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CYANOALKYL COMPLEXES OF TRANSITION METALS

I. PREPARATION AND PROPERTIES OF SOME PALLADIUM COMPLEXES

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SUMMARY

$PdCl(CH_2CN)(PPh_3)_2$ has been synthesized by the reaction of $Pd(PPh_3)_4$ with $ClCH_2CN$. Compounds of the formula $PdX(CH_2CN)L$ ($X=Cl$, Br; $L=PPh_2CH_2CH_2PPh_2$, $PPh_2CH{=}CHPPh_2$, $PPh_2CH_2CH_2AsPh_2$ and *o*-phenanthroline) have been obtained by an exchange reaction of $PdCl(CH_2CN)(PPh_3)_2$ with the ligands. The structures of the complexes are discussed on the basis of IR and NMR spectra. The IR and NMR spectra showed that in the two possible structures of $PdX(CH_2CN)(PPh_2CH_2CH_2AsPh_2)$ the CH_2CN group is situated *cis* to a phosphorus atom.

INTRODUCTION

The reaction of organic halides with complexes of transition metals in low oxidation states is a convenient way of synthesizing organic complexes of transition metals, however, only a few papers describe the reaction of chloroacetonitrile ($ClCH_2CN$) with transition metal complexes. In 1963, Ariyaratne and Green[1] obtained (π-$C_5H_5Fe(CO)_2CH_2CN$) in low yield by the reaction of Na[π-$C_5H_5Fe(CO)_2$] with $ClCH_2CN$. They also reported the formation of a ketenimine complex by treating the cyanomethyl complex with dry HCl. Recently, Faraone *et al.*[2] prepared $[\pi\text{-}C_5H_5Rh(CO)(CH_2CN)PPh_3]^+$ by the reaction of π-$C_5H_5Rh(CO)PPh_3$ with $ClCH_2CN$ and assigned the stability of the cationic species to the presence of the electron withdrawing CN group bonded to the methylenic group. In this paper, we report the preparation and spectroscopic properties of some palladium complexes containing a cyanomethyl group, and nitrogen, phosphorus or arsenic attached to the metal.

RESULTS AND DISCUSSION

Preparation and properties

The reaction of $Pd(PPh_3)_4$ with $ClCH_2CN$ gives *trans*-$PdCl(CH_2CN)(PPh_3)_2$ which is a light yellow crystalline solid. If the complex is treated with a chelating agent, two triphenylphosphine molecules are replaced to give $PdCl(CH_2CN)L$ [where $L=PPh_2CH_2CH_2PPh_2$ (P–P), $PPh_2CH_2CH_2AsPh_2$ (P–As), *cis*-$PPh_2CH{=}$

CHPPh$_2$ (PCH=CHP) and *o*-phenanthroline (*o*-Phen)]. With ethylenediamine and its derivatives a more complex reaction takes place, the products of which are under investigation. The bromide PdBr(CH$_2$CN)(PPh$_3$)$_2$ which was obtained by treatment of the corresponding chloride with LiBr in acetone was used in the preparation of PdBr(CH$_2$CN)L (L=P–P and P–As).

All the complexes prepared appear to be stable indefinitely in the solid state. Most of them are soluble in CHCl$_3$ and CH$_2$Cl$_2$ and slightly soluble in acetone. It is interesting to note that PdX(CH$_2$CN)(PPh$_3$)$_2$ (X=Cl or Br) changes colour when exposed to light but reverts to its original yellow colour in the dark or on heating.

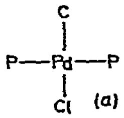
$$\underset{\text{(yellow)}}{\mathrm{PdX(CH_2CN)(PPh_3)_2}} \xrightleftharpoons[\text{dark or heat}]{\text{light}} \underset{\text{(peach)}}{\mathrm{PdX(CH_2CN)(PPh_3)_2}}$$

The reason for this photochromism is not yet clear.

