Journal of Organometallic Chemistry, 224 (1982) 407—420
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

METALS IN ORGANIC SYNTHESES

VII *. THE ISOLATION OF *trans*-$[PtCl(COPr\text{-}n)(PPh_3)_2]$ (I) AND *trans*-$[Pt(SnCl_3)(COPr\text{-}n)(PPh_3)_2]$ (II), ACTIVE INTERMEDIATES IN THE HYDROFORMYLATION OF PROPENE CATALYZED BY A $[PtCl_2(PPh_3)_2]$-$SnCl_2$ PRECURSOR. THE CRYSTAL AND MOLECULAR STRUCTURE OF COMPLEX I AND A COMPARISON WITH ITS PALLADIUM ANALOG

R. BARDI, A.M. PIAZZESI,

Biopolymer Research Centre, CNR, University of Padova, Via Marzolo 1, 35100 Padova, (Italy)

G. CAVINATO, P. CAVOLI and L. TONIOLO **

Istituto di Chimica Generale ed Inorganica e di Chimica Inorganica Industriale, University of Padova, Via Loredan 4, 35100 Padova (Italy)

(Received June 11th, 1981)

Summary

trans-$[PtCl(COPr\text{-}n)(PPh_3)_2]$ (I) has been isolated in good yield from the mixtures obtained by treating a mixture of propene, *cis*-$[PtCl_2(PPh_3)_2]$ and $SnCl_2 \cdot H_2O$ with carbon monoxide in the presence or absence of hydrogen in an alcohol in which no significant hydroformylation or hydroxycarboalkylation actually occurs. The *cis*-$[PECl_2(PPh_3)_2]$-$SnCl_2 \cdot 2\ H_2O$ system is highly active in the catalytic hydroformylation in methyl isobutyl ketone, and from reaction mixtures in this medium *trans*-$[Pt(SnCl_3)(COPr\text{-}n)(PPh_3)_2]$ (II) has been isolated (33% yield). The presence of a Pt—Sn bond in a complex of type II plays a key role in promoting the formation of the aldehyde from the acyl derivative, but it is not necessary for the formation of intermediate I, since this can be isolated in good yield even in the absence of the tin compound. The higher regioselectivity observed using intermediate I or II, compared with that when the precursor is used is discussed in terms of steric effects of the ligands competing for coordination to the platinum atom. The catalytic properties of complex I are compared also with those of its palladium analog, which catalyzes only the hydrocarbo-

---

* Part VI: see reference 1.

** Author to whom correspondence should be addressed.

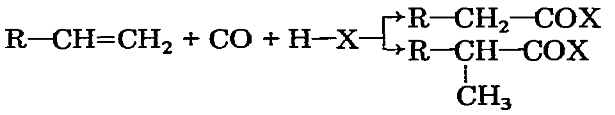
0022-328X/82/0000—0000/$02.75

alkoxylation but does this even in the absence of $SnCl_2$.

The crystal and molecular structures of the title complex I and its palladium analogue have been determined from three dimensional X-ray diffractometer data. Both complexes are isostructural and crystallize in the monoclinic space group $P2_1/n$. Cell parameters are as follows: $[PtCl(COPr\text{-}n)(PPh_3)_2]$, (I), a = 13.266(8), b = 24.029(10), c = 12.142(8) Å, β = 115.4(1)°, Z = 4; $[PdCl(COPr\text{-}n)(PPh_3)_2]$, (III), a = 13.292(8), b = 23.800(10), c = 12.196(8) Å, β = 115.2(1)°, Z = 4. Full-matrix least-squares refinement converged at R = 0.048 (I) and R = 0.054 (III). The structures have approximately square-planar geometry and the dimensions are not unusual.

Introduction

The hydroformylation and hydrocarboalkoxylation reactions (eq. 1) have been the subject of several reports, especially in the patent literature [2,3].



$$R{-}CH{=}CH_2 + CO + H{-}X \begin{cases} \rightarrow R{-}CH_2{-}COX \\ \rightarrow R{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}COX \end{cases} \qquad (1)$$

X = H, OR′

Most of these deal with the long established cobalt and rhodium catalysis since it is these metals which are used industrially.

