Journal of Organometallic Chemistry, 73 (1974) 131—136
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CYANOALKYL COMPLEXES OF TRANSITION METALS

II. PREPARATION AND PROPERTIES OF SOME PLATINUM COMPLEXES CONTAINING PHOSPHORUS AS A DONOR ATOM

KEINOSUKE SUZUKI, HISASHI YAMAMOTO and SHIGEKI KANIE
Inorganic Chemistry Laboratory, Faculty of Science, Nagoya University, Chikusa, Nagoya (Japan)

(Received December 6th, 1973)

Summary

cis-$PtCl(CH_2CN)(PPh_3)_2$ was obtained by the reaction of $Pt(PPh_3)_4$ with $ClCH_2CN$ in acetone. A solution of $Pt(PPh_3)_4$ and $ClCH_2CN$ in benzene was heated under reflux to give *trans*-$PtCl(CH_2CN)(PPh_3)_2$. The reaction of the *trans*-isomer with Br^-, I^-, $Ph_2PCH_2CH_2PPh_2$, $Ph_2PCH_2CH_2AsPh_2$ and *cis*-$Ph_2PCH{=}CHPPh_2$ has been examined. The *trans*-influence of a ligand *trans* to the CH_2CN group seems to be indicated by the ^2J(Pt—H) of the CH_2CN protons. The τ values of *trans*-$PtX(CH_2CN)(PPh_3)_2$ and $PtX(CH_2CN)$(P—P) (X = Cl, Br, I) are related by a linear function.

Introduction

Recently several complexes containing a CH_2CN group have been reported. They include Fe^{II} [1], Rh^{III} [2], Ir^{III} [2], Pd^{II} [3] and Pt^{II} [4] as a central metal atom. The palladium complexes reported by us were stable in air as expected due to the presence of the electron-withdrawing cyano group on the methylenic ligand. Faraone et al. [2] demonstrated that the CH_2CN group in $[\pi\text{-}C_5H_5M(CO)(PPh_3)CH_2CN]^+$ (M = Rh, Ir) is less electrophilic than the CO group by the reaction of CH_3O^- or N_3^- with the complexes. Very recently Bennett et al. [4] obtained $Pt(CH_3)(CH_2CN)$(P—P) (P—P = $Ph_2PCH_2CH_2PPh_2$) by the reaction of $Pt(OH)(CH_3)$(P—P) with CH_3CN. In this paper we describe the preparation and spectroscopic properties of some platinum complexes containing a cyanomethyl group and phosphorus or arsenic donor ligands attached to the metal. It is also demonstrated that platinum—hydrogen coupling constant, ^2J(Pt—H) in the complexes studied here is influenced by the σ-donor property of a ligand *trans* to the cyanomethyl group.

Experimental

IR and NMR spectra were recorded as reported in the previous paper [3].

$Pt(PPh_3)_4$ was prepared by the method described in the literature [5]. All the ligands used were obtained commercially. Analytical data are summarized in Table 1.

trans-$PtCl(CH_2CN)(PPh_3)_2$ (I)

To a solution of $Pt(PPh_3)_4$ (2.0 g) in benzene (100 ml) was added $ClCH_2C$ (0.5 ml) at room temperature under nitrogen. The mixture was heated under reflux for a few hours. After cooling to room temperature, *trans*-$PtCl(CH_2CN)(PPh_3)_2$ was obtained as white crystals containing one molecule of benzene.

trans-$PtBr(CH_2CN)(PPh_3)_2$ (II) and *trans*-$PtI(CH_2CN)(PPh_3)_2$ (III)

LiBr (0.6 g) and 1.0 g of I was heated under reflux in ethanol for 24 h. The product, II, was recrystallized from benzene. It contained one molecule of benzene. The corresponding iodide III was prepared similarly using $LiI \cdot 3H_2O$ instead of LiBr and recrystallizing from dichloromethane.

cis-$PtCl(CH_2CN)(PPh_3)_2$ (IV)

A mixture of $Pt(PPh_3)_4$ (3.8 g) and $ClCH_2CN$ (0.3 ml) in acetone (150 ml) was stirred for 4 h under nitrogen at room temperature. The resulting precipitat was filtered off and recrystallized from chloroform/acetone. It contained one molecule of acetone. *cis*-$PtCl(CH_2CN)(PPh_3)_2$ was converted into *trans*-$PtCl(CH_2CN)(PPh_3)_2$ by heating under reflux in benzene containing a small amount of triphenylphosphine.

