Journal of Organometallic Chemistry, 139 (1977) 355—359
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HYDRIDOCYANOMETHYL COMPLEXES OF PLATINUM(II) *

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(Received May 25th, 1977)

Summary

The preparation and spectroscopic properties are described of some novel platinum(II) complexes having a hydride ligand *cis* or *trans* to an sp^3 carbon, vis. $PtH(CH_2CN)(PPh_3)_2$ and $PtH(CH_2CN)(L—L)$ with L—L = bis(diphenylphosphino)-ethene, -ethane, -propane and bis(diphenylarsino)ethane.

We previously reported the preparation, spectroscopic properties and reactions of various complexes of platinum(II) of the type $PtX(YCN)L_2$ (L = tertiary phosphine; Y = $(CH_2)_n$, $n = 1, 2, 3$, o-$CH_2C_6H_4$; X = Cl, Br) and their cationic derivatives $[Pt(YCN)L_2]_m(BF_4)_m$ [2] in which the CN group is σ-coordinated. We have now shown that while heating the cationic complexes in methanol leads to nucleophilic attack at the CN group, yielding iminoether complexes, methanolic NaOH gives good yields of the novel hydrido complex *trans*-$PtH(CH_2CH_2CH_2CN)(PPh_3)_2$. The enhanced strength of the Pt—C bond of cyanoalkyl complexes compared to that of the parent alkyl complexes allows the coexistence of Pt—H and σ-Pt—C bonds in the same compound.

However, this preparation is not a general one. Indeed, the first product formed in methanolic NaOH is the hydroxo complex $PtOH(YCN)L_2$; its hydroxo group may then react intramolecularly with the CN group giving $[Pt(YCONH)L_2]_2$ in cases in which the cyanoalkyl ligand has a favourable geometry to give dimeric imido complexes. This prevents any further reaction, as the imido complexes are particularly stable in basic media. When Y = CH_2 or o-$CH_2C_6H_4$, this reaction gives negligible yields of hydrido complexes and the classical route to hydrides starting with the chloro complexes $PtCl(YCN)L_2$ and $NaBH_4$ is preferred. Treatment of *trans*-$PtCl(CH_2CN)(PPh_3)_2$ (Ia) [2] with

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[*] For a preliminary account see ref. [1].

[**] Abstracted in part from the Ph.D. thesis of R. Bataillard, University of Lausanne (1977).

[***] Centro Chimica e Tecnologia Composti Metallorganici Elementi Transizione C.N.R.

TABLE 1

^1H AND ^{31}P NMR SPECTRAL DATA FOR CYANOMETHYL COMPLEXES OF PLATINUM(II)

Complex	δ(CH_2)[a] (ppm)	^2J(PtCH); (Hz)	^3J(PPtCH) (Hz)	δ(H) (ppm)	^1J(PtH); (Hz)	^2J(PPtH) (Hz)	δ(P)[h] (ppm)	^1J(P—Pt); (Hz)	^2J(PP) (Hz)
Ib PtCl(CH_2CN)($Ph_2PCH{=}CHPPh_2$)	b						47.0d 54.6d	3920 [k]; 2175	7
Ic PtCl(CH_2CN){$Ph_2P(CH_2)_2PPh_2$}	b						43.1d 44.1d	3887; 2158	3
IdPtCl(CH_2CN){$Ph_2P(CH_2)_3PPh_2$}	1.35dd [c] 2.45 m [d]	76;	4.4 (*cis*) 8.2 (*trans*)				−1.0d −2.7d	3769 [k]; 2019	26
Ie PtCl(CH_2CN){$Ph_2As(CH_2)_2AsPh_2$}	2.3 m								
Ih PtCl(CH_2CN)(PPh_3)($PPhMe_2$)	1.30dd 1.30d [e]	73;	5.6 (*cis*) 9.2 (*trans*)				16.2d [i] −11.5d	4147; 2068	19
IIa trans-PtH(CH_2CN)(PPh_3)$_2$	0.63td	70;	6.2	−7.32tt	746;	16 [g]	32.2t	3034	
IIb PtH(CH_2CN)($Ph_2PCH{=}CHPPh_2$)	2.20dd	97;	7.4 (*cis*) 9.3 (*trans*)	−1.40dd	1154;	17 (*cis*) 205 (*trans*)	60.0d 61.2d	1735 [l] 2322	
IIc PtH(CH_2CN){$Ph_2P(CH_2)_2PPh_2$}	2.2 m			−1.70dd	1132;	15 (*cis*) 200 (*trans*)	48.2t [j] 51.2t	1744 2372	
IId PtH(CH_2CN){$Ph_2P(CH_2)_3PPh_2$}	1.48t [f] 2.55 m [d]	95	8.8	−2.6 dd	1092;	19 (*cis*) 198 (*trans*)	5.0d 1.7d	1713; 2344	21
IIe PtH(CH_2CN){$Ph_2As(CH_2)_2AsPh_2$}	2.47t 2.25 m	109		−6.08t	1309				