In recent years palladium and platinum complexes have been receiving much attention as active and regioselective catalysts. Palladium complexes in combination with Group 4B metal halides have been found to be particularly effective in providing highly regioselective bimetallic catalysts in hydrocarboalkoxylation [4]. The regioselectivity can be directed towards one isomer or the other in the absence of $SnCl_2$ and using as reaction medium the reagent alcohol or an additional solvent [1,5]. Ligand-stabilized platinum(II)-Group 4B metal halide complexes (for example of the type $[PtCl_2(PPh_3)_2]$-$SnCl_2$) have been found to be excellent regioselective catalysts for both reactions [6—10]. It has been suggested that these bimetallic catalytic systems are highly regioselective because of the steric hindrance around the central metal [4,6].

Here we report the catalytic properties of *trans*-$[PtCl(COPr\text{-}n)(PPh_3)_2]$ (I) and *trans*-$[Pt(SnCl_3)(COPr\text{-}n)(PPh_3)_2]$ (II) which were isolated from reactions under propene hydroformylation and hydrocarboalkoxylation conditions employing *cis*-$[PtCl_2(PPh_3)_2]$-$SnCl_2 \cdot 2\,H_2O$ as catalyst precursor. The structure of complex(I) is reported, and compared to that of its palladium analogue [11].

Experimental section

Materials

Carbon monoxide and hydrogen were purchased from the S.I.O. Company. Propene was kindly supplied by the Montedison S.p.A.; it contained about 5% propane, traces of propyne and allene, but no C_2 or higher hydrocarbons. Alcohols and $SnCl_2 \cdot 2\ H_2O$ * were commercial grade. The catalyst precursor *cis*-$[PtCl_2(PPh_3)_2]$ was prepared from $[H_2PtCl_6]\ 6\ H_2O$ and PPh_3 [12].

General procedure

The yields and the isomeric compositions of the reaction products were determined by GLC, using a Hewlett-Packard gas chromatograph Model 5830 A equipped with a Hewlett-Packard GC terminal Model 18850. Analyses were carried out using a 6 ft long column of SE 30 25% on Chrom. P followed by a 6 ft column of Porapak N at 170°C.

Carbonylations were carried out in a stainless steel stirred autoclave of about 75 ml, thermostated in an oil bath. Catalyst and reagents were contained in a Pyrex bottle placed in the autoclave to prevent contamination by other metallic species and to avoid effects of the metal surface of the autoclave.

Synthesis of trans-[PtCl(COPr-n)(PPh$_3$)$_2$] (I)

80 mg of *cis*-$[PtCl_2(PPh_3)_2]$ (0.1 mmol) together with 26 mg of PPh_3 (0.1 mmol) and 5 ml of alcohol (MeOH, EtOH or n-BuOH) were introduced into the bottle in the autoclave. The autoclave was cooled in an ice bath and purged with carbon monoxide. Then was pressurized with 10 atm of propene and with 100 atm of CO at room temperature. The autoclave was then placed in a thermostated oil bath and the temperature was raised to 100°C during ca. 10 min. After 4 hours the autoclave was cooled in an ice bath. After ca. 1 day at r.t. the autoclave was depressurized. White crystals of complex I were filtered off, washed with EtOH and dried under vacuum. Yield 75%. Found: C, 57.95; H, 4.60; Cl, 4.14. $C_{40}H_{37}ClOP_2Pt$ Calcd.: C, 58.15; H, 4.51; Cl, 4.29%.

Practically the same result was obtained using 0.5 mmol of $SnCl_2$ in place of PPh_3.

Propene hydroformylation

In a typical experiment, 0.05 mmol of complex I, 0.25 mmol of $SnCl_2$ and 9.4 ml of methyl isobutyl ketone (MIK) were introduced in the bottle placed in the autoclave (whose free volume was reduced to ca. 50 ml). After purging with CO, propene (10 mmol), molecular hydrogen (50 atm), and carbon monoxide (50 atm) were introduced into the autoclave at r.t. Then the autoclave was placed in a thermostated oil bath at 70°C. After 3 h the autoclave was cooled in an ice bath and slowly depressurized. The content of the bottle was analyzed by GLC after the usual work up. The linear/branched isomer ratio was found to be 13.

The bottle was set aside for several hours out of the autoclave, and yellow crystals of $[Pt(SnCl_3)(COPr\text{-}n)(PPh_3)_2]$ (II) separated. Yield 33%. Found: C, 47.51; H, 3.58; Cl, 10.99. $C_{40}H_{37}Cl_3OP_2PtSn$ Calcd.: C, 47.30; H, 3.67; Cl, 10.47%.