$PtCl(CH_2CN)(P—P)$ (V)

To a suspension of *trans*-$PtCl(CH_2CN)(PPh_3)_2$ (0.4 g) in benzene (100 ml) was added P—P (0.2 g) in the same solvent (20 ml). After stirring for 2 h, the product was filtered and recrystallized from dichloromethane/petroleum ether.

$PtBr(CH_2CN)(P—P)$ (VI)

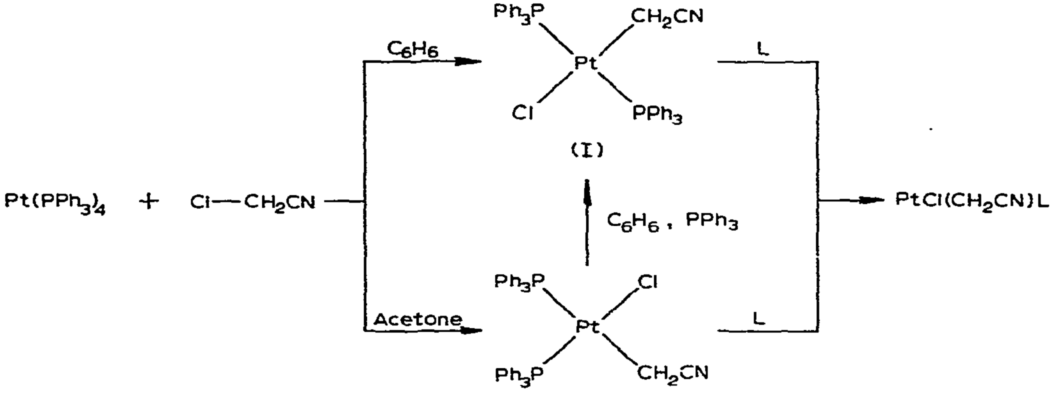
A mixture of the complex V and LiBr in acetone was stirred for 17 h at room temperature. The resulting mixture was filtered. The filtrate was concentrated. Addition of water precipitated a white solid. It was washed with acetone and ether and dried in air.

$PtI(CH_2CN)(P—P)$ (VII), $PtCl(CH_2CN)(P—As)$ (VIII) and $PtCl(CH_2CN)(PCH{=}CHP)$ (IX)

These three complexes were synthesized in a manner similar to that described for the complex V. The complexes VII and VIII were recrystallized from dichloromethane/petroleum ether. The complex IX was obtained as a benzene solvate.

Results and discussion

The reaction of $Pt(PPh_3)_4$ suspended in acetone with $ClCH_2CN$ gave *cis*-$PtCl(CH_2CN)(PPh_3)_2$ IV. The corresponding *trans*-$PtCl(CH_2CN)(PPh_3)_2$ I was obtained by heating the *cis*-isomer with a small amount of PPh_3 under reflux in benzene or by performing the reaction of $Pt(PPh_3)_4$ with $ClCH_2CN$ in refluxing benzene since the reaction conducted at room temperature usually gave a mixture of the *cis*- and *trans*-isomer. This result indicates that the first product of the reaction is the *cis*-isomer even in benzene solution. If the complex $PtCl(CH_2CN)(PPh_3)_2$ (*cis* or *trans*) was treated with a chelating agent, $PtCl(CH_2CN)L$ (L = $Ph_2PCH_2CH_2PPh_2$ = P—P; $Ph_2PCH_2CH_2AsPh_2$ = P—As; *cis*-$Ph_2PCH{=}CHPPh_2$ = PCH=CHP) was obtained. However, 1,10-phenanthroline did not form the expected complex $PtCl(CH_2CN)(phen)$, although the palladium analogue was prepared by the corresponding reaction [3]. The metathesis reaction of the *trans*-$PtCl(CH_2CN)(PPh_3)_2$ and $PtCl(CH_2CN)$(P—P) with LiBr or LiI gave the corresponding bromide and iodide respectively.



