Terminal Phosphido-complexes of Co-ordinatively Saturated and Unsaturated Platinum(II)

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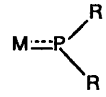
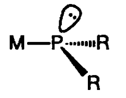
Reactions of $[Pt\{PPh(CH_2CH_2PPh_2)_2\}Cl]Cl$ or $[Pt\{P(CH_2CH_2PPh_2)_3\}Cl]Cl$ with PR_2H (R = Ph or C_6H_{11}) and $Tl(O_3SCF_3)$ give secondary phosphine complexes $[Pt\{PPh(CH_2CH_2PPh_2)_2\}(PR_2H)][O_3SCF_3]_2$ or $[Pt\{P(CH_2CH_2PPh_2)_3\}(PR_2H)][O_3SCF_3]_2$. The corresponding terminal phosphido complexes were prepared by deprotonation with aqueous KOH or $Na[N(SiMe_3)_2]$. The new complexes were characterised by ^{31}P and ^{195}Pt n.m.r. spectroscopy. Phosphorus-31 n.m.r. spectra indicate that the geometry at the terminal phosphido phosphorus is pyramidal.

Interest in transition-metal terminal-phosphido complexes $M(PR_2)L_n$ stems from the fact that metal–phosphorus multiple bonding may or may not be involved depending on the electronic requirements of the ML_n part. In co-ordinatively unsaturated metal fragments the phosphido-ligand lone pair may be delocalised to a suitable empty metal orbital, which generates a planar geometry at phosphorus, (**a**).[1–6] In co-ordinatively saturated metals the phosphido lone pair should remain non-bonding, leading to a pyramidal geometry at phosphorus, (**b**).[7–13] In this paper we report on terminal-phosphido complexes of co-ordinatively saturated and unsaturated platinum(II). The sole terminal phosphido complex of platinum reported so far is $[PtCl(PEt_3)_2(PCl_2)]$.[14]



(**a**)



(**b**)

Experimental

All manipulations were performed under an inert atmosphere (N_2 or Ar) in dried solvents. N.m.r. spectra were recorded on a Bruker WP-80 spectrometer. Elemental analyses were provided by the Institut für Physikalische Chemie der Universität Wien. The compounds $[Pt\{PPh(CH_2CH_2PPh_2)_2\}Cl]Cl$ and $[Pt\{P(CH_2CH_2PPh_2)_3\}Cl]Cl$ were prepared by literature methods;[15,16] all other reagents are commercially available.

Preparations.—$[Pt\{PPh(CH_2CH_2PPh_2)_2\}(PPh_2H)][O_3SCF_3]_2$ (**1a**). The salt $Tl(O_3SCF_3)$ (77.7 mg, 0.22 mmol) in MeOH (0.1 cm^3) was added to $[Pt\{PPh(CH_2CH_2PPh_2)_2\}Cl]Cl$ (80.1 mg, 0.1 mmol) and PPh_2H (17.4 μl, 0.1 mmol) in CH_2Cl_2 (1 cm^3). After stirring for 1 h, the volatiles were removed *in vacuo*. The residue was extracted with CH_2Cl_2, TlCl and excess of $Tl(O_3SCF_3)$ were filtered off. Evaporation to dryness afforded 116 mg (96%) of colourless microcrystals of complex (**1a**). Crystals may be obtained from CH_2Cl_2–MeOH (Found: C, 47.5; H, 3.6. Calc. for $C_{48}H_{44}F_6O_6P_4PtS_2$: C, 47.50; H, 3.65%).

The same procedure was used for $[Pt\{PPh(CH_2CH_2PPh_2)_2\}\{P(C_6H_{11})_2H\}][O_3SCF_3]_2$ (**2a**) (Found: C, 46.5; H, 4.6. Calc. for $C_{48}H_{56}F_6O_6P_4PtS_2$: C, 47.00; H, 4.60), $[Pt\{P(CH_2CH_2PPh_2)_3\}(PPh_2H)][O_3SCF_3]_2$ (**3a**) (Found: C, 49.3; H, 3.8. Calc. for $C_{56}H_{53}F_6O_6P_5PtS_2$: C, 49.80; H, 3.95%), and $[Pt\{P(CH_2CH_2PPh_2)_3\}\{P(C_6H_{11})_2H\}][O_3SCF_3]_2$ (**4a**) (Found: C, 48.6; H, 4.7. Calc. for $C_{56}H_{65}F_6O_6P_5PtS_2$: C, 49.40; H, 4.80%).