Essentially the same results were obtained using complex II or *trans*-$[PtHCl(PPh_3)_2]$ in place of complex I. With *cis*-$[PtCl_2(PPh_3)_2]$ the linear/branched isomer ratio was 4.9. Using complex I together with an equimolecular amount of

---

* Hereafter simply referred to as $SnCl_2$.

TABLE 1

CRYSTAL DATA

a (Å)	Complex I	Complex III
a (Å)	13.266(8)	13.292(8)
b (Å)	24.029(10)	23.800(10)
c (Å)	12.142(8)	12.196(8)
β(°)	115.4(1)	115.2(1)
Formula wt	826.35	737.81
$\rho_{obsd.}$ (gcm^{-3})	1.57	1.40
$\rho_{calcd.}$ (gcm^{-3})	1.569	1.403
Z	4	4
Unit cell volume (Å^3)	3496.5	3491.0
Space group	$P2_1/n$	$P2_1/n$
Crystal dimensions (mm)	0.2 × 0.3 × 0.7	0.2 × 0.2 × 0.8
Absorption coeff. (cm^{-1})	44.34 (Mo-*Kα*)	7.30 (Mo-*Kα*)

HCl gave results similar to those obtained with *cis*-[$PtCl_2(PPh_3)_2$].

When these complexes were employed in EtOH in place of MIK, complex I was recovered in each case, and no significant amounts of aldehydes or ethyl butyrates were detected.

When *trans*-[$PdCl_2(PPh_3)_2$) or *trans*-[PdCl(COPr-n)(PPh_3)$_2$], (III), were used in MIK or EtOH no aldehyde was formed.

Propene hydrocarboalkoxylation

This was carried out by the procedure reported above for the propane hydroformylation, but in the absence of molecular hydrogen.

Using complex I, at 70°C, under P_{CO} = 120 + 140 atm; for 3 h, using as solvent either (a) the alcohol or (b) MIK and a alcohol/propene ratio slightly over 1, no significant amounts of ester was detected by GLC. After 6 h at 100°C small amounts of n-butyrrate and *iso*-butyrrate were found (ca. 10 catalytic cycles).

Collection and reduction of X-ray intensity data

Suitable crystals for X-ray analysis of complexes I and III were obtained directly from the reaction media (in EtOH).

TABLE 2

DETAILS OF DATA COLLECTION

	Complex I	Complex III
Radiation	Mo-*Kα*, λ 0.7107 Å	Mo-*Kα*, λ 0.7107 Å
Monochromator	graphite crystal	graphite crystal
Scan method	θ—2θ	θ—2θ
Scan speed (° min^{-1})	0.03	0.03
Scan width (°)	1.20	1.20
"Standard" reflections	2 every 180 min	2 every 180 min
"Standard" indices	(040), (0$\bar{4}$0)	($\bar{2}$14), (21$\bar{4}$)
2θ scan limit (°)	44	46
No. of data	4273	4713
No. of data with $I > 3\sigma$ (*I*)	2267	3354

TABLE 3

FRACTIONAL ATOMIC POSITIONAL PARAMETERS (X10^4)

