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PREPARATION OF PLATINUM(II) CYANO-COMPLEXES CONTAINING σ-CARBYL, HYDRIDO- OR ORGANOSILYL-LIGANDS *

JOAQUIM F. ALMEIDA and ALAN PIDCOCK *
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

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Summary

Chloride, cyclo-octa-1,5-diene, and uni- and bi-dentate organophosphine ligands have been displaced from platinum(II) complexes by KCN in an organic solvent in presence of 18-crown-6. Reactions with methyl and aryl complexes give $[K(18\text{-crown-}6)]_2[Pt(CN)_{4-n}R_n]$ ($n = 1, 2$; R = Me, aryl) at ambient temperature and $[K(18\text{-crown-}6)][Pt(CN)_3(SiPh_3)]$ was obtained from *trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$. Hydrido-complexes gave only $[K(18\text{-crown-}6)]_2[Pt(CN)_4]$ at ambient temperature but $[K(18\text{-crown-}6)]_2[PtH(CN)_3]$ was obtained from *trans*-$[PtH(Cl)(AsPh_3)_2]$ at —45°C. ^1H NMR and infrared spectra were recorded.

Introduction

Cyanide is well known to displace anionic ligands such as chloride from platinum(II) complexes and although its tendency to displace neutral ligands is recognised in the use of stoichiometric proportions of cyanide for the displacement of anionic ligands, this characteristic has been relatively little exploited in synthetic work. Previously, *trans*-$[Pt(CN)_2(GePh_3)_2]^{2-}$ has been obtained by treatment of $[Pt(GePh_3)_2(PEt_3)_2]$ with KCN[1] and work in this group has shown that complexes $[K(18\text{-crown-}6)]_2[Pt(CN)_2R_2]$ ** (R = Me, Ph, 2-thienyl, benzofuran-2-yl, C_6H_4OMe-4) may be obtained from KCN and $[PtR_2(COD)]$ (COD = cyclo-octa-1,5-diene) in presence of 18-crown-6[2]. We now report that the latter method can be used to obtain complexes $[K(18\text{-crown-}6)]_2[Pt(CN)_3R]$ (R = a variety of σ-carbyl ligands), $[K(18\text{-crown-}6)]_2[PtH(CN)_3]$ and $[K(18\text{-crown-}6)]_2[Pt(CN)_3(SiPh_3)]$.

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* No reprints available for distribution.

** 18-crown-6 = 1,4,7,10,13,16-hexa-oxacyclo-octadecane.

Results and discussion

Platinum(II) complexes containing σ-carbyl, hydrido- or organosilyl ligands are generally uncharged complexes which are soluble in organic solvents but insoluble in water. Reactions with KCN may be carried out under phase transfer conditions using the complex in an organic solvent with KCN in water in presence of a phase transfer reagent such as 18-crown-6. However, our earlier work [2] had shown that products containing the cation $[K(18\text{-crown-}6)]^+$ were hygroscopic and difficult to isolate in presence of water, so for this work we treated the platinum complex and 18-crown-6 dissolved or suspended in an organic solvent with solid KCN under anhydrous conditions.

The mixture was generally stirred at ambient temperature for several hours. For most of the complexes, benzene was used as the solvent, when the solid

TABLE 1

PREPARATIONS AND PROPERTIES OF COMPOUNDS $[K(18\text{-crown-}6)]_2[Pt(CN)_{4-n}R_n]$

