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THE PREPARATION AND PROPERTIES OF SOME *cis*-PLATINUM(II) CARBONYLPHOSPHINE COMPLEXES, $PtX_2(CO)(PR_3)$

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SUMMARY

A series of substituted platinum(II) carbonyl complexes, *cis*-$[PtX_2(CO)(PR_3)]$ has been prepared. The effects of various X and R groups on the carbonyl stretching frequency and the dipole moment are discussed. A modified general procedure for the preparation of dimeric platinum(II) complexes, $[Pt_2Cl_4(PR_3)_2]$ has been developed.

INTRODUCTION

In a continuation of our studies on the structure and properties of Pt^{II} carbonyl complexes[1], we were led to expand the number and variety of complexes $[PtCl_2(CO)(PR_3)]$ (R=Et, n-Pr, n-Bu) prepared in 1964 by Chatt, Johnson and Shaw[2]. The dipole moment of these complexes confirmed their *cis*-configuration. In the present study, we have developed a modified general procedure for the synthesis of the precursors of such complexes and have extended the series. The carbonyl stretching frequencies and the dipole moments of the compounds *cis*-$[PtX_2(CO)(PR_3)]$ (I) as a function of X and R have been of particular interest.

The starting compounds required for some of the preparations of (I) are the dimeric complexes, $Pt_2Cl_4(PR_3)_2$. Previously[3] these compounds have been obtained by melting together the mononuclear complex $[PtCl_2(PR_3)_2]$ and platinum(II) chloride. This method is unsuccessful, however, if either the starting material or the product decomposes before melting. Recently[4] it was reported that these difficulties are minimized by employing a slurry of the reactants in a hydrocarbon solvent consisting of varying proportions of naphthalene and xylene depending on the desired reflux temperature. In our procedure, tetrachloroethane is used as the solvent and thus the necessity of adjusting the proportions of the hydrocarbons is obviated. The conversions of the dimers to the desired carbonyl complexes (I) are detailed in the Experimental section. The new carbonyl complexes and their properties are listed in Table 1.

DISCUSSION

The methods employed for preparing the desired carbonyl complexes (I) might be expected to lead to the *trans*-isomer. However, the carbonyl complexes all have dipole moments of about 10 D, and thus the cleavage of the dimeric complex (for

TABLE I

PROPERTIES OF $PtX_2(CO)(PR_3)$

Compound[a]		Analysis[b] found (calcd.) (%)		Color	M.p. (or dec.) (°C)	$\nu(C\equiv O)$		μ (D)
X	PR_3	C	H			Nujol	$CHCl_3$	
Cl	PPh_3	41.0 (41.0)	2.9 (2.7)	colorless	220–230	2103	2117	9.65
Cl	$PPh_2(C_6H_{11})$	40.1 (40.6)	3.9 (3.8)	colorless	252–254	2090	2111	[c]
Cl	$PPh(C_6H_{11})_2$	40.3 (40.1)	4.8 (4.8)	colorless	235–245	2085	2103	10.1
Cl	$P(C_6H_{11})_3$	39.8 (39.7)	5.8 (5.8)	orange	250	2075	2093	[c]
Cl	PBu_3[d]			colorless	114–116	2086	2105	9.7
Br	PBu_3	26.8 (26.7)	4.6 (4.6)	colorless	104–106	2090		9.7
I	PBu_3	23.0 (23.0)	4.0 (4.0)	yellow	54–55	2083		9.15
I	PPh_3	31.0 (30.9)	2.1 (2.0)	yellow	[e]	2095		9.15
I	$PPh(C_6H_{11})_2$	30.3 (30.4)	3.4 (3.6)	yellow	> 250	2083		9.1
Cl[f]	PMe_2Ph			colorless	184–191	2105		
I	PMe_2Ph	18.3 (17.6)	2.0 (1.8)	yellow	92–94[g]	2083		9.1
I	PBu_2Ph	25.9 (25.8)	3.4 (3.3)	yellow	83–85	2076		
$[Ph(C_6H_{11})_2PPtCl_2]_2$		39.7 (40.0)	5.0 (5.0)	orange	289–291			
$[Ph_2(C_6H_{11})PPtCl_2]_2$		40.2 (40.5)	4.0 (4.0)	orange	248–251			

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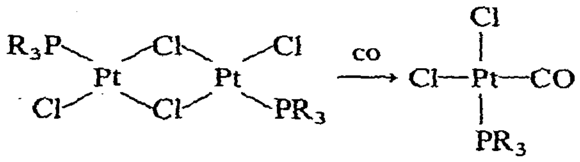
[a] Each prepared by both method (*a*) and method (*b*), see experimental. [b] Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. [c] Too insoluble to determine. [d] See ref. 2. [e] Complex changes color to red, melts with gas evolution 130–150°, then solidifies to a red solid m.p. 250–300°. [f] This chloride[11] was prepared only from the dimeric complex $[Pt_2Cl_4(PR_3)_2]$. [g] On cooling resolidifies to an orange solid m.p. 272–275°, which is probably $[Pt_2I_4(PMe_2Ph)_2]$.

example) must lead to the *cis*-isomer:



I

The *cis*-isomers are expected to be more stable thermodynamically because tertiary phosphines as well as carbon monoxide are strong double bonding ligands and the PR_3 and CO would form stronger bonds to the metal when they are in a mutual *cis*-relationship and thus *trans* to the weakly-double-bonding chlorine atoms.

