Novel Ring Opening and Halogen Transfer from Platinum(II) to Phosphorus in the Reaction of $[PtCl_2(CNR)_2]$ (R = Bu^t, *p*-$MeOC_6H_4$) with the Phosphirene Ring PPhCPh=CPh. Crystal and Molecular Structure of the Dimeric Chlorophosphane Complex $[PtCl(PClPhCPh{=}CPh)(CNBu^t)]_2$

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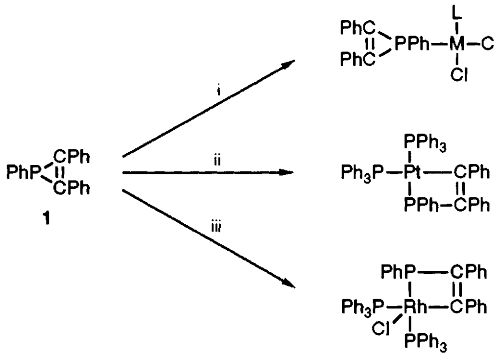
A new type of ligating behaviour of the phosphirene ring system PPhCPh=CPh is described, in which novel dimeric platinum(II) chlorophosphane complexes result from phosphirene ring opening and a Pt–Cl bond-insertion reaction.

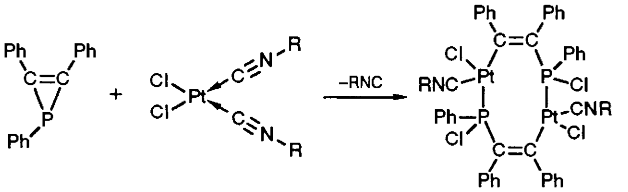
There is considerable current interest in the chemistry of phosphirene ring systems.[1–5] Previously,[1,6–7] we have described the different ligating behaviour exhibited by the phosphirene ring PPhCPH=CPh **1** towards transition metal centres. Thus, whereas κ*P*-coordinated phosphirene complexes of Pd^{II} and Pt^{II} are quantitatively formed with $[MCl_2L]$ fragments (M = Pd, Pt; L = PEt_3, PPhCPh=CPh), zerovalent platinum and Rh^I metal complexes, on the other hand, readily insert into the P–C bond of the phosphirene to afford Pt^{II} and Rh^{III} products, respectively[2,3] (see Scheme 1).

Very recently, in attempting to extend the range of κ*P*-ligated phosphirene complexes of Pt^{II} containing coordinated isonitrile ligands, we unexpectedly observed a different reaction type, in which novel dimeric platinum(II) halogenophosphane complexes are obtained (Scheme 2).

Thus, $[PtCl_2(CNR)_2]$ **2** (R = Bu^t) and **3** (R = *p*-$MeOC_6H_4$) readily react with **1** at room temperature to afford $[PtCl(PClPhCPh{=}CPh)(CNR)]_2$ **4** (R = Bu^t) and **5** (R = *p*-$MeOC_6H_4$), respectively, [ν(C≡N) *ca.* 2198 cm^{-1}], essentially quantitatively. The dimeric nature of the complexes **4** and **5** was suggested by analysis and simulation of their $^{31}P\{^1H\}$ NMR spectra, which are AA′XX′ spin systems (A = ^{31}P, 100% abundant; X = ^{195}Pt, 34% abundant, *e.g.* for **4** ($^1J_{PtP}$ 4694, $^2J_{PtP}$ 187, $^4J_{PP'}$ 27 Hz).



Scheme 1 *Reagents*: i, M = Pd, Pt; L = PPhCPh=CPh, PEt_3; $[MCl_2(PEt_3)]_2$ or $[MCl_2(cod)]$ (cod = cyclooctadiene); ii, $[Pt(PPh_3)_2(C_2H_4)]$; iii, $[RhCl(PPh_3)_3]$