Complex I				Complex III			
Atom	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	Atom	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$
Pt	1950(1)	1414(1)	279(1)	Pd	1971(1)	1396(1)	306(1)
Cl	2254(4)	417(2)	724(4)	Cl	2272(2)	392(1)	744(2)
P(1)	1955(3)	1586(2)	2157(4)	P(1)	1977(2)	1591(1)	2190(2)
P(2)	1834(4)	1213(2)	8359(4)	P(2)	1849(2)	1215(1)	8366(2)
C(7)	1713(16)	2229(8)	9927(14)	C(7)	1694(7)	2213(3)	9923(8)
C(8)	2709(13)	2569(7)	156(17)	C(8)	2720(9)	2563(4)	215(10)
C(9)	2562(19)	3200(10)	67(19)	C(9)	2553(12)	3196(5)	136(12)
C(10)	1898(20)	3384(9)	8750(22)	C(10)	1949(14)	3391(7)	8874(15)
O	771(11)	2433(5)	9479(11)	O	766(5)	2395(3)	9503(6)
Phenyl ring 1							
C(1)	3071(7)	1224(5)	3429(10)	C(1)	3066(4)	1228(2)	3453(5)
C(11)	2976	1127	4514	C(11)	2971	1138	4536
C(12)	3840	865	5486	C(12)	3827	873	5504
C(13)	4800	700	5374	C(13)	4779	696	5390
C(14)	4895	797	4290	C(14)	4874	786	4707
C(15)	4031	1059	3318	C(15)	4018	1052	3339
Phenyl ring 2							
C(2)	654(8)	1368(4)	2201(8)	C(2)	681(4)	1374(2)	2244(4)
C(21)	309	1609	3027	C(21)	330	1613	3067
C(22)	—690	1442	3046	C(22)	—669	1442	3079
C(23)	—1344	1034	2239	C(23)	—1317	1032	2268
C(24)	—999	793	1412	C(24)	—966	793	1445
C(25)	0	960	1393	C(25)	33	965	1433
Phenyl ring 3							
C(3)	2129(7)	2309(5)	2658(9)	C(3)	2137(3)	2326(2)	2692(5)
C(31)	1207	2663	2214	C(31)	1220	2685	2248
C(32)	1334	3223	2551	C(32)	1344	3249	2592
C(33)	2382	3429	3332	C(33)	2386	3454	3381
C(34)	3304	3074	3776	C(34)	3303	3095	3825
C(35)	3178	2515	3439	C(35)	3178	2531	3481
Phenyl ring 4							
C(4)	3031(10)	796(4)	8482(10)	C(4)	3024(5)	794(2)	8460(5)
C(41)	4093	1006	9198	C(41)	4088	1001	9165
C(42)	5036	723	9264	C(42)	5020	709	9226
C(43)	4916	230	8613	C(43)	4889	209	8584
C(44)	3854	20	7897	C(44)	3825	1	7879
C(45)	2912	302	7832	C(45)	2893	293	7818
Phenyl ring 5							
C(5)	1790(8)	1787(5)	7360(10)	C(5)	1811(4)	1794(2)	7354(5)
C(51)	2684	1902	7079	C(51)	2707	1917	7083
C(52)	2607	2336	6283	C(52)	2634	2362	6308
C(53)	1636	2654	5768	C(53)	1666	2683	5803
C(54)	742	2539	6049	C(54)	770	2560	6074
C(55)	819	2105	6845	C(55)	843	2115	6849
Phenyl ring 6							
C(6)	562(9)	834(5)	7424(10)	C(6)	576(4)	837(2)	7436
C(61)	275	748	6189	C(61)	274	751	6204
C(62)	—707	467	5464	C(62)	—709	467	5499
C(63)	—1402	271	5974	C(63)	—1389	269	6025
C(64)	—1115	356	7209	C(64)	—1087	355	7257
C(65)	—133	638	7934	C(65)	—104	639	7962

Approximate unit cell dimensions for both complexes were obtained from preliminary Weissenberg and precession photographs. Systematic absence of the types $h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$) observed in both cases uniquely define the centrosymmetric, monoclinic space group $P2_1/n$ (C_{2h}^5, no. 14). For $Z = 4$ neither molecule has any imposed crystal symmetry. Full details of the crystal data for both complexes are listed in Table 1.

Reflection data for I and III were collected on a Philips PW 1100 four-circle diffractometer. Accurate unit cell dimensions and crystal orientation matrices, together with their estimated standard errors, were obtained from least-squares refinement of the 2θ, ω, χ and φ values of 20 carefully centered high-angle reflections. Full details of the experimental conditions and data collection method used are given in Table 2.

Solution and refinement of the structures

The structures were readily solved by conventional Patterson and Fourier syntheses. The refinement of the structural models, which was by the method of full-matrix least-squares, was carried out with the phenyl rings treated as rigid groups and restricted to their normal geometry (D_{6h} symmetry, C—C = 1.395 Å), using the group-refinement procedure [13]. Each ring was assigned six variable positional parameters and each ring carbon atom was assigned an individual thermal parameter. The remaining non-hydrogen atoms were allowed to vibrate anisotropically. Hydrogen atoms could not be located from electron density difference maps and therefore were included in the scattering models in calculated idealized positions (C—H = 0.95 Å), but not varied.

