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

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

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

The complexes $[Pd_2Cl_2\{\mu\text{-}PPh_2CH(R)PPh_2\}_2]$, where R = H or Me, react with H_2Se or elemental Se to yield the bridging-selenide derivatives $[Pd_2Cl_2(\mu\text{-}Se)\{\mu\text{-}PPh_2CH(R)PPh_2\}_2]$; these, on treatment with Bu^tOOH, yield the corresponding μ-SeO (dimetallic selenoxide) species.

We have reported recently[1] on reaction (1) [X = S, dpm = bis(diphenylphosphino)methane], which allows for the quantitative recovery of H_2 from H_2S, and it was of considerable interest to see if such chemistry existed for the X = Se and O systems.

$$\underset{(\mathbf{1})}{[Pd_2Cl_2(\mu\text{-}dpm)_2]} + H_2X \rightarrow \underset{(\mathbf{2a})\,(X = Se)}{[Pd_2Cl_2(\mu\text{-}X)(\mu\text{-}dpm)_2]} + H_2 \quad (1)$$

A corresponding reaction does occur with H_2Se, although accompanying replacement of the terminal chloride ligands by SeH^- is also observed, which is presumably related to the higher acidity of H_2Se compared to that of H_2S; the reaction† gives a mixture of the A-frame complexes (**2a**), $[Pd_2Cl(SeH)(\mu\text{-}Se)(\mu\text{-}dpm)_2]$ (**2b**), and $[Pd_2(SeH)_2(\mu\text{-}Se)(\mu\text{-}dpm)_2]$ (**2c**). Complex (**2a**) can be made independently by treatment of (**1**) with elemental, amorphous selenium.‡ The ^1H 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[3] for $[Pd_2Cl_2(\mu\text{-}S)(\mu\text{-}dpm)_2]$; the resonance for co-ordinated SeH^- in (**2b**) and (**2c**) is seen, respectively, at δ −3.52 (t, J_{HP} 13.00 Hz) and δ −3.56 (qn, J_{HP} 6.39 Hz), differences in splitting resulting from coupling to two and four P atoms, respectively. The recently isolated *anti*-isomer of

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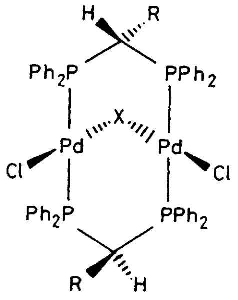
† H_2Se, generated *in situ* from Al_2Se_3, was transferred *via* Schlenk-tube techniques to cooled CH_2Cl_2 solutions of (**1**) [or (**2a**)]; after *ca.* 1 h at 20 °C, addition of MeOH to a concentrated solution precipitated a mixture of (**2a**), (**2b**), and (**2c**).

‡ Complex (**1**) was stirred with freshly prepared red selenium[2] [Se : (**1**) = 3] in CH_2Cl_2 for 1.5 h under 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[a] for the dinuclear palladium complexes.

Compound		^1H, δ_H splitting pattern (J_{HH}, J_{HP}, Hz)	$^{31}P\{^1H\}$, δ_P p.p.m.
(**2a**)	CH_2:	4.91 d.qn. (13.05, 5.76), 3.63 d.qn. (13.05, 3.51)	4.0 s
(**2b**)[b]	CH_2:	4.98 d.qn. (13.07, 6.15), 3.80 d.qn. (13.07, 3.44)	AA′BB′[c]
(**2c**)[d]	CH_2:	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′[e]
	$C(CH_3)$:	1.33 d.t. (7.29, 13.16), 0.98 d.t. (7.83, 10.07)	
(**4**)	CH_2:	6.09 d.t. (13.13, 13.29), 4.01 d.t. (14.25, 8.50) 2.64 m, 2.53 m	[f]
(**5**)[g]	CH:	6.97 t.qt. (7.33, 15.47), 3.53 t.qt.t. (7.00, 15.00, 2.50[h])	[f]
	$C(CH_3)$:	1.13 d.t. (7.33, 12.70), 1.00 d.t. (7.00, 10.26)	
(**6**)	CH_2:	4.90 d.qn. (13.0, 5.6),[i] 2.53 d.qn. (13.0, 3.54)[i]	—

[a] Measured at ambient temperatures in CD_2Cl_2 or $CDCl_3$; δ_H; proton integrations were correct in every system; δ_P downfield relative to external 85% H_3PO_4; s = singlet, d = doublet, t = triplet, qt = quartet, qn = quintet, un = unresolved multiplet, m = overlapping multiplets. [b] δ(Se*H*) −3.52 t, J_{HP} = 13.00 Hz. [c] Major peaks centred at δ 11.2 and 5.7. [d] δ(Se*H*) −3.55 qn, J_{HP} = 6.39 Hz. [e] δ 40.49, 22.83, and 20.21, 2.50. [f] Decomposition in solution during free induction decay (FID) accumulation. [g] 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. [h] Long range coupling to remote P atoms. [i] 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

$[Pd_2Cl_2(\mu\text{-dpmMe})_2]$ [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][4] 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^tOOH.§ The incorporation of the O-atom makes inequivalent all four of the $-CH_2-$ protons in (**4**), and the sets of $-CH(CH_3)$ protons in (**5**) (Table 1). The n.m.r. data for (**4**) resemble closely those for the corresponding μ-SO complex.[1] In contrast to the latter, no further oxidation to the $\mu\text{-SeO}_2$ 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_3-SeO moiety within an Fe_2Pt species.[5] I.r. bands found at ~770 cm^{-1} (Nujol) for (**4**) and (**5**) are assigned to ν_{SeO}.

Compound (**1**) in CH_2Cl_2–MeOH does react with H_2O [*cf.* equation (1)], but the reaction is complex and ^{31}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 $[Pd_2Cl_2(\mu\text{-O})(\mu\text{-dpm})_2]$, (**6**), is almost certainly formed at −50 °C in CD_2Cl_2 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.[3] 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 $[Os_2Cl_6(\mu\text{-O})(\mu\text{-dpm})_2]$ complex was not identified,[6] although extraction of oxygen from H_2O to give μ-oxo complexes is well documented for the early transition metals.[7]

Clearly, extraction of the main group element from H_2X (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_2 recovery.

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§ For example, (**2a**) was stirred with a 10-fold excess of Bu^tOOH in CH_2Cl_2 for 1 h; addition of diethyl ether yielded orange crystals of (**4**) in 85% yield. Elemental analysis, including O and Se, is satisfactory.