1

2; R = Bu^t
3; R = p-MeOC$_6$H$_4$

4; R = Bu^t
5; R = p-MeOC$_6$H$_4$

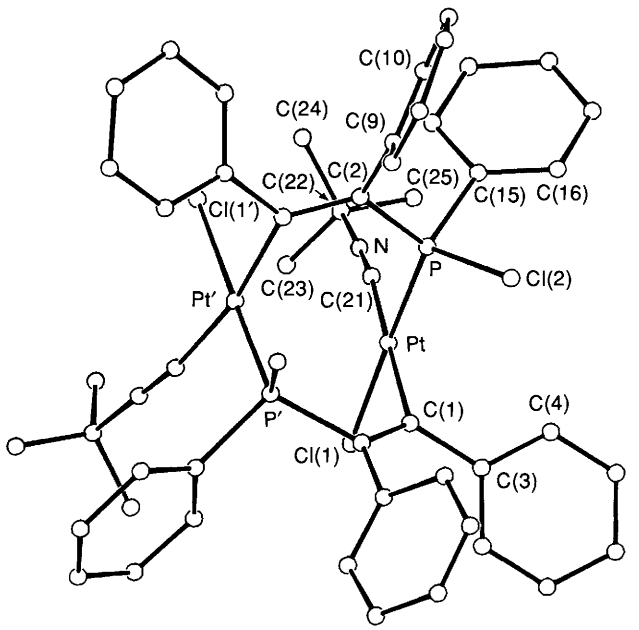


Fig. 1 Molecular structure of [PtCl(PClPhCPh=CPh)(CNBu^t)]$_2$. Important bond lengths (Å) and bond angles (°) are: Pt–Cl (1) 2.354(5), Pt–P 2.250(3), Pt–C(1) 2.041(12), Pt–C(21) 1.988(14), P–Cl(2) 2.065(5), P–C(2) 1.803(10), Cl(1)–Pt–P 178.1(1), Cl(1)–Pt–C(1) 85.3(3), Cl(1)–Pt–C(21) 86.2(4), P–Pt–C(1) 85.3(3), Cl(1)–Pt–C(21) 86.2(4), P–Pt–C(1) 93.1(3), P–Pt–C(21) 95.3(4), C(1)–Pt–C(21) 170.3(5), Pt–P–Cl(2) 114.2(2), Pt–P–C(2) 121.8(4), Pt–P–C(15) 110.4(4).

The large value observed for $^1J_{\mathrm{PtP}}$ is especially significant, and is typical for the presence of a halogenophosphane ligand occupying a *trans*-position to chloride in a square-planar platinum(II) complex.[8] The migration of Cl from Pt to P and the dimeric nature of the complexes **4** and **5** were subsequently established by a single-crystal X-ray crystallographic study on **4** (see Fig. 1).† Further mechanistic studies of these reactions are planned, but it seems that, unlike the Pt^0 and Rh$^{\mathrm{I}}$ systems previously reported,[1,6,7] the reaction may not involve direct insertion of the metal into the phosphirene ring, since this would result in a Pt$^{\mathrm{IV}}$ intermediate. The reaction could proceed by initial κ*P* coordination of the phosphirene (with loss of RNC), followed by chloride ion displacement prior to the insertion step and Cl$^-$ attack at phosphorus.

Interestingly, whereas with phosphirenes, the isonitrile simply acts as a spectator ligand, analogous reactions of isonitrile complexes of Pd$^{\mathrm{II}}$ and Pt$^{\mathrm{II}}$ with related ring systems such as aziridines, thiiranes, and oxiranes led to neutral five-memered ring cyclic diamino-, aminothio- and aminooxy-carbene complexes.[9]

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† *Crystal data*: C$_{50}$H$_{40}$Cl$_4$N$_2$P$_2$Pt$_2$, M = 1270.9, monoclinic, space group $C2/c$ (No. 15), a = 22.284(9), b = 12.157(5), c = 18.250(6) Å, β = 100.31(3)°, U = 4864.2 Å^3, Z = 4, D_c = 1.74 g cm^{-3}. The structure was solved by heavy-atom methods, using 3049 reflections (from a total of 4500 unique reflections, having $|F^2| > 2\sigma(F^2)$ collected on an Enraf-Nonius CAD4 diffractometer, using Mo-Kα radiation, λ = 0.71069 Å, μ = 61.3 cm^{-1}. The final residuals were R = 0.054, R_w = 0.065. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.