$[Pt\{PPh(CH_2CH_2PPh_2)_2\}(PPh_2)]O_3SCF_3$ (**1d**). Aqueous KOH (0.5 cm^3, 4 mol dm^{-3}) was added to complex (**1a**) (121.4 mg, 0.1 mmol) in CH_2Cl_2 (1 cm^3) and stirred for 5 min. The CH_2Cl_2 phase turned red and was separated and concentrated *in vacuo* to *ca.* 0.1 cm^3. The product (**1b**) (95 mg, 89%) was precipitated as red crystals by addition of hexane (1 cm^3) (Found: C, 52.7; H, 4.0. Calc. for $C_{47}H_{43}F_3O_3P_4PtS$: C, 53.05; H, 4.05%).

The same procedure as above was used for $[Pt\{PPh(CH_2CH_2PPh_2)_2\}\{P(C_6H_{11})_2\}]O_3SCF_3$ (**2b**) (Found: C, 50.7; H, 5.3. Calc. for $C_{47}H_{55}F_3O_3P_4PtS{\cdot}0.5CH_2Cl_2$: C, 50.95; H, 5.05%) and $[Pt\{P(CH_2CH_2PPh_2)_3\}(PPh_2)]O_3SCF_3$ (**3b**) (Found: C, 52.1; H, 4.0. Calc. for $C_{55}H_{52}F_3O_3P_5PtS{\cdot}CH_2Cl_2$: C, 52.35; H, 4.25%).

$[Pt\{P(CH_2CH_2PPh_2)_3\}\{P(C_6H_{11})_2\}]O_3SCF_3$ (**4b**). The salt $Na[N(SiMe_3)_2]$ (18.3 mg, 0.1 mmol) was added to complex (**4a**) (136.2 mg, 0.1 mmol) in CH_2Cl_2 (1 cm^3). After stirring for 1 h the volatiles were removed *in vacuo*. The residue was extracted with CH_2Cl_2 and $Na(O_3SCF_3)$ was filtered off. Complex (**4b**) could not be crystallised.

Results and Discussion

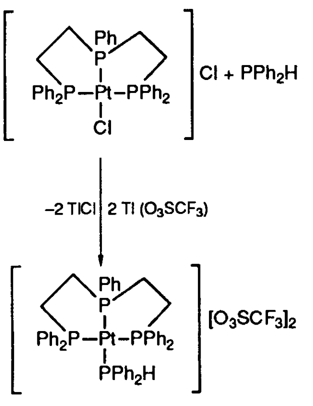
Reaction of $[Pt\{PPh(CH_2CH_2PPh_2)_2\}Cl]Cl$ with diphenylphosphine and $Tl(O_3SCF_3)$ gave the secondary phosphine complex (**1a**) in almost quantitative yield [equation (1)]. In the absence of $Tl(O_3SCF_3)$, $[Pt\{PPh(CH_2CH_2PPh_2)_2\}(PPh_2H)Cl_2]$ (**1b**) is formed in a temperature-dependent equilibrium. Lowering the temperature shifts the reaction to the product side. Below 233 K, (**1b**) is present exclusively. The n.m.r. parameters of (**1a**), (**1b**), and the similarly formed iodide $[Pt\{PPh(CH_2CH_2PPh_2)_2\}(PPh_2H)I_2]$ (**1c**) are markedly different indicating the presence of five-co-ordinate platinum complexes $[Pt\{PPh(CH_2CH_2PPh_2)_2\}(PPh_2H)X]X$ (X = Cl or I) (Table)

The dicyclohexylphosphine complex $[Pt\{PPh(CH_2CH_2PPh_2)_2\}\{P(C_6H_{11})_2H\}][O_3SCF_3]_2$ (**2a**) and the complexes $[Pt\{P(CH_2CH_2PPh_2)_3\}(PPh_2H)][O_3SCF_3]_2$ (**3a**) [equation (2)] and $[Pt\{P(CH_2CH_2PPh_2)_3\}\{P(C_6H_{11})_2H\}][O_3SCF_3]_2$ (**4a**) were prepared analogously. The secondary phosphine