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) IN COMPLEXES I and III

Distance	I	III	Distance	I	III
M—Cl[a]	2.450(4)	2.446(1)	P(2)—C(4)	1.830(12)	1.817(4)
M—P(1)[a]	2.314(4)	2.340(1)	P(2)—C(5)	1.820(13)	1.836(4)
M—P(2)[a]	2.320(4)	2.342(1)	P(2)—C(6)	1.824(12)	1.824(4)
M—C(7)[a]	2.002(19)	1.996(6)	C(7)—O	1.231(18)	1.197(6)
P(1)—C(1)	1.837(11)	1.821(4)	C(7)—C(8)	1.475(22)	1.505(8)
P(1)—C(2)	1.825(11)	1.827(4)	C(8)—C(9)	1.536(22)	1.521(9)
P(1)—C(3)	1.823(12)	1.835(4)	C(9)—C(10)	1.515(24)	1.475(11)
Angle	**I**	**III**	**Angle**	**I**	**III**
P(1)—M—P(2)[a]	176.3(2)	176.5(1)	C(1)—P(1)—C(2)	105.7(5)	104.9(2)
P(1)—M—Cl[a]	91.6(1)	92.7(1)	C(1)—P(1)—C(3)	103.2(5)	103.5(2)
P(1)—M—C(7)[a]	88.2(4)	87.7(2)	C(2)—P(1)—C(3)	104.5(5)	103.5(2)
P(2)—M—C(7)[a]	93.0(4)	91.0(2)	C(4)—P(2)—C(5)	104.4(5)	103.5(2)
P(2)—M—Cl[a]	87.3(1)	88.5(1)	C(4)—P(2)—C(6)	108.4(5)	108.2(2)
Cl—M—C(7)[a]	179.5(4)	178.8(2)	C(5)—P(2)—C(6)	101.9(5)	101.5(2)
M—P(1)—C(1)[a]	113.9(3)	114.0(1)	M—C(7)—O[a]	121.4(15)	120.5(4)
M—P(1)—C(2)[a]	112.0(3)	111.7(1)	M—C(7)—C(8)[a]	117.2(13)	115.1(4)
M—P(1)—C(3)[a]	116.5(4)	117.9(1)	C(8)—C(7)—O	121.4(18)	124.4(6)
M—P(2)—C(4)[a]	110.5(4)	110.5(1)	C(7)—C(8)—C(9)	114.5(13)	116.1(7)
M—P(2)—C(5)[a]	118.8(4)	120.7(1)	C(8)—C(9)—C(10)	111.1(11)	112.2(8)
M—P(2)—C(6)[a]	112.0(3)	111.5(1)			

[a] M = Pt, (I): M = Pd, (III).

The function minimized was $\Sigma w\Delta^2$, ($\Delta = |F_0| - |F_c|$), and w were 2.49 $[\sigma^2(F_0) + 0.0009\ F_0^2]^{-1}$ (III) and 2.05 $[\sigma^2(F_0) + 0.0003\ F_0^2]^{-1}$ (I). Weighting-scheme analyses showed no significant dependence of the mean $w\Delta^2$ on either $|F_0|$ and λ^{-1} sin θ. The final electron density difference maps showed no unusual features. Atomic scattering factors were taken from ref. 14. Allowance was made for the anomalous scattering of platinum, palladium, chlorine and phosphorus atoms, using values of $\Delta f'$ and $\Delta f''$ from ref. 15. The final conventional R values for the observed reflections with $I \geqslant 3\sigma(I)$ were 0.048 (I) and 0.054 (III), [$R_w = 0.046$ (I), $R_w = 0.058$ (III)].

Final atomic parameters and a selection of functions derived from them are presented in Tables 3 and 4. Final atomic thermal parameters and tables of structure factors are available as supplementary material. All calculations were carried out on the CYBER 76 computer of the "C.I.N.E.C.A." with the SHELX-76 program for crystal structure determination [16].

Results and discussion

By pressurizing [*cis*-$PtCl_2(PPh_3)_2$] in EtOH, in the presence or absence of added PPh_3, with carbon monoxide and propene, white crystals of *trans*-[$PtCl(COPr\text{-}n)(PPh_3)_2$] (I) are obtained in satisfactory yield (75%). The IR spectrum of complex I shows ν(C=O) at 1659 cm^{-1}, close to the value found in other alkanoyl complexes of platinum(II) (17,18).