Anion $[Pt(CN)_{4-n}R_n]^{2-}$	Starting complex	Solvent (Temperature, °C)	M.p.(°C)
$[Pt(CN)_3Me]^{2-}$	*trans*-$[PtMe(Cl)(PEt_3)_2]$ [c]	C_6H_6(250)	205—280 [a]
$[Pt(CN)_3Ph]^{2-}$	$[PtPh(Cl)(COD)]$	C_6H_6/CH_2Cl_2(25)	206—210
$[Pt(CN)_3(C_6H_4SiMe_3\text{-}4)]^{2-}$	$[Pt(C_6H_4SiMe_3\text{-}4)Cl(COD)]$	C_6H_6(25)	207—209
$[Pt(CN)_3(C_6H_4Cl\text{-}3)]^{2-}$	$[Pt(C_6H_4Cl\text{-}3)Cl(COD)]$	C_6H_6(25)	176—180
$[Pt(CN)_3(C_6H_4Me\text{-}3)]^{2-}$	$[Pt(C_6H_4Me\text{-}4)Cl(COD)]$	C_6H_6(25)	210—220
$[Pt(CN)_3(C_6H_4Ph\text{-}3)]^{2-}$	$[Pt(C_6H_4Ph\text{-}3(Cl(COD)]$	C_6H_6(25)	220—225
$[Pt(CN)_3(C_4H_3S)]^{2-}$ [g]	$[Pt(C_4H_3S)Cl(COD)]$ [g]	CH_2Cl_2(25)	215—217
$[Pt(CN)_3(C_8H_5S)]^{2-}$ [i]	$[Pt(C_8H_5S)Cl(COD)]$ [i]	CH_2Cl_2(25)	114—115
$[Pt(CN)_3(C_8H_7)]^{2-}$ [j]	$[Pt(C_8H_7)Cl(COD)]$ [j]	C_6H_6(25)	200—210
$[Pt(CN)_3(C_8H_5O)]^{2-}$ [k]	$[Pt(C_8H_5O)Cl(COD)]$ [k]	C_6H_6(25)	240—245
$[Pt(CN)_3(C_4H_3O)]^{2-}$ [l]	$[Pt(C_4H_3O)Cl(COD)]$ [l]	C_6H_6(50)	240—245
cis-$[Pt(CN)_2Ph_2]^{2-}$	*cis*-$[PtPh_2(PMe_2Ph_2)]$	C_6H_6/CH_2Cl_2(50)	245—255
cis-$[Pt(CN)_2(C_6H_4Ph\text{-}3)_2]^{2-}$	$[Pt(C_6H_4Ph\text{-}3)_2(COD)]$	C_6H_6(25)	
cis-$[Pt(CN)_2(C_6H_4Br\text{-}4)_2]^{2-}$	$[Pt(C_6H_4Br\text{-}4)_2(COD)]$	C_6H_6(25)	118—120
cis-$[Pt(CN)_2(C_{10}H_7)_2]^{2-}$ [m]	$[Pt(C_{10}H_7)_2(COD)]$ [m]	C_6H_6(50)	197—198
$[PtH(CN)_3]^{2-}$	*trans*-$[PtH(Cl)(AsPh_3)_2]$	MeOH(—45)	163—165
$[Pt(CN)_3(SiPh_3)]^{2-}$	*trans*-$[PtCl(SiPh_3)(PMe_2Ph)_2]$	CH_2Cl_2(25)	180—182
$[Pt(CN)_4]^{2-}$	*trans*-$[PtH(Cl)(AsPh_3)_2]$	C_6H_6(5)	240 [d]

[a] In $CDCl_3$ solutions; positive shifts are to high frequency of the internal reference ($SiMe_4$); an additional resonance due to 18-crown-6 was present in all spectra (see text). [b] In Nujol; additional bands due to 18-crown-6 were present in all spectra (see text). [c] Also prepared from *trans*-$[PtMe(Cl)(PMe_2Ph)_2]$ and

crude product was obtained by filtration and purified by recrystallisation from dichloromethane-diethyl ether. The complexes $[K(18\text{-crown-6})]_2[Pt(CN)_3R]$ (R = Me, Ph, $C_6H_4SiMe_3$-4, C_6H_4Br-4, C_6H_4Cl-3,2-benzofuryl, 2-benzothienyl, 2-thienyl) were obtained and characterised spectroscopically and by analysis, and a number of analogous complexes were obtained (R = C_6H_4Me-3, C_6H_4Ph-3, 2-benzofuryl, 2-benzothienyl, 2-furyl, 3-(1,2-dihydrobenzocyclobutenyl)) and characterised spectroscopically. Details of the starting complexes used and of the spectroscopic and analytical results are given in Table 1 together with some further results for complexes of the type $[K(18\text{-crown-6})]_2[Pt(CN)_2R_2]$ (R = Ph, C_6H_4Ph-3, C_6H_4Br-4, 2-naphthyl). The complex $[K(18\text{-crown-6})]_2$-$[Pt(CN)_3Me]$ was obtained from *trans*-$[PtMe(Cl)(PEt_3)_2]$ and the ^1H NMR spectrum comprised a very intense resonance at δ 3.8 ppm from the protons of the 18-crown-6 ligand and a ca. 1 : 4 : 1 triplet δ 0.33 ppm from the PtMe group. The relative intensity of these resonances was in agreement with the