Table. N.m.r. data[a]

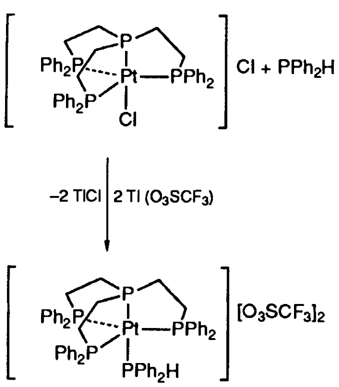
	$\delta(P_A)$	$J(PtP_A)$	$\delta(P_B)$	$J(PtP_B)$	$\delta(P_X)$	$J(PtP_X)$	$J(P_BP_X)$	$\delta(Pt)$	T/K
(1a)	41.5	2 272	99.4	2 230	−18.1	2 393	288	−5 272[d]	213
(1b)	38.6	2 550	93.4	2 332	−14.5	2 479	304		213
(1c)	31.2	2 741	84.0	2 252	−19.3	2 319	320		213
(1d)	40.0	2 826	92.0	1 637	−2.2	987	96	−4 989[b]	273
(2a)	43.6	2 304	102.9	2 126	9.4	2 231	267	−5 306[b]	213
(2b)	37.9	2 880	88.7	1 457	−11.1	860	64	−4 998[b]	300
(3a)	25.3	2 365	133.5	1 784	−33.2	1 960	288	−5 288[c]	300
(3b)	13.7	2 768	114.4	1 498	−39.8	937	53	−5 029[c]	300
(4a)	25.8	2 454	131.1	1 613	−24.3	*d*	260		183
(4b)	34.5	2 876	111.7	1 369	−19.1	819	44		193

[a] Chemical shifts in p.p.m. relative to 85% H_3PO_4 or 1 mol dm^{-3} $Na_2[PtCl_6]$; coupling constants in Hz. Notation: $P_BPh(CH_2CH_2P_APh_2)_2$, $P_B(CH_2CH_2P_APh_2)_3$, and P_X indicates the unidentate phosphorus ligand (PR_2H or PR_2). [b] ddt (d = doublet, t = triplet). [c] ddq (q = quartet). [d] Not resolved.



(1)

(1a)



(2)

(3a)

complexes were characterised by microanalysis and n.m.r. (^{31}P, ^{195}Pt) spectroscopy (Table).

In solutions of **(4a)** there is a temperature-dependent equilibrium between the five-co-ordinate isomer and the four-co-ordinate isomer in which one terminal phosphine group of $P(CH_2CH_2PPh_2)_3$ remains non-bonded. The interconversion of the two species is rapid on the ^{31}P n.m.r. time-scale. In the four-co-ordinate species the $P(CH_2CH_2PPh_2)_3$ ligand undergoes rapid exchange involving the co-ordinated and free terminal phosphorus atoms, presumably *via* the five-co-ordinate isomer as an intermediate. A related dynamic behaviour has been reported for $[PtMe_2\{PPh(CH_2CH_2PPh_2)_2\}]$ and $[PtMe_2\{P(CH_2CH_2PPh_2)_3\}]$.[17]

