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Chemistry of Metal Hydrides. X. The Effect of Trans Ligands on Cationic Platinum(II) Carbonyls

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The preparation of $PtCl(X)L_2$ complexes by cleavage of the cationic dimeric species $[Pt_2Cl_2L_4][BF_4]_2$ by the simple salts NaX is described, where X = anionic ligand and L = $P(C_2H_5)_3$, $P(C_6H_5)_3$, or $P(CH_3)_2(C_6H_5)$. These compounds react readily to form new cationic carbonyl species $[PtX(CO)L_2]BF_4$. A comparison of the physical properties and spectroscopic data for these cations is made with regard to the trans influence of X. The reaction of *trans*-$[PtX(CO)L_2]BF_4$ with water to give *trans*-$PtH(X)L_2$ occurs only for L = $P(C_2H_5)_3$ and $P(C_6H_5)_3$, with X = halide, but reaction with methanol to give alkoxycarbonyls, *trans*-$PtX(COOCH_3)L_2$, occurs only for L = $P(C_6H_5)_3$ and X = NO_3, C_6F_5, or SCN. Differences in X cause differences in the chemical reactivity of these new derivatives.

Introduction

Several types of cationic platinum(II) complexes have been described recently,[1,2] including the carbonyl species[3] *trans*-$Pt(X)(CO)L_2{}^+$, where X is a halide and L is a tertiary phosphine, arsine, or stibine. Previous work[4] has examined the effect on physical properties and chemical reactivities of these complexes and their derivatives caused by changes of L. Attempts have also been made to correlate various parameters such as $^{31}P-^{195}Pt$ coupling constants[5] or the chemical shift of hydridic protons[6] with the trans effect of various anionic ligands in other complexes of platinum(II). We now describe the preparation and physical properties of a series of cationic carbonyl species $Pt(X)(CO)L_2{}^+$, where L = $P(C_2H_5)_3$, $P(C_6H_5)_3$, or $P(CH_3)_2(C_6H_5)$ and X = anionic ligand, and their alkoxycarbonyl derivatives $Pt(X)(COOCH_3)L_2$ for L = $P(C_6H_5)_3$.

Results and Discussion

In a reaction similar to the reported cleavage of the cationic dimeric complexes of platinum(II) with carbon monoxide, the neutral species $PtCl(X)L_2$ for L = $P(C_2H_5)_3$, $P(C_6H_5)_3$, and $P(CH_3)_2(C_6H_5)$ were formed by reaction with the anionic ligands X = SCN, NO_3, and NO_2. (See eq 1.) These derivatives are all air-stable, white, crystalline products; proton nmr spectra of the derivatives of L = $P(CH_3)_2(C_6H_5)$ are consistent with cis configurations (Table IV).

$$[Pt_2Cl_2L_4][BF_4]_2 + 2NaX \longrightarrow 2PtCl(X)L_2 + 2NaBF_4 \quad (1)$$

The syntheses of cationic diplatinum cations, $[Pt_2X_2L_4][BF_4]_2$, containing X as a bridging group, by reaction of the monomeric species with boron trifluoride were successful for X = SCN and L = $P(C_2H_5)_3$ and $P(C_6H_5)_3$ and for X = NO_3 and L = $P(C_6H_5)_3$. These new dimeric cations, like the analogs for X = halide, react in chloroform suspension with carbon monoxide to yield well-defined carbonylplatinum(II) salts, presumably in the trans configuration[7] (eq 2). These cationic carbonyl complexes may also be prepared directly from the monomeric species (a) *cis*-$PtCl(X)L_2$ for X = Cl, NO_2, and NO_3 and L = $P(C_2H_5)_3$ and $P(CH_3)_2(C_6H_5)$ or (b) *trans*-$PtCl(X)L_2$ for X = H, CH_3, C_6H_5, and C_6F_5 and L = $P(C_2H_5)_3$ and for X = H, CH_3, CF_3, and C_6F_5 and L = $P(C_6H_5)_3$ by displacement of chloride ion with carbon monoxide in the presence of sodium or silver tetrafluoroborate (eq 3). The products from eq 3, using *trans*-$PtCl(X)L_2$, are all well-defined, crystalline solids except those for X = H. For X = NO_2 and NO_3, eq 3 with *cis*-$PtCl(X)L_2$ proceeds with decomposition, and the products are isolated as dark, amber oils. For L = $P(CH_3)_2(C_6H_5)$, the proton nmr spectrum of the product for X = NO_2 showed the presence of impurities, while for X = Cl, the product was identified as the trans isomer. For X = SCN an nmr spectrum of the carbonyl cation is consistent with a cis configuration.