Analytical results found (calcd.)(%)			^1H NMR [a] δ(ppm)	IR(cm^{-1})	
C	H	N		ν(CN) [b]	Other bands
37.2 (37.6)	5.7 (5.6)	4.6 (4.7)	0.3 [e]	2115w, 2105(sh), 2095m	530, 500m
41.2 (41.4)	5.9 (5.6)	4.4 (4.4)	6.0	2125w, 2100s	1552m, 1025w, 732(sh), 700(sh)
39.3 (39.9) [f]	5.3 (5.6) [f]	4.1 (3.9) [f]	0.1, 7.2	2160s(br), 2130s(sh), 2110(sh)	1570s(br), 1060s, 1020w 805s, 755m, 725s
48.8 (48.7)	6.3 (6.3)	3.5 (3.5)	6.8	2160m(br), 2120s	1561m, 1495m, 930(br) 810w, 765m
			2.4, 6.8	2160s, 2130(sh), 2110s	1595m, 1550m
			6.5, 7.4	2160m, 2110s	1600m, 1550m, 1505m 1500m, 760s, 710m
36.6 (36.7) [f]	5.3 (5.1) [f]	4.1 (4.0) [f]	6.9, 7.6	2125w, 2112s	675, 530m, 500w
41.0 (41.5)	5.3 (5.3)	4.0 (4.1)	6.8, 7.4	2120s	725s
			2.6, 2.7	2160m(br), 2120(sh), 2100(sh)	1570m, 785m, 750s 725s, 400(br)
			7.5	2180s, 2140m 2170(br), 2120s	1600w, 1500s, 1250(sh) 730s, 610w, 535w
46.1 (45.3)	5.6 (5.8)	2.4 (2.8)	6.9	2130s	720s, 505m, 495m
			7.2, 7.3	2130s	1500s, 790m, 750vs, 700s
36.7 (37.5) [f]	4.6 (4.7) [f]	2.4 (2.2) [f]	7.2	2120s(br)	810vs, 730s, 700m 415m, 400m
49.5 (49.9)	5.5 (5.6)	2.9 (2.5)	7.2, 7.8	2100s, 1900s	1590m, 790m, 770s 720s(br)
35.7 (36.8)	5.5 (5.6)	4.7 (4.8)	—12.97 [l]	2120(sh), 2100(sh)	ν(PtH)230(sh)
46.9 (47.4)	5.5 (5.6)	3.5 (3.7)	7.1, 7.8	2140w, 2110s, 2100s	905w, 740s, 720m 700(sh), 520(sh), 500(sh)
37.6 (37.1)	5.4 (5.3)	5.5 (6.2)		2130	530

$[PtMe(Cl)(DPPE)]$ in CH_2Cl_2-C_6H_6. [a] With decomposition. [e] ^2J(PtCH) 65.7 Hz. [f] Containing 1 mol CH_2Cl_2 of crystallisation. [g] Counterion [K dicyclohexyl-(18-crown-6)]$^+$. [h] C_4H_3S = 2-thienyl. [i] 2-benzothienyl. [j] 3-(1,2-dihydrobenzocyclobutenyl). [k] 2-benzofuryl. [l] 2-furyl. [m] = 2-naphthyl. [n] ^1J(PtH) 738 Hz.

assigned formula and the coupling constant for the PtMe group ^2J(PtCH) (65.7 Hz) is similar to those for other complexes with Me *trans* to CN, viz. *trans*-[PtMe(CN)(PEt$_3$)$_2$] (60.2 Hz [3]) and *trans*-[PtMe(CN)(PMe$_2$Ph)$_2$] (61 Hz [4]). The ^{31}P-{^{1}H} NMR spectrum of the complex gave no indication of phosphorus-containing impurities derived from the starting complexes. The ^{1}H NMR spectra of the aryl complexes [K(18-crown-6)]$_2$[Pt(CN)$_3$R] had features expected for the aryl groups R and the strong resonance for the protons of the 18-crown-6 ligand (Table 1).

