

Chemical Communications

Number 22
1986

Selenium Extrusion from a Pt–Se–P Bond Sequence and Selenium Insertion into a Pt–P Bond

Paul Peringer* and Johanna Schwald

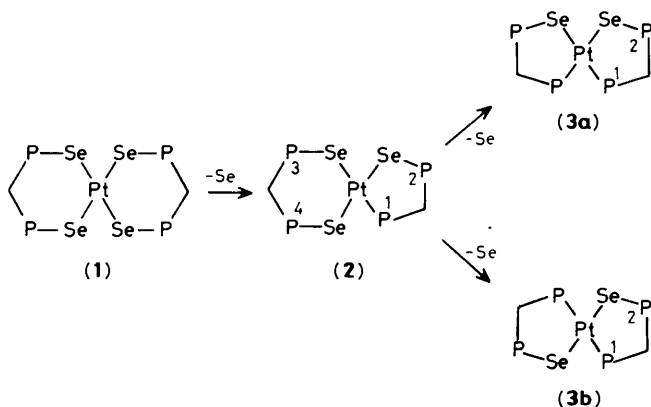
Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria

$[\text{Pt}(\eta^2\text{-dppmSe}_2)_2](\text{O}_3\text{SCF}_3)_2$ decomposes by stepwise selenium extrusion via $[\text{Pt}(\eta^2\text{-dppmSe}_2)(\eta^2\text{-dppmSe})](\text{O}_3\text{SCF}_3)_2$ to $[\text{Pt}(\eta^2\text{-dppmSe})_2](\text{O}_3\text{SCF}_3)_2$; the latter compound is also formed by the reaction of $[\text{Pt}(\eta^2\text{-dppm})_2]\text{Cl}_2$ and selenium or by rearrangement of $[\text{Pt}(\eta^2\text{-dppm})(\eta^2\text{-dppmSe}_2)](\text{O}_3\text{SCF}_3)_2$ [dppm = bis(diphenylphosphino)methane].

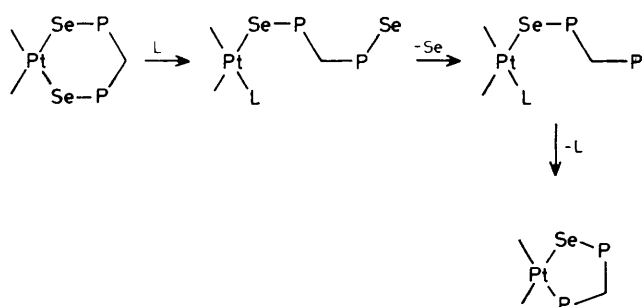
Tertiary phosphines readily react with elemental selenium to yield phosphine selenides.¹ We report here on the unprecedented reverse reaction where a metal-co-ordinated phosphine selenide decomposes into a co-ordinated phosphine and selenium. We observed that $[\text{Pt}(\eta^2\text{-dppmSe}_2)_2](\text{O}_3\text{SCF}_3)_2$ (**1**); from PtCl_2 , 2 dppmSe₂, and 2 TiO_3SCF_3 , which has two 6-membered PtSePCPSe chelate rings, converts in the presence of Cl⁻ or dppmSe₂ as catalyst via (**2**) into (**3a**) and (**3b**) each having 5-membered PtPCPSe rings (Scheme

1†). A possible mechanism is outlined in Scheme 2. The first step in Scheme 2 could proceed via a five-co-ordinate platinum intermediate and is slow, since the Pt–Se bond is kinetically stable on the n.m.r. time scale of $^2J(\text{Pt-P})$.

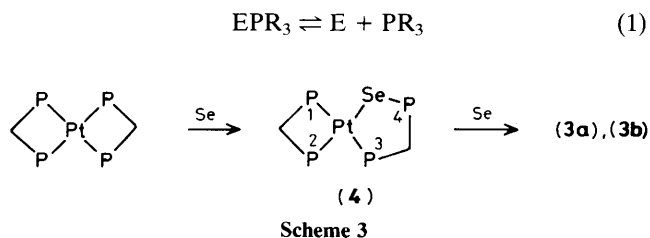
The second step in Scheme 2 seems to contradict the known behaviour of selenium with phosphines,¹ although another reaction which involves the breaking of a P–Se bond is known *i.e.* the transfer of selenium from tertiary phosphine selenides to tertiary phosphines.² Tellurium behaves similarly but leaves much more readily.³ These reactions were thought to proceed either via a $\text{R}_3\text{P} \cdots \text{E} \cdots \text{PR}_3$ intermediate (E = Se, Te), or by the establishment of a rapid equilibrium (1), E = Te.⁴ The reaction of selenium with phosphines is commonly seen as a P^{III}/P^V redox reaction.¹ The homologous phosphine tellurides have alternatively been described as phosphine complexes of tellurium(0) because of the kinetic lability of the P–Te bond.³ From this point of view the opening of a P–Te bond, equation (1), would be a dissociation as previously observed for other metal phosphine complexes. A dissociation equilibrium according to equation (1), E = Se, as the second step in Scheme 2 is thought to precede the co-ordination of phosphorus to platinum (third step in Scheme 2), which perhaps again involves a five-co-ordinate platinum intermediate. The favourable steric configuration, *i.e.* the formation of a 5-membered chelate ring, certainly facilitates this step.