$$[Pt_2X_2L_4][BF_4]_2 + 2CO \longrightarrow 2[Pt(X)(CO)L_2]BF_4 \quad (2)$$

$$PtCl(X)L_2 + AgBF_4 + CO \longrightarrow [Pt(X)(CO)L_2]BF_4 + AgCl \quad (3)$$

Unlike their analogs for X = halide, none of the carbonyl cations *trans*-$[Pt(X)(CO)L_2][BF_4]$ for L = $P(C_2H_5)_3$ react with methanol to give the alkoxycarbonyl species, *trans*-$Pt(X)(COOCH_3)L_2$. However, for X = SCN, NO_3, and C_6F_5 and L = $P(C_6H_5)_3$ reaction occurs at room temperature to yield white crystalline derivatives (eq 4). Similarly, for the platinum(II) carbonyl cation or alkoxycarbonyl species, reaction with water or aqueous methanol does not take place for L = $P(C_2H_5)_3$ and $(C_6H_5)_3P$, and the hydride–platinum(II) complex is not formed as reported for X = halide[3] (eq 5). The physical properties of these new derivatives are qualitatively similar to those of other carbonyl cations of platinum.[3,4]

$$trans\text{-}[Pt(X)(CO)L_2]BF_4 + CH_3OH \longrightarrow Pt(X)(COOCH_3)L_2 + HBF_4 \quad (4)$$

$$trans\text{-}[Pt(X)(CO)L_2]BF_4 + H_2O \longrightarrow trans\text{-}PtH(X)L_2 + CO_2 + HBF_4 \quad (5)$$

For X = SCN, the infrared spectra of *cis*-$PtCl(SCN)L_2$, with ν_{CN} at 2106–2110 cm^{-1}, suggest an S-bonded thiocyanate group;[8] an N-bonded group shows ν_{CN} below 2100 cm^{-1}. The marked increase in ν_{CN} in going to the dimeric complexes $[Pt_2X_2L_4][BF_4]$ is

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TABLE I

PROPERTIES OF $Pt^{II}Cl(X)L_2$ AND $[Pt^{II}_2X_2L_2][BF_4]_2$

					Anal., %				
					Calcd		Found		ν_{CN}, cm^{-1} (Nujol)
L	Compound	Mp, °C	Color	Recrystn solvents	C	H	C	H	
$P(C_2H_5)_3$	$L_2PtCl(SCN)$	160–152	White	CH_2Cl_2–$(C_2H_5)_2O$	29.8	5.8	29.7	5.7	2110
	$L_2PtCl(NO_2)$	198–200	White	CH_2Cl_2–$(C_2H_5)_2O$	28.1	5.9	28.8	5.8	
	$L_2PtCl(NO_3)$	128–132, 200 dec[a]	Off-white	Evap CH_3OH	27.3	5.7	27.3	5.8	
$P(CH_3)_2(C_6H_5)$	$L_2PtCl(SCN)$	160–163	White	CH_2Cl_2–$(C_2H_5)_2O$	36.1	3.9	35.7	4.0	2106
	$L_2PtCl(NO_2)$	199–201	White	CH_2Cl_2–$(C_2H_5)_2O$	34.8	4.0	34.2	4.1	
	$L_2PtCl(NO_3)$	178–180	White	Evap CH_3OH	33.8	3.9	34.1	4.0	
$P(C_6H_5)_3$	$L_2PtCl(SCN)$	254–257	White	CH_2Cl_2–$(C_2H_5)_2O$	54.7	3.7	55.1	4.0	2109
	$L_2PtCl(NO_2)$	222–224	White	CH_2Cl_2–$(C_2H_5)_2O$	54.0	3.8	53.2	3.8	
	$L_2PtCl(NO_3)$	226–228	White	CH_2Cl_2–$(C_2H_5)_2O$	53.0	3.7	52.2	3.7	
$P(C_2H_5)_3$	$[L_4Pt_2(SCN)_2][BF_4]_2$	232–234	White	CH_2Cl_2–$(C_2H_5)_2O$	27.1	5.3	27.2	5.6	2165
$P(C_6H_5)_3$	$[L_4Pt_2(SCN)_2][BF_4]_2$	277–279	White	CH_2Cl_2–$(C_2H_5)_2O$	51.4	3.5	51.2	3.6	2170
$As(C_6H_5)_3$	$[L_4Pt_2(SCN)_2][BF_4]_2$	b	Pale yellow	CH_2Cl_2–$(C_2H_5)_2O$	...		...		2170
$P(C_6H_5)_3$	$[L_4Pt_2(NO_3)_2][BF_4]_2$[c]	285–288	White	CH_2Cl_2–$(C_2H_5)_2O$	49.8	3.5	50.5	3.6	

[a] Melts to viscous oil before decomposing. [b] Not analyzed. [c] Nitrogen analysis: calcd, 1.6; found, 1.3.

consistent with similar infrared data for thiocyanate as a bridging ligand in other complexes of platinum[9] and palladium.[8] However, for the carbonyl cation where X = SCN and L = $P(C_6H_5)_3$, two sharp infrared absorptions are observed at 2130, 2180 cm^{-1}. Assignment of the lower frequency to ν_{CN} is consistent with a terminal S-bonded thiocyanate group and is further supported by the retention of this frequency in the thiocyanate alkoxycarbonyl. However, this is inconsistent with assignment of the higher frequency to ν_{CO}, since $\nu_{C=O}$ is 2143 cm^{-1} for free carbon monoxide.[10] However, the opposite assignment does not allow a rational relationship to the thiocyanate ligand, unless dimerization through a bridging thiocyanate group is thought to occur in solution. Jennings and Wojcicki[11] proposed a dinuclear thiocyanate bridging species in solution for $Rh(AsR_3)(CO)NCS$.