All these complexes are stable both in the solid state and in soluiton like the palladium analogues. They are soluble in $CHCl_3$ and CH_2Cl_2 and slightly soluble in acetone. Generally the triphenylphosphine complexes were more soluble than the complexes of chelating phosphines. Some of the complexes contained one molecule of lattice solvent. However, none of them showed any color change similar to that observed for the palladium complexes reported previously [3]. The reason is not clear yet.

Infrared spectra

All the complexes reported here show a storng band due to $\nu(CN)$ at ca. 2200 cm^{-1} indicating the presence of a cyanomethyl group. The platinum—chlorine stretching frequency of the complexes is useful in determining the structure of the complexes. They are summarized in Table 2 together with NMR data.

The complex I (whose structure was confirmed by NMR) showed a strong band at 293 cm^{-1}. The band was assigned to $\nu(Pt—Cl)$ because of its disappearance in the corresponding bromide and iodide. The stretching frequency is a little higher than the $\nu(Pd—Cl)$ of the corresponding palladium complex (288 cm^{-1}). In the complexes *cis*-$PtCl(CH_2CN)(PPh_3)_2$ IV, $PtCl(CH_2CN)$(P—P) V, and $PtCl(CH_2CN)$(PCH=CHP) VIII where Cl is *trans* to P, the $\nu(Pt—Cl)$ appeared at 304, 301, and 303 cm^{-1} respectively. These stretching frequencies are ca. 10 cm^{-1} higher than that of I. This result is similar to that obtained for the corresponding palladium complexes and indicates that the *trans* influence of carbon is larger than that of phosphorus in the platinum complexes, too.

TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA

Complex		Colour	M.p. (dec. °C)	Analysis found (calcd.) (%)		
				C	H	N
I	*trans*-$PtCl(CH_2CN)(PPh_3)_2 \cdot C_6H_6$	White	245—250	60.62 (60.52)	4.23 (4.39)	1.68 (1.60)
II	*trans*-$PtBr(CH_2CN)(PPh_3)_2 \cdot C_6H_6$	White	242—248	57.59 (58.11)	4.17 (4.22)	1.53 (1.73)
III	*trans*-$PtI(CH_2CN)(PPh_3)_2 \cdot CH_2Cl_2$	Pale orange	234—242	48.21 (48.38)	3.53 (3.50)	1.44 (1.59)
IV	*cis*-$PtCl(CH_2CN)(PPh_3)_2 \cdot (CH_3)_2CO$	White	244—250	57.99 (57.71)	4.40 (4.49)	1.61 (1.64)
V	$PtCl(CH_2CN)$(P—P)	White	246—250	51.06 (50.27)	3.71 (3.92)	2.11 (2.09)
VI	$PtBr(CH_2CN)$(P—P)	White	252—255	47.18 (47.14)	3.70 (3.67)	2.03 (1.96)
VII	$PtI(CH_2CN)$(P—P)	Pale yellow	260—280	44.38 (44.22)	3.35 (3.45)	1.83 (1.84)
VIII	$PtCl(CH_2CN)(PCH{=}CHP) \cdot C_6H_6$	White	236—240	54.43 (54.81)	3.82 (4.06)	1.64 (1.88)
IX	$PtCl(CH_2CN)$(P—As)	White	247—251	46.97 (47.17)	3.48 (3.31)	1.74 (1.96)

TABLE 2

IR AND NMR SPECTRAL DATA OF THE COMPLEXES $PtX(CH_2CN)L$

Complex	L	X	$\tau(CH_2CN)$ (ppm)	*J*(Pt—H) (Hz)	*J*(P—H) (Hz)	ν(Pt—Cl) (cm^{-1})
I	$(PPh_3)_2$ [a]	Cl	9.04(t)	106.0	7.5	293
II	$(PPh_3)_2$ [b]	Br	8.98(t)	103.5	7.5	
III	$(PPh_3)_2$ [c]	I	8.88(t)	102.0	7.5	
IV	$(PPh_3)_2$ [d]	Cl	8.36(q)	78.0	9.0 (*trans*) 6.0 (*cis*)	304
V	(P—P) [e]	Cl	8.41(q)	*f*	10.0 (*trans*) 4.5 (*cis*)	301
VI	(P—P) [e]	Br	8.27(q)	*f*	10.0 (*trans*) 4.5 (*cis*)	
VII	(P—P) [e]	I	8.03(q)	*f*	9.0 (*trans*) 5.0 (*cis*)	
VIII	(PCH=CHP) [g]	Cl	8.23(q)	≈ 80	10.5 (*trans*) 4.0 (*cis*)	303
IX	(P—As)	Cl	8.28(d)	92.0	4.5	298

The complex $PtCl(CH_2CN)(P—As)$ IX can take two different structures i.e. with P *trans* to Cl or with As *trans* to Cl. It was hoped that the structure of IX could be determined by its far infrared spectrum, but this was not possible. Therefore the configuration of IX is discussed on the basis of NMR data alone.