The infra-red spectrum of [K(18-crown-6)]$_2$[Pt(CN)$_3$Me] exhibited a strong and sharp band ν(CN) at 2105 cm^{-1} flanked by two bands of medium intensity at 2095 and 2115 cm^{-1}. The presence of three bands ν(CN) is consistent with the presence of an ion [Pt(CN)$_3$Me]$^{2-}$ of C_{2v} symmetry. Strong bands in the spectrum at 1350, 1100 and 955 cm^{-1} were assigned to vibrations of the 18-crown-6 ligand. The infra-red spectra of the compounds [K(18-crown-6)]$_2$-[Pt(CN)$_3$R] were similar to that of the compound with R = Me; in some instances fewer than three ν(CN) bands were observed, presumably because of accidental degeneracy, and the presence of aryl groups was confirmed by the observation of bands in the regions 1600—1500 cm^{-1} and 1000—650 cm^{-1} (Table 1). The spectra of the compounds containing the anions [Pt(CN)$_2$R$_2$]$^{2-}$ were similar to those recorded previously and are consistent with a *cis*-configuration of the anion [2]. The complex [K(18-crown-6)]$_2$[Pt(CN)$_3$Me] was also obtained with satisfactory analytical and spectroscopic results from [PtMe(Cl)-(DPPE)] [DPPE = 1,2-bis(diphenylphosphino)ethane], showing that the greater stability of the chelate complex does not prevent the displacement reaction with cyanide.

Considerable difficulty was experienced in the preparation of [K(18-crown-6)]$_2$[Pt(CN)$_3$H] and from a variety of complexes *trans*-[PtH(Cl)(PR$_3$)$_2$]; the method described above gave only [K(18-crown-6)]$_2$[Pt(CN)$_4$]. However, the AsPh$_3$ ligands in *trans*-[PtH(Cl)(AsPh$_3$)$_2$] proved to be sufficiently labile for the displacement reaction with KCN and 18-crown-6 to proceed at —45°C in dry methanol. The compound is stable in air at ambient temperature and gave satisfactory analytical results (Table 1). The ^{1}H NMR spectrum of a solution in CDCl$_3$ was obtained with a Fourier Transform instrument and comprised a strong resonance at δ 3.7 ppm from the 18-crown-6 protons and a ca. 1 : 4 : 1 triplet at δ —12.97 ppm from the hydride ligand. The coupling constant ^1J(Pt—P) 738 Hz is smaller than for most platinum(II) hydrido-complexes but is similar to that in *trans*-[PtH(CN)(PMePh$_2$)$_2$] (768 Hz [s]) where H is also *trans* to CN. The infra-red spectrum exhibited two strong bands at 2120 and 2100 cm^{-1} assigned to ν(CN) and a band at 2030 cm^{-1} which was assigned to ν(PtH); in complexes *trans*-[PtH(CN)(PR$_3$)$_2$] the band ν(CN) lies in the range 2130—2145 cm^{-1} and ν(PtH) in the range 2039—2070 cm^{-1} [5,6]. In CDCl$_3$ the complex decomposed after ca. 50 h, and in the solid state it readily absorbs moisture.

The complex [K(18-crown-6)]$_2$[Pt(CN)$_3$(SiPh$_3$)] was obtained straightforwardly from *trans*-[PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$] in CH$_2$Cl$_2$ and the solid showed less tendency to absorb moisture than the other complexes [K(18-crown-6)]$_2$[Pt-(CN)$_3$R]. A reaction between KCN and [PtCl(SiMePh$_2$)(DPPE)] at 50°C gave [K(18-crown-6)]$_2$[Pt(CN)$_4$], whereas several complexes containing Pt—R bonds (R = aryl) were obtained under similar conditions (Table 1), so it appears that the Pt—Si bond is more labile than the Pt—R bond in the cyanide complexes.