Our assignment of the higher frequency to ν_{CO} recognizes that the stretching of other bonds may also be involved. For L = $P(CH_3)_2(C_6H_5)$ analytical results, conductivity data and an ^1H nmr spectrum suggest a carbonyl cation in the cis configuration, while for X = Cl, reaction 3 with *cis*-$PtCl(X)L_2$ results in the formation of the trans isomer (Table IV).

In considering the effect of various anionic ligands, many workers have established an order[12a] of trans effect:[12b] $P(C_2H_5)_3 \sim H > CH_3 > C_6H_5 > SCN > NO_2 > I > Br > C_6F_5$[13] $> Cl > CF_3$[14] $> NO_3$, in accordance with their ability to activate a trans position to substitution.[15] This effect may be accounted for in two ways:[12b] (a) the σ-inductive effect or trans influence which causes polarization of the metal ion by electron release or (b) the π effect, whereby electron density is pulled away from the metal by π-acceptor orbitals on the ligand. For the ligands (X) considered here, the π component of the Pt–X bond is small, and a directional σ effect is assumed to be mainly responsible for the trans influence. Previous workers[5] have studied the effect on the spectroscopic properties and reactivities of Pt–X[1] bonds for different anionic ligands in the position trans to X.[1] It has been found more difficult here to relate the trans influence of X to the C–O infrared stretching frequencies of the trans platinum(II) carbonyl cations. The changes in $\nu_{C=O}$ are small, although a trend to higher frequencies is observed in descending the order of trans influence of X for L = $P(C_2H_5)_3$ and L = $P(C_6H_5)_3$ (Table II). A low value of ν_{CO} for X = H is consistent with the high trans influence for the hydride ligand. However, $\nu_{C=O}$ increases markedly for both X = CH_3 and C_6H_5, which also have a high trans influence. Church and Mays[1] reported a similar increase in cationic carbonyl complexes for X = H and X = D, ligands which have a similar high trans influence. This suggests that the low value of ν_{CO} observed for X = H could be accounted for by coupling with ν_{PtH}, which would affect both frequencies. For X = D, coupling of ν_{PtD} with ν_{CO} does not occur.

There are no significant differences in $\nu_{C=O}$ for the new alkoxycarbonyl complexes *trans*-$Pt(X)(COOCH_3)L_2$ with L = $P(C_6H_5)_3$. In contrast to the effects of ligand basicity on the nmr spectra of these species,[4] chemical shifts of the methyl protons and J_{PtH} are virtually unaffected by changes in the trans ligand X. Previous work[3,4] has shown that the nature of L affects the reactivity of *trans*-$Pt(X)(CO)L_2^+$ for X = halide in eq 4. In addition, the reactivities of the carbonyl cations with various anionic ligands decrease in descending the trans-influence series. For L = $P(C_6H_5)_3$, only the compounds with X = SCN, NO_3, and C_6F_5 undergo reaction to the alkoxycarbonyl derivatives. This decreased reactivity is consistent with a greater σ-inductive effect where X has a high trans influence, thereby lowering the reactivity of carbonyl carbon toward a nucleophile.

The failure of eq 5 to produce previously reported stable hydride species[16] could well be due to factors other than the σ-inductive effects of X.

Experimental Section

Previously described techniques and instrumentation[3,7] were used. Physical properties and analytical data for prepared derivatives are summarized in Tables I–IV.

1. **Preparation of $PtCl(X)L_2$.**—All monomeric species *cis*-$PtCl(X)L_2$ were formed by cleavage of the dichloro-bridged diplatinum cations $[Pt_2Cl_2L_4][BF_4]_2$ in solution by the simple salts