NMR spectra

NMR spectra of the complexes were recorded at room temperature in $CDCl_3$ using TMS as internal standard. The cyanomethyl protons of the complexes I—III appeared as a triplet (1/2/1) with satellites due to coupling with ^{195}Pt indicating the *trans* configuration of two triphenylphosphines. The chemical shift of the CH_2CN protons and the coupling constant J(P—H) of the platinum complexes are similar to those of the corresponding palladium complexes reported previously [3].

The cyanomethyl protons of the complexes IV—VIII showed a quartet (1/1/1/1) as expected from the *cis* configuration of two phosphorus atoms. In the NMR spectrum of $Pt(NO_3)(CH_3)$ (P—P), Bennett et al. [6] have found that the $|J(\text{P—H})|$ for *trans*-coupling is larger than that for *cis*-coupling, although the sign for the former is negative and positive for the latter. Therefore the larger J(P—H) in the complexes IV—VIII is tentatively assigned to coupling with the *trans*-phosphorus and smaller J(P—H) to coupling with the *cis*-phosphorus.

The J(Pt—H) of *trans*-$PtCl(CH_2CN)(PPh_3)_2$ I is larger than that of *cis*-isomer IV. A similar result has been reported in the *cis* and *trans* platinum complexes of the type $PtX(CH_3)(PPh_3)_2$ [7] (X = Cl, Br, N_3, NCS, and NO_2). Using a series of platinum complexes Clark et al. [8] showed that the increase of the *trans*-influence of a ligand *trans* to CH_3 caused the decrease of J(Pt—H). Therefore, it is reasonable to ascribe the change of J(Pt—H) observed for I and IV to the difference of *trans*-influence of PPh_3 and Cl.

As shown in Table 2, $\tau(CH_2CN)$ of I—III (*trans*) and V—VII (*cis*) decreased in the same order Cl > Br > I. The values of the corresponding halide complexes in these two series are related to each other by the equation $\tau_t = 5.44 + 3/7\ (\tau_c)$, where τ_t is the $\tau(CH_2CN)$ of the complexes I—III and τ_c is that of the complexes V—VII.

In the complex IX, it was difficult to determine the structure on the basis of ν(Pt—Cl) as mentioned before, but the NMR spectrum suggests that the structure in which P is *trans* to Cl is preferable. This is because the J(P—H) of IX is close to the *cis* J(P—H) found for the complexes IV--VII suggesting the configuration where P is *cis* to the CH_2CN group. Furthermore, J(Pt—H) of IX is larger than that of IV. This fact also supports the configuration mentioned above because in this structure As must be *trans* to the CH_2CN group causing the increase of J(Pt—H) owing to the weaker σ-donor property of As than that of P.

References

1 J.K. Ariyaratne and M.L.H. Green, J. Chem. Soc., (1963) 2976.
2 F. Faraone, C. Ferara and E. Rotando, J. Organometal. Chem., 33 (1971) 221;
F. Faraone, F. Cusmano, P. Piraino and R. Pietropaolo, J. Organometal. Chem., 44 (1972) 391.
3 K. Suzuki and H. Yamamoto, J. Organometal. Chem., 54 (1973) 385.
4 A.G. Appleton and M.A. Bennett, J. Organometal. Chem., 55 (1973) C88.
5 R. Ugo, F. Cariati and G. La Monica, Inorg. Syn., 11 (1968) 105.

6 M.A. Bennett, R. Brameley and I.B. Tomkins, J. Chem. Soc. A, (1973) 166.
7 F.H. Allen and A. Pidcock, J. Chem. Soc. A, (1970) 2700.
8 H.C. Clark and L.E. Manzer, Inorg. Chem., 11 (1972) 2749.