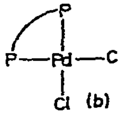
Infrared spectra

The IR spectra in the region 4000–700 cm^{-1} show a strong band due to ν(CN) at ca. 2200 cm^{-1}. The presence of the band indicates the existence of the cyanomethyl group but no useful structural information was derived from the spectra. Thus the bands in this region were used only for analytical purposes. A possible way of determining the structure of a complex is to examine the Pd–Cl stretching frequencies of the complexes because these depend on the ligand *trans* to the Cl atom. The values are summarized in Table 1 together with NMR data.

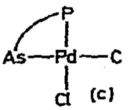
The complex PdCl(CH$_2$CN)(PPh$_3$)$_2$ (I) shows a strong band at 288 cm^{-1} which disappears in the corresponding bromide, indicating that the band is due to ν(Pd–Cl). A *trans* geometry of the two triphenylphosphine ligands in (I) is shown by the NMR spectrum which implies that the Cl atom must be *trans* to the CH$_2$CN group (structure (a)).



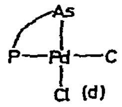
(a)



(b)



(c)



(d)

The complexes PdCl(CH$_2$CN)(P–P) (II) and PdCl(CH$_2$CN)(PCH=CHP) (III) are expected to have similar values of ν(Pd–Cl) because the arrangement of the coordinating atoms around palladium is the same (structure (b)). In fact, the band assignable to ν(Pd–Cl) was observed at 295 in (II) and 296 cm^{-1} in (III) although the complex (II) also contained two additional medium intensity bands at 288 and 240 cm^{-1}. The Pd–Cl stretching frequency in (I) is ca. 10 cm^{-1} lower than those of (II) and (III) suggesting that the *trans* effect of carbon is much larger than that of phosphorus, since the Cl atom is *trans* to CH$_2$CN in (I) and *trans* to P in (II) and (III). The same order (C > P) is also found in other metal complexes[3].

TABLE 1

IR AND NMR SPECTRA OF THE COMPLEXES $PdCl(CH_2CN)L$

Complex	*L*	*X*	$\tau(CH_2CN)$[a] *(ppm)*	*J(P–H)* *(Hz)*	$\nu(Pd\text{–}Cl)$ *(cm^{-1})*
(I)	$(PPh_3)_2$	Cl	9.13 (t)	7.5	288
(II)	P–P[b]	Cl	8.42 (dd)[c]	11.0 (*trans*) 4.0 (*cis*)	295
(III)	PCH=CHP[d]	Cl	8.26 (dd)	10.5 (*trans*) 3.5 (*cis*)	296
(IV)	P–As	Cl	8.27 (d)	4.0 (*cis*)	296
(V)	*o*-Phen	Cl	8.02 (s)[e]		334
(VI)	$(PPh_3)_2$[f]	Br	9.02 (t)	7.0	
(VII)	P–As	Br	8.20 (d)	4.0	

[a] s, Singlet; t, triplet; dd, double doublet; solvent, $CDCl_3$. [b] $PdBr(CH_2CN)(P\text{–}P)$ was insoluble in solvents used here. [c] τ 8.76 (DMSO-d_6); values of *J*(P–H) were same as those in $CDCl_3$. [d] $\tau(C_6H_6)$ 2.74 (s). [e] solvent DMSO-d_6 [f] $\tau(CH_3)_2CO$ 7.85 (s).

Complex $PdCl(CH_2CN)(P\text{–}As)$, (IV), has two possible structures, (c) and (d). The far infrared spectrum shows a strong band assignable to $\nu(Pd\text{–}Cl)$ at 296 cm^{-1} which is absent in the corresponding bromide. This stretching frequency is in agreement with those observed for (II) and (III) as mentioned above and strongly suggests that the complex (IV) has the structure (c). If the structure of (IV) is (d), $\nu(Pd\text{–}Cl)$ will be higher than those reported for (II) and (III) (ca. 20–30 cm^{-1}) since phosphorus is reported[4] to be a better σ-donor than arsenic.