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TABLE II

PROPERTIES OF CATIONIC CARBONYL SPECIES $[Pt^{II}(X)(CO)L_2][BF_4]$

					Anal., %				$\nu_{C=O}$, cm^{-1}	
					Calcd		Found			
L	X	Mp, °C	Color	Recrystn solvents	C	H	C	H	Nujol	$CHCl_3$
$P(C_2H_5)_3$	H	Oil	Amber	Evap CH_2Cl_2	*a*				2058	2043
	CH_3	110–111	White	Acetone–$(C_2H_5)_2O$	30.0	5.9	30.1	5.9	2085	2103
	C_6H_5	164–167	White	Acetone–$(C_2H_5)_2O$	36.6	5.6	36.8	5.6	2110	2102
	SCN	129–131	White	CH_2Cl_2–$(C_2H_5)_2O$	27.8	5.0	27.6	4.7	2100 b	
	NO_2	Oil	Amber	Evap CH_2Cl_2	*c*				2050	2046
	Br	158–160	White	Ethyl acetate	*a*				2110	2112
	C_6F_5		Off-white	Evap CH_3OH	32.0	4.3	31.8	4.5	2118	2123
	Cl	168–171	White	Ethyl acetate	*a*				2100	2098
	NO_3	Oil	Amber	Evap CH_2Cl_2	*c*				2120	
$P(CH_3)(C_6H_5)_2$	Cl	Oil	Colorless	Evap CH_2Cl_2	*b*				2118	
$P(CH_3)_2(C_6H_5)$	SCN	102–107	White	Evap CH_2Cl_2	33.6	3.4	33.5	3.7	2175	
	NO_2	Oil	Amber	Evap CH_2Cl_2	*c*				2080	
	Cl	Oil	Colorless	Evap CH_2Cl_2	*a*				2120	
$P(C_6H_5)_3$	H	Oil	Amber	Evap CH_2Cl_2	*b*				2070	2068
	CH_3	234–237 dec	White	CH_2Cl_2–$(C_2H_5)_2O$	53.8	3.9	52.9	3.9	2095	2100
	SCN	252–257 dec	White	CH_2Cl_2–$(C_2H_5)_2O$	51.2	3.4	51.4	4.1	2180	
	I	270	Yellow	CH_2Cl_2–$(C_2H_5)_2O$	*a*					2120
	Br	270	White	C_6H_6	*a*					2111
	C_6F_5	86–89	Orange	Evap C_6H_6	51.6	3.0	51.9	3.7	2115	2117
	Cl	270	White	C_6H_6	*a*					2120
	CF_3	Dec (oil)	Yellow	Evap C_6H_6	*b*				2120	
	NO_3[d]	118 dec	White	CH_2Cl_2–$(C_2H_5)_2O$	49.6	3.3	47.6	3.3	2130	

[a] Previously reported. [b] Not analyzed. [c] Isolated impure. [d] Nitrogen analysis: calcd, 1.6; found, 1.4.

TABLE III

PROPERTIES OF ALKOXYCARBONYL SPECIES $Pt^{II}(X)(COOCH_3)L_2$

					Anal., %				$\nu_{C=O}$, cm^{-1}	
					Calcd		Found			
L	X	Mp, °C	Color	Recrystn solvents	C	H	C	H	Nujol	$CHCl_3$
$P(C_2H_5)_3$	Cl	Oil	White	Evap CH_3OH	*a*				1600	1600
$P(C_6H_5)_3$	Cl	222–227	White	CH_2Cl_2–$(C_2H_5)_2O$	*a*				1664	1637
	Br	226–231	Cream	CH_2Cl_2–$(C_2H_5)_2O$	*a*				1665	1637
	I	226–229	Pale yellow	CH_2Cl_2–$(C_2H_5)_2O$	*a*				1655	1648
	SCN	230–233	White	CH_2Cl_2–$(C_2H_5)_2O$	56.0	4.0	55.4	4.0	1645	1639
	NO_3[c]	215–218	Off-white	CH_2Cl_2–$(C_2H_5)_2O$	55.0	4.0	52.4	3.7	1642	1645
	C_6F_5	242–245	Cream	CH_2Cl_2–$(C_2H_5)_2O$	*b*				1660	1646
	CF_3	...	Cream	...	*b*				1645	

[a] Previously reported. [b] Not analyzed. [c] Nitrogen analysis: calcd, 1.7; found, 1.3.

TABLE IV

NMR DATA FOR PLATINUM(II) COMPLEXES

				Phosphine methyls			Alkoxy methyls	
Compound	L	X	Solvent	$\delta(CH_3)$[a]	J_{P-H}[b]	J_{Pt-H}	$\delta(CH_3)$	J_{Pt-H}
$Pt(X)(COOCH_3)L_2$	$P(C_2H_5)_3$	Cl	C_6H_6				2.9 t[c]	7
	$P(C_6H_5)_3$	Cl	CH_2Cl_2				2.4 t	7
	$P(C_6H_5)_3$	Br	CH_2Cl_2				2.4 t	7
	$P(C_6H_5)_3$	SCN	CH_2Cl_2				2.4 t	6
	$P(C_6H_5)_3$	NO_3	CH_2Cl_2				2.4 t	6
	$P(C_6H_5)_3$	C_6F_5	CH_2Cl_2				2.4 t	5.6
$PtCl(X)L_2$	$P(CH_3)_2(C_6H_5)$	Cl	CH_2Cl_2	1.71 d	10.8	34.2		
	$P(CH_3)_2(C_6H_5)$	NO_2	CH_2Cl_2	1.72, 1.66 dd	11	41		
	$P(CH_3)_2(C_6H_5)$	SCN	CH_2Cl_2	1.66 d	11	36		
	$P(CH_3)_2(C_6H_5)$	NO_3	CH_2Cl_2	1.62 d	11	36		
trans-$[PtX(CO)L_2][BF_4]$	$P(CH_3)_2(C_6H_5)$	Cl	CH_2Cl_2	2.18 t	8.6	26.0		
cis-$[PtX(CO)L_2][BF_4]$	$P(CH_3)_2(C_6H_5)$	SCN	CH_2Cl_2	1.85 d	11.0	36		
cis-$[PtX(CO)L_2][PF_6]$	$P(CH_3)_2(C_6H_5)$	SCN	CH_2Cl_2	1.90 d	11.0	36		
trans-$[PtX(CO)L_2][BF_4]$	$P(CH_3)(C_6H_5)_2$	Cl	Acetone	2.55 t	8.2	24.8		

[a] Chemical shifts (δ) in ppm; d, doublet; t, triplet. [b] Coupling constauts (J) in Hz. [c] The methyl protons are split by ^{195}Pt (34% abundance) with $I = 1/2$ into a 1:4:1 triplet.