In (I) where X=Cl and PR_3 is $(C_6H_5)_3P$, $(C_6H_{11})(C_6H_5)_2P$, $(C_6H_{11})_2(C_6H_5)P$

and $(C_6H_{11})_3P$, the carbonyl stretching frequency of the $(C_6H_5)_3P$ complex is highest and that of the $(C_6H_{11})_3P$ complex is lowest. Presumably, the less basic $(C_6H_5)_3P$ competes most effectively for the metal *d*-electrons, thus reducing donation of metal *d*-electrons into the anti-bonding orbitals of carbon monoxide. Our results are in accord with the "spectrochemical series" for π-bonding ligands recently proposed[5].

The data of Table 1 show that the dipole moments and carbonyl stretching frequencies of the iodo complexes are significantly lower than those of the corresponding chloro complexes. This fact may be reasonably attributed to the smaller electronegativity of iodine compared to chlorine.

Dipole moment calculations may be made from group vectors[6]. For the complexes *cis*-$[PtCl_2(CO)PR_3]$, the dipole moment is made up of the group vectors $\overrightarrow{P{-}Pt{-}Cl}$ and $\overrightarrow{OC{-}Pt{-}Cl}$. The dipole moments of the complexes *cis*-$[PtCl_2(CO)PR_3]$ $= 10.7$ D[7]; thus the group vector $\overrightarrow{P{-}Pt{-}Cl} = [0.5 \cdot (10.7)^2]^{\frac{1}{2}} = 6.5$ D. This value is considerably higher than the $\overrightarrow{OC{-}Pt{-}Cl}$ group vector obtained from the bis[carbonyl] complex *cis*-$[Pt(CO)_2Cl_2]$ ($\mu = 4.6$), which is $[0.5 \cdot (4.6)^2]^{\frac{1}{2}} = 3.25$ D[8]. It would appear that in *cis*-$[PtCl_2(CO)PR_3]$ the carbonyl group acts as a much better donor (or poorer acceptor) of electrons than the carbonyl groups in *cis*-$[Pt(CO)_2Cl_2]$.

EXPERIMENTAL

Preparation of the complexes

Dichlorobis(tert-phosphine)platinum(II) complexes, $[PtCl_2(PR_3)_2]$, were prepared by methods similar to those reported by Jensen[9].

Di-μ-chloro-1,3-dichloro-2,4-bis(tert-phosphine)diplatinum(II), $[Pt_2Cl_4(PR_3)_2]$

Platinum(II) chloride (1.1 mmole) was added to a solution of dichlorobis(tert-phosphine)platinum(II) (0.9 mmole) in tetrachloroethane (25 ml). The solution was refluxed for 1 h under an atmosphere of nitrogen. After cooling the solution was filtered and reduced to small volume (25 ml) by evaporation under reduced pressure. The product was then precipitated by the addition of hexane. The product was purified by dissolving it in chloroform and then reprecipitating it with hexane.

Compounds prepared by this method were: $[(C_6H_{11})_2C_6H_5PPtCl_2]_2$, $[C_6H_{11}(C_6H_5)_2PPtCl_2]_2$, $[(n\text{-}C_4H_9)_3PPtCl_2]_2$, $[(C_6H_5)_3PPtCl_2]_2$ and $[(CH_3)_2C_6H_5PPtCl_2]_2$. In all cases, yields ranging from 50 to 80% were obtained.

Dichlorocarbonyl(tert-phosphine)platinum(II), $[PtCl_2(CO)PR_3]$

Compounds of this type were prepared by two general methods:

(*a*) *From Zeise's Salt, $K[PtCl_3(C_2H_4)]$*. Carbon monoxide was bubbled through a stirred solution of Zeise's Salt, $K[PtCl_3(C_2H_4)]$ (1 mmole) in acetone (10 ml) until the color of the solution changed from yellow to pale green, indicating the formation of $K[Pt(CO)Cl_3]$. To this solution, a solution of the tertiary phosphine (0.95 mmole) in benzene (10 ml) was added. The solution was evaporated to dryness under reduced pressure and the residue was extracted with dichloromethane. After filtration, the solution was reduced in volume and the product was precipitated by the addition of hexane.

(*b*) *From the dimeric platinum(II) complexes, $[Pt_2Cl_4(PR_3)_2]$*. A solution or suspension of the dimeric complex $[Pt_2Cl_4(PR_3)_2]$ in benzene (20 ml) was stirred while carbon monoxide was bubbled through for 1–3 h. The solvent was then removed by evaporation under reduced pressure, the residue was dissolved in chloroform and the product was precipitated by the addition of hexane. The complex $[(n\text{-}C_4H_9)_3PPt(CO)Cl_2]$ was recrystallized from ethanol.

Di-iodocarbonyl(tert-phosphine)platinum(II), $[PtI_2(CO)PR_3]$

Compounds of this type were prepared either by treating the corresponding chloro complexes $[PtCl_2(CO)PR_3]$ with sodium iodide in acetone or[2] by the action of carbon monoxide on the complexes di-μ-iodo-1,3-di-iodo-2,4-bis(tert-phosphine)-diplatinum(II), $[Pt_2I_4(PR_3)_2]$.

Treating the corresponding chloro complex with lithium bromide in acetone led to the only bromo complex prepared, $[PtBr_2(CO)(C_4H_9)_3P]$.

Determination of spectra

Infrared spectra were obtained with a Perkin–Elmer Model 337 grating spectrophotometer calibrated with polystyrene film.

Dipole moments were obtained as described by Chatt and Shaw[10] except that a W.T.W. Dipolmeter equipped with a D.F.L. 1 cell was used.

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