[a] In CD_2Cl_2 at room temperature; TMS as internal standard. [b] see [3]. [c] d: doublet, m: multiplet, t: triplet. [d] P—CH_2 protons. [e] P—CH_3 protons: ^2J(PH) 9.7 Hz, ^3J(PtPH) 19.6 Hz. [f] Accidental degeneracy of the two ^3J(PPtCH). [g] ^3J(HCPtH) 3 Hz for IIa, 0.8 Hz for IIb. [h] In CD_2Cl_2 at room temperature; positive sign for a resonance at lower field than 85% H_3PO_4 (external reference). [i] PPh_3 *trans* to Cl. [j] ^2J(PP) < 1 Hz. [k] P trans to Cl. [l] P *trans* to H: a ^2J(PPtH) 200 Hz centered at 60.0 ppm is observed in the undecoupled spectrum.

$NaBH_4$ in methanol yields *trans*-$PtH(CH_2CN)(PPh_3)_2$ (IIa), the first example of a platinum(II) complex with a hydride ligand *trans* to an sp^3 carbon. *cis*-Hydrido complexes are obtained from reactions $PtCl(CH_2CN)(L—L)$ (L—L $= Ph_2PCH{=}CHPPh_2$ [3] Ib, $Ph_2P(CH_2)_2PPh_2$ [3] Ic, $Ph_2P(CH_2)_3PPh_2$ Id, $Ph_2As(CH_2)_2AsPh_2$ Ie) with $NaBH_4$ in ethanol yielding $PtH(CH_2CN)(L—L)$ (IIb—e). IIb—d are also obtained by displacing PPh_3 from IIa by L—L in benzene. This last reaction is a good example of a *trans*—*cis* isomerization around platinum(II) occurring without the formation of a cationic 4-coordinated intermediate.

No hydrido complexes could be isolated from $PtCl(CH_2CN)(PPh_3)(PPhMe_2)$ (Ih) or from complexes with nitrogen donor atoms $PtCl(CH_2CN)$(*o*-phen) (If) and $PtCl(CH_2CN)$(bipy) (Ig).

The complexes were characterized by ^1H and ^{31}P NMR (Table 1), IR and Raman spectra and elemental analysis (Table 2). The $^{31}P\{^1H\}$ FT NMR spectra of Ib—d show two doublets with additional splitting due to ^{195}Pt; the higher coupling constant $^1J(Pt—P)$ is attributed to the phosphorus atom *trans* to Cl since chloride has a smaller *trans* influence than carbon. In the mixed phosphine complex Ih, PPh_3 is *trans* to chloride since the lower ^{31}P signal is associated with the greater coupling constant $^1J(Pt—P)$ (the ^{31}P resonance of $PPhMe_2$ appears generally at higher field than that of PPh_3 [4]). The hydrido complexes IIa—e are white crystalline solids stable in air, soluble in chloroalkanes and insoluble in alcohols. The *trans* geometry of IIa is deduced from its NMR spectra: a triplet of triplets for the hydride resonance due to coupling with two equivalent phosphorus nuclei and two methylene protons, and a single ^{31}P resonance. All the other hydrido complexes have a *cis* geometry: the $^{31}P\{^1H\}$ FT