NaSCN, $NaNO_2$, and $NaNO_3$, for L = $P(C_2H_5)_3$, $P(CH_3)_2(C_6H_5)_3$, and $P(C_6H_5)_3$.

(a) For L = $P(C_2H_5)_3$ an aqueous solution (2 ml) of NaSCN (0.030 g) was added dropwise to a refluxing solution of $[Pt_2Cl_2L_4][BF_4]_2$ (0.200 g) in methylene chloride and stirred for 5 hr. The organic layer was dried, filtered, and then reduced to small volume before crystallization was induced with diethyl ether. The white, solid product was filtered, washed with cold methanol, and recrystallized as above, affording pure *cis*-$PtCl(SCN)L_2$ (0.180 g); $NaBF_4$ (0.031 g) was recovered from the aqueous layer.

(b) Similarly the monomeric species *cis*-$PtCl(NO_2)L_2$ and *cis*-$PtCl(NO_3)L_2$ were formed from reaction with $NaNO_2$ and $NaNO_3$, respectively.

(c) For L = $P(C_6H_5)_3$ and $P(CH_3)_2(C_6H_5)$, the dimeric salts $[Pt_2Cl_2L_4][BF_4]_2$ were produced *in situ* by the addition of an acetone solution (5 ml) of $AgBF_4$ to an equimolar quantity of *cis*-$PtCl_2L_2$ in CH_2Cl_2 (20 ml). After filtration to remove the AgCl precipitate, the procedures were similar to that in (a). For X = SCN and NO_2, the products were recrystallized as above, while for X = NO_3 the white, solid product $PtCl(NO_3)L_2$ was filtered from the reaction mixture. The ^1H nmr spectra of the products for L = $P(CH_3)_2(C_6H_5)$ were consistent with a cis configuration. See Table IV.

2. Preparation of $[Pt_2X_2L_4][BF_4]_2$.—(a) For L = $P(C_2H_5)_3$ and X = SCN, $PtCl(X)L_2$ (0.260 g) in CH_2Cl_2 (20 ml) was stirred with an acetone solution (5 ml) of $AgBF_4$ (0.096 g) for 1 hr at 25°. The white precipitate of AgCl was filtered off, and crystallization in the filtrate was induced by the addition of diethyl ether. The white, solid product $[Pt_2(SCN)_2L_4][BF_4]_2$ (0.240 g) was similarly recovered for L = $P(C_6H_5)_3$ and L = $As(C_6H_5)_3$.

(b) For L = $P(C_6H_5)_3$ and X = NO_3, $[PtCl(X)L_2]$ (0.200 g) and boron trifluoride (0.300 g) were maintained in dried chloroform at 25° for 8 hr in a silica Carius tube. A yellow oil separated from solution after 2 hr, but shaking was continued for 6 hr. After removal of volatiles and extraction with methylene chloride, precipitation in solution was induced with diethyl ether. Recrystallization as above afforded pure $[Pt_2(NO_3)_2L_4][BF_4]_2$ (0.140 g), ν_{NO_3} 1525, 1350 cm^{-1}.

A similar procedure was also successful for X = SCN and L = $P(C_6H_5)_3$ and $P(C_2H_5)_3$.

(c) Procedures similar to (2b), using $PtCl(X)L_2$, yielded $[Pt_2Cl_2L_4][BF_4]_2$ for L = $P(C_6H_5)_3$ and X = NO_2 and for L = $P(C_2H_5)_3$ and X = NO_3 and NO_2.

3. Preparation of $Pt(X)(CO)L_2^+$. (a) **For L = $P(C_2H_5)_3$.**—(i) For X = H,[17] *trans*-$Pt(H)ClL_2$ (0.200 g) was stirred with $AgBF_4$ (0.083 g) in acetone solution under 1 atm of carbon monoxide for 1 hr at 25°. After filtration to remove NaCl and evaporation of volatiles, $[Pt(H)(CO)L_2][BF_4]$ (0.200 g) was isolated as an amber oil identified by its infrared spectrum, ν_{PtH} 2158 and $\nu_{C=O}$ 2058 cm^{-1}.

(ii) For X = CH_3, $AgBF_4$ (0.091 g) in acetone (2 ml) was stirred with an acetone solution of *trans*-$Pt(CH_3)ClL_2$[18] (0.200 g) under 1 atm of carbon monoxide. A white precipitate of silver chloride formed almost immediately but stirring was continued for 2 hr. After filtration and evaporation to small volume, crystallization in solution was induced with diethyl ether. Recrystallization from a methylene chloride–diethyl ether mixture afforded pure *trans*-$[Pt(CH_3)(CO)L_2][BF_4]$ (0.200 g). In addition to the anticipated ethyl proton resonance, the ^1H nmr spectrum in methylene chloride solution consisted of a 1:4:1 triplet (J_{Pt-H} = 64 cps) centered at δ_{CH_3} 0.66 ppm, each component of which was split into a 1:2:1 triplet (J_{Pt-H} = 8 cps).