Complex I forms also when *trans*-[$PtHCl(PPh_3)_2$] is used. Thus it appears that the butanoyl complex is formed as follows:

$$[PtCl_2(PPh_3)_2] \xrightarrow{CH_3CH_2OH} [PtHCl(PPh_3)_2] \xrightarrow{CH_3CH{=}CH_2}$$

$$[PtCl(CH_2CH_2CH_3)(PPh_3)_2] \xrightarrow{CO} [PtCl(COCH_2CH_2CH_3)(PPh_3)_2] \qquad (2)$$

The capacity of alcohols to act as hydride sources is well documented [19]. The olefin inserts into a Pt—H bond to form a Pt-alkyl intermediate, which in turn reacts with CO to yield the final complex I.

The reaction in EtOH does not proceed further to ester formation:

$$[PtCl(COPr\text{-}n)(PPh_3)_2] + EtOH \nrightarrow [PtHCl(PPh_3)_2] + n\text{-}PrCOOEt \qquad (3)$$

contrary to what happens in the presence of the palladium analog [$PdCl(COPr\text{-}n)(PPh_3)_2$], which has been recognised as an active intermediate precursor in the hydrocarboalkoxylation of propene [11]. With the platinum complex I in EtOH as solvent, even in the presence of $SnCl_2$ no detectable amounts of ester were observed, even though [$PtCl_2(PPh_3)_2$] in combination with $SnCl_2$ is known to catalyze the hydrocarbomethoxylation of α-olefins in suitable solvents of low or moderately low polarity [6]. Again, complex I can be isolated.

Complex I, in combination with $SnCl_2$, and with MeOH as hydrogen source and MIK as solvent catalyzes the synthesis of esters, though only to a small extent (ca. 10 catalytic cycles at 100°C, after 6 h, under $P_{CO} = 130$ atm, see Experimental). Thus a complex of this type may act as precursor intermediate in the hydrocarboalkoxylation of α-olefins catalyzed by ligand-stabilized platinum(II)-Group 4B metal halide complexes [6]. Among these, [$PtCl_2(AsPh_3)_2$]-$SnCl_2$

is the most active. With this catalytic system it has been established that the rate of carbonylation of 1-heptene is independent of the initial alcohol concentration (at least with MeOH), provided that sufficient is present to satisfy the stoichiometry of the reaction [6]. Thus it seems that with this system the alkanol does not prevent the catalysis to give the esters, which are formed at temperature as low as 80°C [6].

For the catalytic carbonylation, a mechanism has been proposed similar to the reaction sequencies 2 and 3 in which the active species contains at least one Pt—Sn bond. No attempt has been made to correlate the activity with the nature of the solvent, but a range of nonpolar and moderately polar solvents has been found suitable. The fact that *N,N*-dimethylformamide inhibits carbonylation has been explained by assuming that formation of stable DMF adducts with the platinum complex prevent the interaction with the olefin [8,20]. In the cases reported here, EtOH does not prevent such an interaction, since $[PtCl_2(PPh_3)_2]$ is recovered as $[PtCl(COPr\text{-}n)(PPh_3)_2]$ in good yield.

In an attempt to carry out the hydroformylation of propene by $[PtCl_2(PPh_3)_2]$-$SnCl_2$, propene, carbon monoxide and molecular hydrogen were pressurized (5 atm, 50 atm, 50 atm, respectively) in ethanol as solvent at 70°C for 3 h. No aldehyde was detected, and complex I was recovered. The same result was obtained in the absence of $SnCl_2$. Thus it can be concluded that, with EtOH as solvent, sequence 2 easily occurs, even in the absence of $SnCl_2$, under both hydrocarboxylation or oxo conditions (in the latter case molecular hydrogen may act as hydride source) but that EtOH prevents the reaction proceeding further by processes 3 or 4 to complete the catalytic cycles:

$$[PtCl(COPr\text{-}n)(PPh_3)_2] \xrightarrow[\text{EtOH, SnCl}_2]{H_2 \; /\!/} [PtHCl(PPh_3)_2] + n\text{-}PrCHO \tag{4}$$

The aldehyde is formed in excellent yield using $[PtCl_2(PPh_3)_2]$-$SnCl_2$ as catalytic precursor under mild conditions when operating in non-polar or moderately polar solvents such as benzene or a ketone, and no significant amount of aldehyde is detected in the absence of $SnCl_2$ [8]. Thus it appears that the presence of $SnCl_2$ and the nature of the solvent play a key role in the hydroformylation.