TABLE 2

ANALYTICAL, IR AND RAMAN SPECTRAL DATA

Complex	M.p. (dec.) (°C)	Analysis found (calcd.)(%)				ν(CN) [c] (cm^{-1})	Others (cm^{-1})
		C	H	N	X		
Id	232—233	50.92	4.13	2.09	P 8.79	IR 2208 s	301 m ν(PtCl)
		(51.00)	(4.13)	(2.05)	(9.07)	R 2192 s	298 m
Ie	238—241	44.55	3.50	1.55	Cl 4.88	IR 2203 s	305 m ν(PtCl)
		(44.43)	(3.46)	(1.85)	(4.68)		
If	285—290	36.44	2.17	8.56		IR 2204 s	340 s ν(PtCl)
		(37.30)	(2.24)	(9.32)			
Ig	273—275	33.07	2.30	9.20		IR 2201 s	337 s ν(PtCl)
		(33.77)	(2.36)	(9.85)			
Ih	205—206	50.14 [a]	4.25	2.11	P 9.40	IR 2203 s	309 s ν(PtCl)
		(50.12)	(4.21)	(2.09)	(9.23)		
IIa	164—165	60.19	4.51	2.03	P 8.01	IR 2183 s	2027 s [b] ν(Pt—H); 808 δ(Pt—H)
		(60.01)	(4.37)	(1.84)	((8.14)	R 2178 s	2033 s
IIb	193—195	52.82	3.90	2.21	P 9.66	IR 2196 s	2020 s [b] ν(Pt—H)
		(53.17)	(3.99)	(2.21)	(9.79)	R 2196 s	2020 s
IIc	200—202	52.99	4.28	2.26	P 9.45	IR 2198 s	2013 s [b] ν(Pt—H); 795 δ(Pt—H)
		(53.00)	(4.29)	(2.21)	(9.76)	R 2190 s	2011s, 2013s ν(Pt—H)
IId	167—168	53.71	4.56	2.25	P 9.28	IR 2199 s	2025 s [b] ν(Pt—H)
		(53.70)	(4.51)	(2.16)	((9.55)	R 2192 s	2018 s
IIe	170—172	46.92	3.90	2.02		IR 2196 s	2063 s [b] ν(Pt—H)
		(46.55)	(3.77)	(1.94)			

[a] Cl 5.44(5.19) for Id, 5.37(5.28) for Ih. [b] broad. [c] IR in nujol mulls, R: powdered samples.

NMR spectra show two doublets; the smaller coupling constant ^{1}J(Pt—P) is attributed to the phosphorus atom *trans* to the hydride ligand, since H$^-$ is known to have a very high *trans* influence. Indeed, the coupled ^{31}P NMR spectra show a large additional ^{2}J(P—Pt—H) of ca. 200 Hz associated with the resonance bearing the smaller ^{1}J(Pt—P) for IIb—e. No correlation between ν(Pt—H) and ^{1}J(Pt—H) was found for these complexes.

We are currently examining the reactivity of the Pt—H bond towards various unsaturated molecules.

Experimental

The spectroscopic techniques were described earlier [2]. The Institute of Organic Chemistry (University of Padova) carried out the microanalyses.

Preparation of complexes

PtCl(CH$_2$CN){Ph$_2$P(CH$_2$)$_3$PPh$_2$} (Id). A mixture of *cis* and *trans*-PtCl(CH$_2$CN)(PPh$_3$)$_2$ (6 g) (obtained by treating Pt(PPh$_3$)$_4$ with chloroacetonitrile in benzene [2,3]) was stirred in benzene (100 ml) with bis(diphenylphosphino)propane (4 g) for 15 h at room temperature. The solid was filtered off, washed with ether, and recrystallized from dichloromethane/methanol. Yield 93%.