(iii) For X = C_6H_5, *trans*-$Pt(C_6H_5)ClL_2$[19] reacted as in (ii) above, affording pure, white *trans*-$[Pt(C_6H_5)(CO)L_2][BF_4]$, recrystallized from an acetone–diethyl ether mixture. The ^1H nmr resonances of the phenyl group bound to platinum were detected at 7.1 ppm.

(iv) As above, for X = C_6H_5, reaction of *trans*-$Pt(C_6H_5)ClL_2$[20] afforded pure *trans*-$[Pt(C_6H_5)(CO)L_2][BF_4]$ as a colorless oil which solidified under vacuum.

(v) For X = SCN, $[PtX_2L_4][BF_4]_2$ (0.200 g) in 5 ml of dried chloroform was maintained at 70° for 12 hr under 2 atm of carbon monoxide in a sealed, evacuated Pyrex Carius tube. After filtration and evaporation to small volume, crystallization in the filtrate was induced with diethyl ether. Recrystallization, as above, yielded pure, white *trans*-$[Pt(SCN)(CO)L_2][BF_4]$ (0.180 g); $\nu_{C=O}$ 2100 cm^{-1} (b); mp 129–131° (dimer), 233–235°.

(vi) For X = NO_2, $Pt(NO_2)ClL_2$ (0.200 g) was stirred with $AgBF_4$ (0.074 g) in acetone solution for 2 hr at 25° under 1 atm of carbon monoxide. The solution quickly became dark amber, yielding a viscous amber oil after filtration, evaporation of volatiles, and extraction with THF. Reaction with an equimolar quantity of $NaPF_6$ in acetone solution, evaporation of volatiles, and extraction of the residue with CH_2Cl_2 gave an impure, dark oil which could not be induced to crystallize; $\nu_{C=O}$ 2046 cm^{-1}.

(vii) For X = NO_3, $Pt(NO_3)ClL_2$ was treated as above. A viscous amber oil was isolated by extraction procedures similar to (vi); $\nu_{C=O}$ 2120 cm^{-1}.

(b) **For L = $P(CH_3)_2(C_6H_5)$.**—(i) For X = Cl,[21] reaction of *cis*-$PtCl_2L_2$ with $AgBF_4$ and carbon monoxide as in (ai) yielded a colorless oil; $\nu_{C=O}$ 2118 cm^{-1}. Methathesis with $NaB(C_6H_5)_4$ as in (avi) afforded solid *trans*-$[PtCl(CO)L_2][B(C_6H_5)_4]$ recrystallized from a methylene chloride–diethyl ether mixture; $\nu_{C=O}$ 2093 cm^{-1}.

(ii) As in (av), for X = SCN, $[Pt_2X_2L_4][BF_4]_2$ was treated with carbon monoxide, to give an amber solution after 12 hr. After filtration and removal of volatiles, an amber oil was isolated, which solidified under vacuum. For $[Pt(SCN)(CO)L_2]$-$[BF_4]$, the proton nmr spectrum in CH_2Cl_2 suggested the cis configuration (see Table IV); ν_{CN} 2110 cm^{-1}, ν_{CO} 2175 cm^{-1}.

As in (avi), $Pt(SCN)ClL_2$ (0.300 g) in acetone–CH_2Cl_2 was treated with $NaPF_6 \cdot H_2O$ (0.099 g) in acetone solution for 12 hr under 1 atm of carbon monoxide. After evaporation of volatiles, extraction with CH_2Cl_2, and filtration, *cis*-$[Pt(SCN)$-$(CO)L_2][PF_6]$ (0.340 g) was isolated as a yellow oil which solidified under vacuum; mp 80–84°. *Anal.* Calcd for $C_{18}H_{22}F_6$-$SNOBP_2Pt$: C, 30.8; H, 3.2. Found: C, 30.9; H, 3.4. ν_{CN} 2105 cm^{-1}, ν_{CO} 2174 cm^{-1}; molar conductance 66 ohm^{-1} cm^2 in methanol.

(iii) For X = NO_2, reaction of $Pt(NO_2)ClL_2$ as in (ii) above yielded an impure viscous amber oil.

(iv) An impure viscous amber oil was similarly isolated for X = NO_3. The proton nmr spectra of these products in methylene dichloride also showed the presence of impurities.

(c) **For L = $P(CH_3)(C_6H_5)_2$.**—For X = Cl, *cis*-$PtCl_2L_2$ (0.200 g) was stirred with $AgBF_4$ (0.058 g) in acetone solution for 1 hr. under 1 atm of carbon monoxide. After filtration and removal of volatiles, a yellow oil was isolated from the filtrate; $\nu_{C=O}$ 2118 cm^{-1}. A pmr spectrum in CH_2Cl_2 suggested the trans configuration for $[PtCl(CO)L_2][BF_4]$. (See Table IV.)

