d.qn. (13.31, 3.45)	13.2 s
(3)	CH: 5.86 t.qt. (7.29, 13.75), 4.09 un	AA'BB' <sup>e</sup>
	C(CH <sub>3</sub> ): 1.33 d.t. (7.29, 13.16), 0.98 d.t. (7.83, 10.07)	
(4)	CH <sub>2</sub> : 6.09 d.t. (13.13, 13.29), 4.01 d.t. (14.25, 8.50)	†
	2.64 m, 2.53 m	
(5) <sup>g</sup>	CH: 6.97 t.qt. (7.33, 15.47), 3.53 t.qt.t. (7.00, 15.00, 2.50 <sup>h</sup> )	†
	C(CH <sub>3</sub> ): 1.13 d.t. (7.33, 12.70), 1.00 d.t. (7.00, 10.26)	
(6)	CH <sub>2</sub> : 4.90 d.qn. (13.0, 5.6), 2.53 d.qn. (13.0, 3.54) <sup>i</sup>	—

<sup>a</sup> Measured at ambient temperatures in CD<sub>2</sub>Cl<sub>2</sub> or CDCl<sub>3</sub>; δ<sub>H</sub>; proton integrations were correct in every system; δ<sub>P</sub> downfield relative to external 85% H<sub>3</sub>PO<sub>4</sub>; s = singlet, d = doublet, t = triplet, qt = quartet, qn = quintet, un = unresolved multiplet, m = overlapping multiplets. <sup>b</sup> δ(SeH) -3.52 t, *J*<sub>HP</sub> = 13.00 Hz. <sup>c</sup> Major peaks centred at δ 11.2 and 5.7. <sup>d</sup> δ(SeH) -3.55 qn, *J*<sub>HP</sub> = 6.39 Hz. <sup>e</sup> δ 40.49, 22.83, and 20.21, 2.50. <sup>f</sup> Decomposition in solution during free induction decay (FID) accumulation. <sup>g</sup> In principle, two isomers are possible for this compound, depending on the orientation of the selenium-bound oxygen atom; however, only one isomer is observed in the n.m.r. spectrum. <sup>h</sup> Long range coupling to remote P atoms. <sup>i</sup> Measured at 0 °C during decomposition.



- (2a) X = Se, R = H  
 (3) X = Se, R = Me  
 (4) X = SeO, R = H  
 (5) X = SeO, R = Me  
 (6) X = O, R = H

[Pd<sub>2</sub>Cl<sub>2</sub>(μ-dpmMe)<sub>2</sub>] [where dpmMe is 1,1-(diphenylphosphino)ethane, and *anti* refers to the disposition of the Me groups with respect to the Pd-C-Pd plane]<sup>4</sup> reacts similarly with Se, but more sluggishly, to give (3), in which the two methyl (and methine) groups are now inequivalent, and coupling occurs only to the adjacent P atoms (Table 1).

Compounds (2a) and (3) were readily converted into their (μ-SeO) derivatives (4) and (5), via a range of O-atom donors, optimum yields being obtained with Bu<sup>t</sup>OOH. § The incorporation of the O-atom makes inequivalent all four of the -CH<sub>2</sub>-protons in (4), and the sets of -CH(CH<sub>3</sub>) protons in (5) (Table 1). The n.m.r. data for (4) resemble closely those for the corresponding μ-SO complex.<sup>1</sup> In contrast to the latter, no further oxidation to the μ-SeO<sub>2</sub> species is observed. To our knowledge, the μ-SeO derivatives are the first such dimetallic selenoxides to be reported, although Rauchfuss and coworkers have reported recently on the transient formation in solution of a μ<sub>3</sub>-SeO moiety within an Fe<sub>2</sub>Pt species.<sup>5</sup> I.r. bands found at ~770 cm<sup>-1</sup> (Nujol) for (4) and (5) are assigned to ν<sub>SeO</sub>.

§ For example, (2a) was stirred with a 10-fold excess of Bu<sup>t</sup>OOH in CH<sub>2</sub>Cl<sub>2</sub> for 1 h; addition of diethyl ether yielded orange crystals of (4) in 85% yield. Elemental analysis, including O and Se, is satisfactory.

Compound (1) in CH<sub>2</sub>Cl<sub>2</sub>-MeOH does react with H<sub>2</sub>O [cf. equation (1)], but the reaction is complex and <sup>31</sup>P n.m.r. data indicate numerous and, as yet, largely uncharacterized products, although a μ-oxo species may well be a precursor to some of these. The complex [Pd<sub>2</sub>Cl<sub>2</sub>(μ-O)(μ-dpm)<sub>2</sub>], (6), is almost certainly formed at -50 °C in CD<sub>2</sub>Cl<sub>2</sub> on treating (1) with an equimolar amount of *m*-chloroperbenzoic acid; there is a rapid colour change from orange to lemon yellow, and the n.m.r. data (Table 1) are similar to those of the μ-Se species (2a), and the μ-S analogue.<sup>3</sup> Decomposition of the μ-oxo species occurs on warming above -50 °C, to give again a complex mixture of unidentified products. Of note, the source of oxygen in a reported [Os<sub>2</sub>Cl<sub>6</sub>(μ-O)(μ-dpm)<sub>2</sub>] complex was not identified,<sup>6</sup> although extraction of oxygen from H<sub>2</sub>O to give μ-oxo complexes is well documented for the early transition metals.<sup>7</sup>

Clearly, extraction of the main group element from H<sub>2</sub>X (X = O, S, Se) as a dianion by transition metal complexes, with concomitant evolution of dihydrogen, now seems to be established, and is of interest from the viewpoints of inorganic syntheses, and H<sub>2</sub> recovery.

We thank N.S.E.R.C. for funding (operating grant to B. R. J., and an International Scientific Exchange award to G. B.), the Isaak Walton Killam Foundation for a postdoctoral fellowship (to C-L. L.) administered by the University of British Columbia, and Johnson Matthey for the loan of Pd.

Received, 30th July 1986; Com. 1088

## References

- C-L. Lee, G. Besenyei, B. R. James, D. A. Nelson, and M. A. Lilga, *J. Chem. Soc., Chem. Commun.*, 1985, 1175.
- G. Gattow, *Z. Anorg. Allg. Chem.*, 1962, **317**, 245.
- A. L. Balch, L. S. Brenner, and M. M. Olmstead, *Inorg. Chem.*, 1979, **18**, 2996.
- C-L. Lee, Y-P. Yang, S. J. Rettig, B. R. James, D. A. Nelson, and M. Lilga, *Organometallics*, 1986, in the press.
- J. E. Hoots, D. A. Lesch, and T. B. Rauchfuss, *Inorg. Chem.*, 1984, **23**, 3130.
- A. R. Chakravarty, F. A. Cotton, and W. Schworzer, *Inorg. Chem.*, 1984, **23**, 99.
- F. Bottomley, D. F. Drummond, G. O. Egharevba, and P. S. White, *Organometallics*, 1986, **5**, 1620; F. Bottomley, G. O. Egharevba, and P. S. White, *J. Am. Chem. Soc.*, 1985, **107**, 4353.