From an experiment under the conditions specified by Schwager et al. [8], using propene and MIK as solvent, we were able to isolate a complex of composition $[Pt(SnCl_3)(COPr)(PPh_3)_2]$ (II). The IR spectrum of II shows $\nu(C{=}O)$ at 1663 cm^{-1} and bands at 324 and 304 cm^{-1} attributable to a $SnCl_3^-$ group with the tin atom bonded to the platinum [21].

Both complex I, in combination with $SnCl_2$, and complex II catalyze the hydroformylation of propene in MIK. Therefore, they are active (precursor) intermediates, which supports the mechanism proposed by Schwager et al. [8]. No aldehyde is formed when complex I is used without $SnCl_2$ or when complex II is used in EtOH. In both cases complex I is recovered.

These facts suggest that the production of the aldehyde with regeneration of the catalyst (eq. 4) occurs only when the solvent promotes the formation of the Pt—Sn bond, as proposed by other authors. It has been suggested that the active catalytic species must contain at least one Pt—Sn bond, as, for example in $[PtH(CO)(SnCl_3)(PR_3)]$ [8], and that the $SnCl_3^-$ ligand, which is a strong π-acceptor and a weak σ-donor, accepts electrons from filled 5*d* orbitals of platinum. This lowering of the electron density on the platinum [22] should favor both initial platinum hydride formation [23] and subsequent attack by nucleophiles such as the multiple bonds of the olefin [24] and CO [8]. However, the presence of a Pt—Sn bond is not essential for attack by such nucleophiles, since from reactions in EtOH, $PtCl_2(PPh_3)_2$ is recovered as complex I (see eq. 2), even in the absence of $SnCl_2$, under both hydrocarboalkoxylation or hydroformylation conditions.

Complexes I or II are significantly more regioselective in favor of the linear isomer (linear/branched isomer ratio = 13 with Pt/Sn = 1/5) than $[PtCl_2(PPh_3)_2]$ (linear/branched = 4.9 under the same conditions, see Experimental). Furthermore, $[PtHCl(PPh_3)_2]$ (IV) is as selective as complexes I or II.

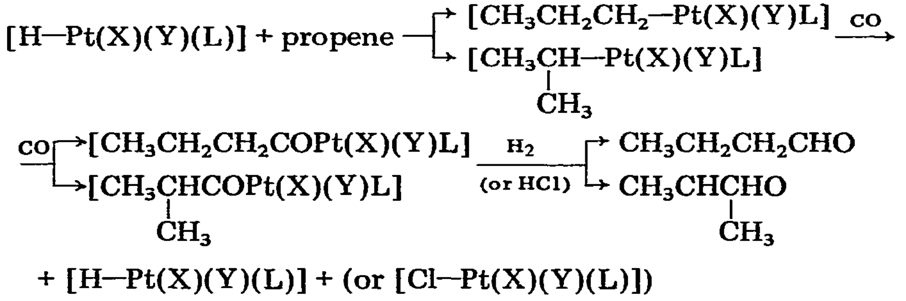
Complexes I, II, IV and their precursor *cis*-$[PtCl_2(PPh_3)_2]$ are equivalent except that they differ by a molecule of HCl.

$$[\mathrm{PtCl_2(PPh_3)_2}] + \mathrm{H_2} \rightarrow \underset{\text{(IV)}}{[\mathrm{PtHCl(PPh_3)_2}]} + \mathrm{HCl}$$

$$\mathrm{IV} + \mathrm{CH_3CH{=}CH_2} + \mathrm{CO} \rightarrow \underset{\text{(I)}}{[\mathrm{PtCl(COPr\text{-}n)(PPh_3)_2}]} \qquad (5)$$

$$\mathrm{I} + \mathrm{SnCl_2} \rightarrow \underset{\text{(II)}}{[\mathrm{Pt(SnCl_3)(COPr\text{-}n)(PPh_3)_2}]}$$

Thus it seems that HCl intervenes (by providing either H^+ and/or Cl^-) in the regioselective steps of the catalysis.