The ^{31}P n.m.r. spectrum of complex **(4a)** consists of an AM_3X pattern. In contrast to **(3a)**, the n.m.r. parameters are strongly temperature dependent. At 300 K the shifts and coupling constants are: $\delta(P_A)$ 25.6, $\delta(P_B)$ 111.7, $\delta(P_X)$ 2.8, $J(PtP_A)$ 1 760, $J(PtP_B)$ 1 949, $J(PtP_X)$ 2 143, and $J(P_BP_X)$ 263 Hz; notation as in the Table. Upon cooling, the data gradually approach those at 183 K, included in the Table. The temperature dependence is due to averaging of the values of the four- and five-co-ordinate isomers present in different concentrations. This is exemplified for the resonance position of the central phosphorus atom of the $P(CH_2CH_2PPh_2)_3$ ligand. Caused by the additive nature of the ring contribution,[18] the central phosphorus of complexes $[Pt\{PPh(CH_2CH_2PPh_2)_2\}(PR_3)][O_3SCF_3]_2$ has resonances at *ca.* 100 p.p.m., whilst for $[Pt\{P(CH_2CH_2PPh_2)_3\}(PR_3)][O_3SCF_3]_2$ $\delta(P)$ values of *ca.* 130 p.p.m. are observed (Table). The resonances $\delta(P)$ of the central phosphorus of tridentate $P(CH_2CH_2PPh_2)_3$ present in the four-co-ordinate species is expected to fall in the same region as for the $PPh(CH_2CH_2PPh_2)_2$ complexes. The ^{31}P shift of $[Pt\{P(CH_2CH_2PPh_2)_3\}\{P(C_6H_{11})H\}][O_3SCF_3]_2$ at 300 K (111.7 p.p.m.) thus indicates a substantial equilibrium concentration of the *P,P′,P″*-bonded isomer. At 183 K the five-co-ordinate isomer dominates as can be seen from the close correspondence of the data with those for **(3a)**.

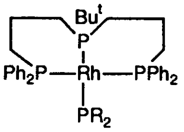
Treatment of the secondary phosphine complexes **(1a)**, **(2a)**, and **(3a)** with aqueous KOH gave the corresponding terminal phosphido complexes **(1d)**, **(2b)**, and **(3b)** which were isolated in good yields. The complete deprotonation of **(4a)** requires $Na[N(SiMe_3)_2]$ as base. The deprotonation of all the secondary phosphine complexes is associated with a change in colour to deep red. The terminal phosphido complexes were characterised as described for the secondary phosphine complexes.

In the four-co-ordinate $PPh(CH_2CH_2Ph_2)_2$ complexes **(1d)** and **(2b)** the phosphido ligand may act either as a two-electron donor involving a 16-electron platinum species or as four-electron σ,π donor involving an 18-electron species. In contrast, the five-co-ordinate $P(CH_2CH_2PPh_2)_3$ complexes **(3b)** and **(4b)** are co-ordinatively saturated implying that the phosphido lone pair is non-bonded.

The ^{31}P n.m.r. chemical shifts of phosphido ligands provide a probe of the bonding mode. Resonances at very high frequencies (up to +400 p.p.m.)[2] appear to be indicative of a metal–phosphorus bond order greater than one. The chemical shifts of complexes **(1d)** and **(2b)** are −2.2 and −11.1 p.p.m.; those of **(3b)** and **(4b)** are −39.8 and −19.1 p.p.m. This clearly demonstrates the presence of a pyramidal geometry (**b**) of the phosphido ligand for both the co-ordinatively saturated and the unsaturated complexes. A pyramidal geometry is also supported by the magnitude of the platinum–phosphorus coupling being reduced from that of the corresponding protonated complexes. This was previously observed for the tungsten complexes [W(cp)$(CO)_2(PMe_3)(PPh_2H)$]Cl and [W(cp)$(CO)_2(PMe_3)(PPh_2)$] (cp = η-C_5H_5) and was rationalised in terms of a decreased *s* character of the tungsten–phosphorus bond caused by the p^3 hybridisation of the terminal phosphido ligand.[19] In contrast, multiple metal–phosphorus bonding should result in a drastic increase in the one-bond metal–phosphorus coupling.[2,5]

The deprotonation of the secondary phosphine complexes is associated with a marked decrease in the two-bond phosphorus–phosphorus *trans* coupling involving the central phosphorus atom of the $PPh(CH_2CH_2PPh_2)_2$ or $P(CH_2CH_2PPh_2)_3$ ligand and the unidentate phosphorus ligand from *ca.* 300 Hz to the unusually small values of 44—96 Hz (Table).

It is interesting that the related rhodium(I) complexes depicted below exhibit a ^{31}P n.m.r. resonance at 26.2 p.p.m. for R = Ph but at 185.8 p.p.m. for R = C_6H_{11}, indicating multiple Rh–P bonding for the cyclohexyl derivative.[1]



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