Recently Nakamoto *et al.*[5] determined $\nu(M\text{–}P)$ (M = Ni or Pd) in some phosphine complexes by a metal isotope technique. Their results indicate that $\nu(Ni\text{–}P)$ (P *trans* to halogen) is shifted to lower frequency (ca. 15 cm^{-1}) on changing the halogen from Cl to Br. We therefore attempted to assign $\nu(Pd\text{–}P)$ by comparison of the far IR spectra of the chlorides (II) and (IV) with those of the corresponding bromides (VII) and (VIII). However it was difficult to find a band assignable to $\nu(Pd\text{–}P)$, because, on changing the halogen, the remaining bands in the region 400–200 cm^{-1} where we would expect to find $\nu(Pd\text{–}P)$ (P *trans* to Cl or Br) assuming that $\nu(Ni\text{–}P) > \nu(Pd\text{–}P)$ and the *trans* influence of P is larger than that of Cl[5], showed no appreciable shift (all were less than ca. 2 cm^{-1}) except for the disappearance of the band assigned to $\nu(Pd\text{–}Cl)$.

NMR spectra

The NMR spectra of the complexes were measured in $CDCl_3$ or DMSO-d_6 using TMS as internal standard at room temperature.

As shown in Table 1, the cyanomethyl protons of complexes (I) and (VI) appeared as a triplet (1/2/1) at τ 9.13 (I) and 9.02 (VI) indicating the *trans* configuration of two triphenylphosphine ligands as mentioned before.

On the other hand, the NMR spectra of the complexes (II) and (III) show a quartet (1/1/1/1) centred at τ 8.42 and 8.26 respectively. This is expected because these two complexes contain two nonequivalent phosphorus atoms which can couple with the cyanomethyl protons. Since it is generally accepted that *trans* coupling in square planar complexes is larger than *cis* coupling[6], the larger J(P–H) is tentatively assigned to coupling with the *trans* phosphorus, and the smaller J(P–H) to coupling with the *cis* phosphorus.

In the complexes (IV) and (VII), a doublet was observed for the CH_2CN group. The coupling constant J(P–H) (4 Hz) is very similar to the *cis* J(P–H) found in the complexes (II) and (III). This result implies that the structure of (IV) and (VII) is (c) which was assigned for the complex (IV) on the basis of the ν(Pd–Cl).

In the complexes (II), (IV) and (VII) methylene protons appeared as a broad complex multiplet centred at ca. τ 7.6. This is presumably due to the increase of J-(P–H) by the coordination of a phosphorus atom as shown by Jenkins and Shaw[7] and to the presence of axial and equatorial protons by chelate ring formation, since the methylene protons of free (P–P) appeared as a triplet at τ 7.92 and those of (P–As) gave a singlet at τ 7.89 and a doublet at τ 7.93[8].

In the complex $PdCl(CH_2CN)$(*o*-Phen), (V), $\tau(CH_2CN)$ appeared as a singlet at τ 8.02 as expected. However, the NMR spectrum of *o*-Phen in the complex was not well resolved and appeared as two broad bands centred at ca. τ 1.2 and 1.9.

We also tried the reaction of dry HCl with the complexes (I), (II) and (V) but were not successful in synthesizing the ketenimine complex of palladium. One of the reasons for the failure might be due to the kinetic stability[9] of the palladium complexes.

EXPERIMENTAL

IR spectra were recorded with DS-402G and EPI-2L spectrophotometer (mull). NMR spectra were obtained in $CDCl_3$ or DMSO-d_6 using a JEOL-C60H spectrophotometer operating at 60 MHz with TMS as internal standard. Chloroacetonitrile and the ligand used were commercially available and were used without further purification. $Pd(PPh_3)_4$ was prepared by the method described in the literature[10].

Chloro(cyanomethyl)bis(triphenylphosphine)palladium (I)

$ClCH_2CN$ (2.0 ml) was added under nitrogen to a solution of $Pd(PPh_3)_4$ (2.5 g) in benzene (200 ml) at room temperature. Within 30 min a white precipitate had started to form. After the solution has been stirred for 3 h the product was filtered and washed with ether. Recrystallization from acetone afforded yellow crystals, m.p. 190–192° (dec.).