Experimental

Methods described in the literature were used to prepare 18-crown-6[7], [PtMe(Cl)(COD)] [8], platinum phenyl complexes [9] and platinum aryl complexes [10]. Dry solvents were used and manipulation of solutions was carried out under nitrogen. The KCN was dried under vacuum at 70°C for 6—7 h.

[K(18-crown-6)]$_2$[Pt(CN)$_3$Me]

To a solution of *trans*-[PtMe(Cl)(PEt$_3$)$_2$] (0.4 g) in benzene (5 cm^3) were added KCN (0.162 g) and 18-crown-6 (0.44 g) and the mixture was stirred at ambient temperature for 12 h. The solid formed was obtained by filtration, washed with diethyl ether and recrystallised from dichloromethane-diethyl ether to give the compound as colourless needles (0.51 g, 68%).

Other complexes [K(18-crown-6)]$_2$[Pt(CN)$_3$R] were prepared in a similar manner; details are given in Table 1. Several of the complexes crystallised with 1 mol CH_2Cl_2 of crystallisation; this is indicated by footnote *f* in the Table and the resonance due to CH_2Cl_2 was also detected in the ^{1}H NMR spectra.

[K(18-crown-6)]$_2$[Pt(CN)$_2$Ph$_2$]

A solution of [PtPh$_2$(COD)] (0.3 g) in benzene-dichloromethane (1 : 1.5 cm^3) was treated with KCN (0.085 g) and 18-crown-6 (0.543 g) and the mixture stirred for 4 h at 50°C. The precipitate was recrystallised from dichloromethane-diethyl ether to give the compound as colourless crystals (0.42 g, 68%). Other complexes [K(18-crown-6)]$_2$[Pt(CN)$_2$R$_2$] were obtained similarly (Table 1).

[K(18-crown-6)]$_2$[PtH(CN)$_3$]

To a suspension of *trans*-[PtH(Cl)(AsPh$_3$)$_2$] (0.25 g) in dry methanol (5 cm^3) at —45°C were added KCN (0.06 g) and 18-crown-6 (0.158 g) and the mixture was stirred at —45°C for 7 h. The mixture was treated with diethyl ether and light petroleum (b.p. 30—40°C), and put aside for 1 h at —45°C to allow the product to precipitate. The supernatant liquor was decanted and the resulting white solid was washed with several portions of a mixture of diethyl ether and light petroleum (b.p. 30—40°C) at —45°C and dried under vacuum to give the product (0.15 g, 58%). A similar complex was obtained using dicyclohexyl-18-crown-6, m.p. 163—165°C. (Analysis. Found: C, 46.9; H, 6.68; N, 3.85. $C_{43}H_{73}N_3O_{12}K_2Pt$ calcd.: C, 47.1; H, 6.7; N, 3.8%.)

[K(18-crown-6)]$_2$[Pt(CN)$_3$(SiPh$_3$)]

A solution of *trans*-[PtCl(SiPh$_3$)(PMe$_2$Ph)$_2$] (0.33 g) in dichloromethane (6 cm^3) was treated with KCN (0.098 g) and 18-crown-6 (0.246 g) and the mixture stirred for 8 h at ambient temperature. The mixture was then evaporated to dryness under reduced pressure and the residue washed with diethyl ether to remove the phosphine. Recrystallisation from dichloromethane-diethyl ether gave colourless crystals of the product.

[K(18-crown-6)]$_2$[Pt(CN)$_4$]

A solution of *trans*-[PtHCl(AsPh$_3$)$_2$] (0.2 g) in benzene (5 cm^3) was treated with KCN (0.037 g) and 18-crown-6 (0.1 g) and the suspension stirred for 12 h at 5°C. The precipitate was filtered off and purified by precipitation from dichloromethane by addition of diethylether. (Analysis. Found: C, 37.6; H, 5.4; N, 5.5. $C_{28}H_{48}N_4O_{12}K_2Pt$ calcd.: C, 37.1; H, 5.3; N, 6.2%.)

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