(d) **For L = $P(C_6H_5)_3$.**—(i) For X = H, *trans*-$Pt(H)ClL_2$ (0.200 g) was stirred with $AgBF_4$ (0.051 g) in CH_2Cl_2–acetone solution under 1 atm of carbon monoxide for 1 hr at 25°. As in (ai) *trans*-$[Pt(H)COL_2][BF_4]$ was isolated as an amber oil; ν_{PtH} 2170 cm^{-1}, $\nu_{C=O}$ 2070 cm^{-1}.

(ii) For X = CF_3, $AgBF_4$ (0.032 g) in acetone solution was added dropwise to a stirring solution of $Pt(CF_3)IL_2$[14] in benzene, under 1 atm of carbon monoxide. After 1 hr at 25°, the white precipitate of AgI was filtered off, and the volatiles were removed under vacuum. $[Pt(CF_3)(CO)L_2][BF_4]$ was isolated as a yellow oil which decomposed on standing; ν_{CO} 2120 cm^{-1}.

(iii) For X = SCN, $[Pt_2X_2L_4][BF_4]_2$ in methylene chloride solution was shaken for 10 hr at 25° under 1 atm of carbon monoxide in an evacuated Pyrex Carius tube. As in (av), recrystallization from a methylene chloride–diethyl ether mixture afforded pure $[Pt(SCN)(CO)_2][BF_4]$; ν_{CN} 2130 cm^{-1}, ν_{CO} 2180 cm^{-1}.

(iv) For X = NO_3, $[Pt_2X_2L_4][BF_4]_2$ was treated as in (iii) above, yielding white, solid $[Pt(NO_3)_2(CO)L_2][BF_4]$; $\nu_{C=O}$ 2130 cm^{-1}, ν_{NO_3} 1520, 1350 cm^{-1}.

(v) An excess of CH_3Br was added to a stirring solution of $Pt^0[P(C_6H_5)_3]_4$[22] in CH_2Cl_2 and maintained at 25° for 3 hr. White, solid *trans*-$Pt(CH_3)BrL_2$ was filtered, washed with methanol, and then dried; mp 281–283°.

trans-$Pt(CH_3)BrL_2$ (0.300 g) in CH_2Cl_2 (20 ml) was stirred with $AgBF_4$ (0.072 g) in acetone (10 ml) for 3 hr at 25° under 1 atm of carbon monoxide. After filtration, crystallization in solution was induced with diethyl ether. Recrystallization as above afforded pure, white *trans*-$[Pt(CH_3)_2(CO)L_2][BF_4]$; mp 234–237°; ν_{CO} 2100 cm^{-1}. In addition to the anticipated phenyl proton resonance, the ^1H nmr spectrum in methylene chloride consisted of a 1:4:1 triplet (J_{PtH} = 61 cps), centered at δ_{CH_3} 0.47 ppm, each component of which was split into a 1:2:1 triplet (J_{PH} = 4 cps).

(vi) As above, for X = C_6H_5, *trans*-$Pt(C_6H_5)BrL_2$ was formed by reaction of excess pentafluorophenyl bromide with $Pt^0[P(C_6H_5)_3]_4$; mp 299–301°. Reaction with $AgBF_4$ and carbon monoxide and recrystallization as above afforded pure, orange *trans*-$[Pt(C_6H_5)(CO)L_2][BF_4]$, mp 86–89°; ν_{CO} 2117 cm^{-1}.

4. Preparation of $Pt(X)(COOCH_3)L_2$. (a) **For L = $P(C_2H_5)_3$ (Attempted).**—(i) For X = H, $[Pt(X)(CO)L_2][BF_4]$ was shaken in neat methanol at 70° in a sealed, evacuated Carius tube. After 18 hr, there was no evidence for formation of alkoxycarbonyl species.

(ii) Similar results were obtained for X = CH_3, C_6H_5, C_6H_5, NO_2, NO_3, and SCN and for the complexes with L = $P(CH_3)_2$-(C_6H_5) and X = SCN, NO_2, and NO_3.

(b) **For L = $P(C_6H_5)_3$.**—(i) For X = SCN, $[Pt_2X_2L_4]$-$[BF_4]$ (0.400 g) in methanol solution was shaken under 1 atm of carbon monoxide for 12 hr at 60° in an evacuated Pyrex Carius tube. The off-white precipitate was filtered, washed with water and methanol, and then recrystallized from a methylene chloride–diethyl ether mixture; $\nu_{C=O}$ 1645 cm^{-1}, ν_{CN} 2100 cm^{-1}.

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Quantitative conversion to the alkoxycarbonyl species $Pt(SCN)(COOCH_3)L_2$ was also carried out as in (ii) below.

(ii) For X = NO_3 and C_6H_5, $[Pt(X)(CO)L_2][BF_4]$ was shaken in neat methanol for 12 hr at 25° in an evacuated Pyrex Carius tube. The off-white precipitate was filtered, washed with water and methanol, and then recrystallized as above, affording pure $Pt(NO_3)(COOCH_3)L_2$ ($\nu_{C=O}$ 1642 cm^{-1}, ν_{NO_3} 1520, 1350 cm^{-1}) and $Pt(C_6H_5)(COOCH_3)L_2$ ($\nu_{C=O}$ 1646 cm^{-1}).