PtCl(CH$_2$CN){Ph$_2$As(CH$_2$)$_2$AsPh$_2$} (Ie), PtCl(CH$_2$CN)(o-phen) (If) and PtCl(CH$_2$CN)(bipy) (Ig). *trans*-PtCl(CH$_2$CN)(AsPh$_3$)$_2$ [2] (1 g) was stirred in dichloromethane (20 ml) with bis(diphenylarsino)ethane (1.4 g), *o*-phenanthroline (1.1 g) or 2,2'-bipyridyl (1 g), at room temperature for 6 h (Ie), 24 h (If) or 5 h (Ig). Ie: ether (50 ml) was added and the mixture was stirred for 15 h; the white product was filtered off and washed with ether, yield 94%. If: the yellow product which separated from the reaction mixture was filtered off and washed with acetone, yield 78%. Ig: the yellow product was stirred with ether (50 ml) for 15 h, filtered off and washed with ether, yield 79%. If and Ig are practically insoluble in chloroalkanes, acetone, alcohols and only slightly soluble in dimethylsulfoxide.

PtCl(CH$_2$CN)(PPh$_3$)(PPhMe$_2$) (Ih) *trans*-PtCl(CH$_2$CN)(PPh$_3$)$_2$ (1.7 g) was stirred at room temperature with phenyldimethylphosphine (0.2 g) in ether (20 ml) for 15 h under nitrogen. The precipitate was filtered off and recrystallized from dichloromethane (1 ml)/ethanol (15 ml) at —10°C. The white crystals were washed with ethanol (2 ml), then ether (2 ml). Yield 25%.

trans-PtH(CH$_2$CN)(PPh$_3$)$_2$ (IIa). NaBH$_4$ (0.15 g in 50 ml ethanol) was added dropwise for 1 h to a suspension of *cis*- or *trans*-PtCl(CH$_2$CN)(PPh$_3$)$_2$ (0.8 g) in dry ethanol (200 ml) at 40°C. The mixture was stirred for 2 h at 40°C; a white solid slowly precipitated from the pale yellow solution which was kept overnight at —20°C. The complex was filtered off and recrystallized from benzene/methanol. Yield 78%.

PtH(CH$_2$CN){Ph$_2$PCH=CHPPh$_2$} (IIb), PtH(CH$_2$CN){Ph$_2$P(CH$_2$)$_2$PPh$_2$} (IIc) and PtH(CH$_2$CN){Ph$_2$P(CH$_2$)$_3$PPh$_2$} (IId). Method A: To a vigorously stirred suspension of Ib [3], Ic [3] or Id (1.4 g), a solution of NaBH$_4$ (0.3 g in 100 ml ethanol) was added dropwise during 2 h at room temperature to give a clear yellow solution. Water (10 ml) was added and the mixture stirred at 0°C. The white precipitate was filtered off, washed with cold ethanol (10 ml), then n-hexane (20 ml), and recrystallized by slow evaporation from dichloromethane/methanol. Yield 75%.

Method B: the appropriate ligand (0.17 g) was added to *trans*-$PtH(CH_2CN)(PPh_3)_2$ (0.27 g) in benzene (20 ml) with stirring. After 10 min a white precipitate began to separate, and the mixture was stirred for 2 h. Ether (100 ml) was added, and the complex filtered off, washed with ether, and recrystallized from dichloromethane/methanol. Yield 86%.

$PtH(CH_2CN)\{Ph_2As(CH_2)_2AsPh_2\}$ (IIe). $NaBH_4$ (0.3 g in 70 ml ethanol) was added dropwise during 4 h to a stirred suspension of Ie (1 g) in ethanol (300 ml). Water (100 ml) was added to the resulting yellow solution and the mixture kept at 0°C for 2 h. The off-white product was filtered off and recrystallized from benzene/ether. White microcrystals. Yield 62%.

Acknowledgement

We acknowledge the generous support of the Swiss National Science Foundation through grant. No. 2.548.76.

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