Chloro(cyanomethyl)-1,2-bis(diphenylphosphino)ethanepalladium (II)

(I) was dissolved in benzene (200 ml) at 70°. After cooling to room temperature, the resulting yellow solution was mixed with a solution of 1,2-bis(diphenylphosphino)-ethane (0.5 g) in benzene (30 ml). A white solid formed almost immediately. The product was filtered and washed with ether. Recrystallization from acetone yielded yellow crystals, m.p. 240° (dec.).

Chloro(cyanomethyl)-cis-1,2-bis(diphenylphosphino)ethylenepalladium (III)

A solution of *cis*-1,2-bis(diphenylphosphino)ethylene (0.3 g) in benzene (20 ml) was added to the suspension of (I) (0.5 g) in benzene (200 ml) at room temperature. After dissolution of (I) was complete, a white precipitate formed again. The mixture was stirred for a further 2 h to complete the reaction. The product was filtered and washed with benzene. The complex contained one molecule of benzene and had m.p. 215° (dec).

Chloro(cyanomethyl)(1-diphenylphosphino-2-diphenylarsino)ethanepalladium (IV) and chloro(cyanomethyl)(o-phenanthroline)palladium (V)

These two complexes were prepared in a manner similar to that described for the complex (II), and recrystallized from acetone. M.p. 215° (dec.) for (IV) and 270° (dec.) for (V) respectively.

Bromo(cyanomethyl)bis(triphenylphosphine)palladium (VI)

A solution of (I) (1.0 g) in acetone (150 ml) prepared by warming at 55° was treated with a solution of $LiBr \cdot 2H_2O$ (0.1 g) in acetone (30 ml) at room temperature. The solution turned deep yellow in colour and was allowed to stand at room temperature for one day, a period during which it afforded yellow crystals of palladium complex, as a solvate of acetone. M.p. 200° (dec.).

Bromo(cyanomethyl)(1-diphenylphosphino-2-diphenylarsino)ethanepalladium (VII)

The complex (VI) (0.5 g) was dissolved in benzene (100 ml) at 70°. After cooling to room temperature, it was added to a solution of 1-diphenylphosphino-2-diphenylarsinoethane (0.25 g) in benzene (30 ml) at room temperature. The solution gave pale yellow materials in a few minutes. Recrystallization from acetone gave pale yellow crystals. The compound was also prepared by treating a solution of $LiBr \cdot 2H_2O$ in acetone with a solution of (IV) in acetone. M.p. 240° (dec.).

Bromo(cyanomethyl)[1,2-bis(diphenylphosphino)ethane]palladium (VIII)

The complex was synthesized in two different ways in a manner similar to that

TABLE 2

ANALYTICAL DATA

Complex		*Analysis found (calcd.) (%)*		
		C	*H*	*N*
(I)	$PdCl(CH_2CN)(PPh_3)_2$	64.4	4.3	1.9
		(64.60)	(4.57)	(1.99)
(II)	$PdCl(CH_2CN)(P{-}P)$	57.3	4.3	2.1
		(57.95)	(4.52)	(2.42)
(III)	$PdCl(CH_2CN)(PCH{=}CHP)C_6H_6$	62.2	4.6	2.1
		(62.38)	(4.31)	(2.08)
(IV)	$PdCl(CH_2CN)(P{-}As)$	54.2	3.9	2.2
		(54.75)	(4.27)	(2.28)
(V)	$PdCl(CH_2CN)(o\text{-}Phen)$	46.4	2.8	11.6
		(46.44)	(2.78)	(11.61)
(VI)	$PdBr(CH_2CN)(PPh_3)_2(CH_3)_2CO$	61.7	5.0	2.1
		(62.09)	(4.84)	(1.77)
(VII)	$PdBr(CH_2CN)(P{-}As)$	50.4	3.9	1.8
		(50.28)	(3.93)	(2.09)
(VIII)	$PdBr(CH_2CN)(P{-}P)$	54.0	4.5	2.4
		(53.82)	(4.20)	(2.24)

described for (VII). Recrystallization from acetone afforded yellow crystals, m.p. 240° (dec.).

Analytical data are summarized in Table 2.

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