Solubility properties were identical with those of the analogs for X = Cl, Br, and I,[3] while ir assignments and pmr absorptions were qualitatively similar (Table IV).

(iii) As above, for X = CF_3, $Pt(CF_3)(COOCH_3)L_2$ was isolated as an off-white solid, which decomposed in solution; $\nu_{C=O}$ 1645 cm^{-1}.

(iv) For X = H, $[PtH(CO)L_2][BF_4]$ in CH_2Cl_2 (1 ml) was stirred with neat methanol for 1 hr at 25°. An insoluble orange-red solid was filtered, washed with water and methanol, and then dried under vacuum; $\nu_{C=O}$ 1800 cm^{-1} (b). Although there was no evidence for the formation of an alkoxycarbonyl derivative, the product could well contain a bridging carbonyl group.[23]

(v) For X = CH_3, $[Pt(CH_3)(CO)L_2][BF]$ was stirred in neat methanol for 12 hr at 25°. There was no evidence for formation of the alkoxycarbonyl species.

(c) For L = $As(C_6H_5)_3$ (Attempted).—Conditions similar to (bi) applied to $[Pt_2(SCN)_2L_4][BF_4]_2$ resulted in pronounced decomposition.

5. Attempted Preparation of $[PtH(X)L_2]$. (a) For L = $P(C_2H_5)_3$.—(i) For X = CH_3, $[Pt(X)(CO)L_2][BF_4]$ was shaken with 20 ml of water–methanol (10:1) solution for 15 hr at 90° in an evacuated Pyrex Carius tube. No evidence for hydride formation was found. A similar reaction conducted at 100° gave pronounced decomposition.

(ii) For X = C_6H_5, identical reactions at 90 and 110° proceeded with less decomposition, yet no hydride was detected in the reaction products.

(iii) As above, reactions were unsuccessful for X = C_6H_5, H, and SCN.

(b) For L = $P(C_6H_5)_3$.—(i) For X = SCN, $Pt(X)(COOCH_3)L_2$ was heated with saturated aqueous sodium thiocyanate solution (5 ml) at 110° for 12 hr in an evacuated Pyrex tube. Carbon dioxide and methanol could not be detected in the volatile products. Extraction of the residue with methylene chloride afforded unreacted starting material. No evidence for hydride formation was found.

(ii) For X = NO_3, $Pt(X)(COOCH_3)L_2$ heated with saturated aqueous potassium nitrate gave similar results.

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Hydrothermal Equilibria and Crystal Growth of Rare Earth Oxides, Hydroxides, Hydroxynitrates, and Hydroxycarbonates

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The equilibria of praseodymium, neodymium, and terbium oxides with water have been examined at temperatures up to 900° and pressures of 1360 atm by hydrothermal techniques. In the trivalent Pr and Nd systems, only hexagonal trihydroxide and oxyhydroxide were observed with the phase boundary near 800°. In the presence of oxygen or oxidizing agent, fcc PrO_2 was found as a product after reaction at temperatures above 600°; under similar conditions diphasic mixtures of rhombohedral $TbO_{1.714}$ and monoclinic $TbO_{1.818}$ were obtained. The equilibria of praseodymium hydroxynitrate and hydroxycarbonate systems have been explored, and monoclinic $Pr(OH)_2NO_3$, hexagonal $Pr_2(OH)_5NO_3$, hexagonal $PrOHCO_3$, and hexagonal $Pr_2O_2CO_3$ have been characterized. Single crystals of trihydroxide, hydroxynitrate, and hydroxycarbonate phases have been prepared and examined by Weissenberg techniques; small crystals of the higher oxides have also been obtained. The use of nitrate ion as an oxidizing agent under high-temperature conditions and as an effective mineralizer at lower temperatures is described and discussed. Tga data for the hydroxy anion phases are presented, and discrepancies between the present hydrothermal results and those of previous reports are discussed.

Introduction

A detailed structural investigation of the intermediate oxides of praseodymium and terbium has been hindered by their unavailability as single crystals. The preparation of hexagonal A-type[1] and monoclinic B-type sesquioxide[2,3] crystals has been achieved by high-temperature techniques, but the oxidation of such samples to the fluorite-related intermediate phases appears to proceed with the loss of crystal integrity.[4] Attempts to employ the lower temperature procedures of chemical transport and flux techniques in this laboratory were unsuccessful. The results of Shafer and Roy,[5] who reported that the oxides of several trivalent rare earths were stable under the hydrothermal conditions, suggested that hydrothermal growth would be the most feasible method for preparing pure oxide crystals in a cubic-related crystallographic form suitable for structural analysis and the investigation of defect chemistry. Since oxygen pressures greater than 10^3 atm are necessary for the preparation of PrO_2 even at 500°[6] and since C-type Nd_2O_3 has been reported to be stable in water under appropriate temperature and pressure conditions, attempts to prepare C-type Pr_2O_3 by hydrothermal techniques were initiated.

After preliminary results for the Pr_2O_3–H_2O system

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