Scheme 1

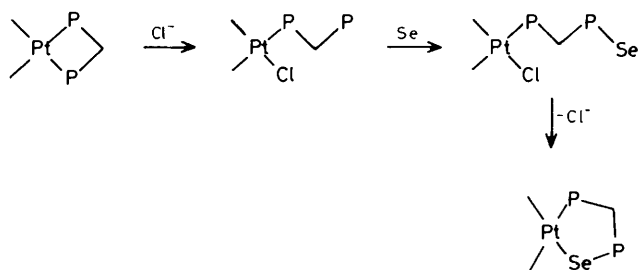


Scheme 2

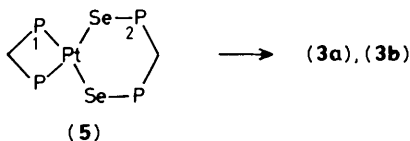


Scheme 3

† In structural formulae, dppm is drawn without the phenyl substituents, *e.g.* P–P = dppm, bis(diphenylphosphino)methane; the formal charges of the platinum(II) compounds are omitted.



Scheme 4



Scheme 5

Compounds (3a) and (3b) are also formed from PtCl_2 and 2 dppmSe₂ or by the reaction of $[\text{Pt}(\eta^2\text{-dppm})_2]\text{Cl}_2$ and selenium followed by conversion into the $[\text{O}_3\text{SCF}_3]^-$ salt by use of TiO_3SCF_3 . The insertion of selenium proceeds stepwise via (4) (Scheme 3), and represents an extension of the interesting chemistry of dppm.⁵ We propose the mechanism shown in Scheme 4. The first step in Scheme 4 is again thought to proceed via a five-co-ordinate platinum intermediate and is slow since the Pt-P bonds are kinetically stable on the n.m.r. time scale.

Compounds (3a) and (3b) are also formed from $[\text{Pt}(\eta^2\text{-dppm})(\eta^2\text{-dppmSe}_2)](\text{O}_3\text{SCF}_3)_2$ ((5), from $[\text{Pt}(\eta^2\text{-dppm})\text{Cl}_2]$, dppmSe₂, and 2 TiO_3SCF_3) in the presence of catalytic amounts of Cl^- (Scheme 5). This reaction is thought to proceed via a combination of extrusion and insertion of selenium.

The structural formulation of the complexes (1)–(5) is based on their characteristic $^{31}\text{P}\{^1\text{H}\}$ and $^{195}\text{Pt}\{^1\text{H}\}$ n.m.r. spectra.‡ Particularly conclusive are the multiplicities of the ^{195}Pt n.m.r. signals and the values of the Pt-P coupling constants.

Satisfactory elemental analyses were obtained for (1) and (5). The reactions did not seem to be sensitive to the presence of dioxygen or light and the analogous insertion of tellurium does not occur.

Received, 2nd April 1986; Com. 436

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‡ ^{31}P shifts are relative to H_3PO_4 , ^{195}Pt shifts are relative to Na_2PtCl_6 , positive being to high frequency of the reference, in p.p.m., *J* in Hz, d = doublet, t = triplet, q = quintet.

- (1): δ_{P} 15.1 (J_{PtP} 111), δ_{Pt} -4283 q.
 (2): δ_{P_1} 23.2 (J_{PtP_1} 3294; $J_{\text{P}_1\text{P}_2}$ 40; $J_{\text{P}_1\text{P}_4}$ 18), δ_{P_2} 37.4 (J_{PtP_2} 69), δ_{P_3} 17.8 (J_{PtP_3} 69), δ_{P_4} 18.0 (J_{PtP_4} 120), δ_{Pt} -4767 ddt.
 (3a): δ_{P_1} 21.3 (J_{PtP_1} 3230; $J_{\text{P}_1\text{P}_2}$ 30), δ_{P_2} 32.7 (J_{PtP_2} 57), δ_{Pt} -4874 tt.
 (3b): δ_{P_1} 22.8 (J_{PtP_1} 2367; $|J_{\text{P}_1\text{P}_2} + J_{\text{P}_1\text{P}_2}'|$ 90), δ_{P_2} 38.6 (J_{PtP_2} 90), a large $J_{\text{P}_1\text{P}_2}$ is indicated by deceptively simple triplet ^{31}P n.m.r. signals, δ_{Pt} -5002 tt.
 (4): δ_{P_1} -41.9 (J_{PtP_1} 1937; $J_{\text{P}_1\text{P}_2}$ 68; $J_{\text{P}_1\text{P}_3}$ 356; $J_{\text{P}_1\text{P}_4}$ 37), δ_{P_2} -46.2 (J_{PtP_2} 2688; $J_{\text{P}_2\text{P}_3}$ -9; $J_{\text{P}_2\text{P}_4}$ -7), δ_{P_3} 27.5 (J_{PtP_3} 2376; $J_{\text{P}_3\text{P}_4}$ 52), δ_{P_4} 40.7 (J_{PtP_4} 102), δ_{Pt} -4581 dddd.
 (5): δ_{P_1} -54.9 (J_{PtP_1} 2645), δ_{P_2} 20.9 (J_{PtP_2} 101), δ_{Pt} -4379 tt.