$$[\mathrm{H{-}Pt(X)(Y)(L)}] + \text{propene} \rightarrow \begin{cases} [\mathrm{CH_3CH_2CH_2{-}Pt(X)(Y)L}] \\ [\mathrm{CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}Pt(X)(Y)L}] \end{cases} \xrightarrow{\mathrm{CO}}$$

$$\xrightarrow{\mathrm{CO}} \begin{cases} [\mathrm{CH_3CH_2CH_2COPt(X)(Y)L}] \\ [\mathrm{CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCOPt(X)(Y)L}] \end{cases} \xrightarrow[\text{(or HCl)}]{\mathrm{H_2}} \begin{cases} \mathrm{CH_3CH_2CH_2CHO} \\ \mathrm{CH_3CH\underset{\underset{\displaystyle CH_3}{|}}{C}HO} \end{cases}$$

$$+ [\mathrm{H{-}Pt(X)(Y)(L)}] + (\text{or } [\mathrm{Cl{-}Pt(X)(Y)(L)}]) \qquad (6)$$

X, Y = $SnCl_3^-$, PPh_3; L = $SnCl_3^-$, PPh_3, CO or Cl^-.

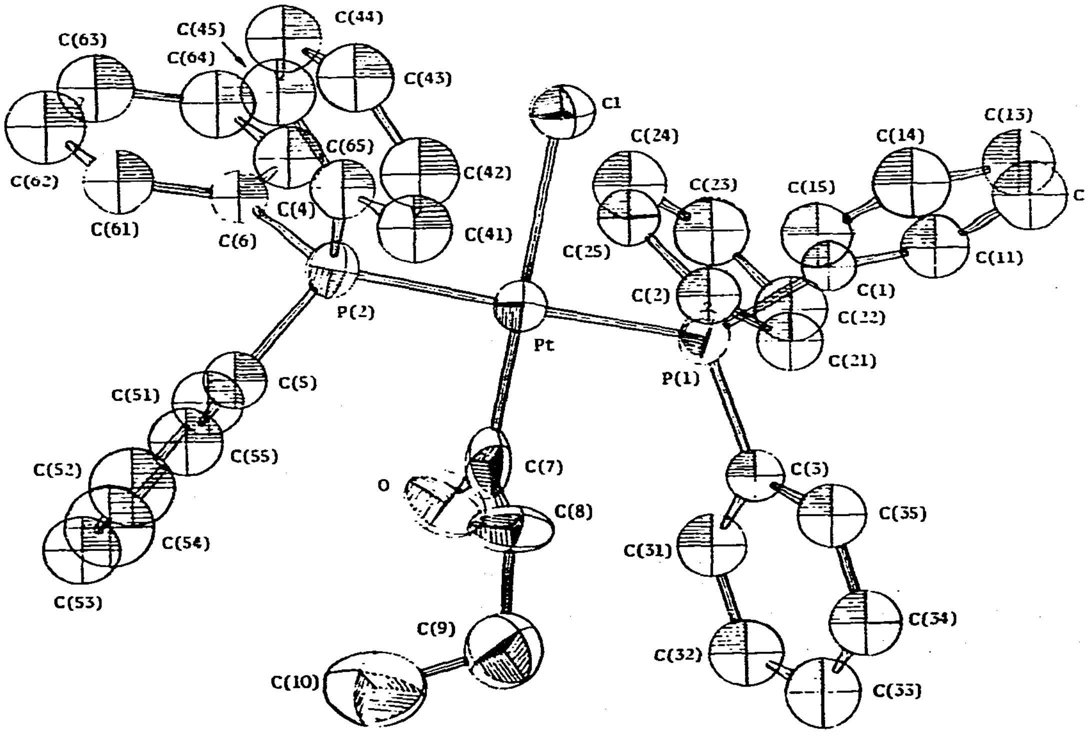
In the presence of a Cl^--rich catalyst, such as $K_2[PtCl_4]$-$SnCl_2$, the regioselectivity is much lower (linear/branched = 2.7, compared with 9 for heptene hydroformylation [8]). This suggests that there are several catalytic species in equilibrium and that Cl^- competes with bulkier ligands to give less sterically hindered intermediates, which lead to a mixture of aldehydes with lower linear/branched isomer ratio.

Structures

The complexes are isostructural. Both have discrete monomeric molecular units and there are no unusually short intermolecular contacts. A somewhat greater efficiency in packing appears to be achieved in the crystals of III, where each molecule occupies a volume of 873 Å^3, compared with 874 Å^3 in I. However, this difference, which is very small, may merely indicate that within individual molecules of III the atoms are more compactly arranged. Intermolecular contacts do not appear to be on average shorter in III than they are in I. Labeled perspective views of I and III are shown in Figs. 1 and 2. In each structure there is satisfactory agreement between chemically equivalent bond lengths and valency angles.

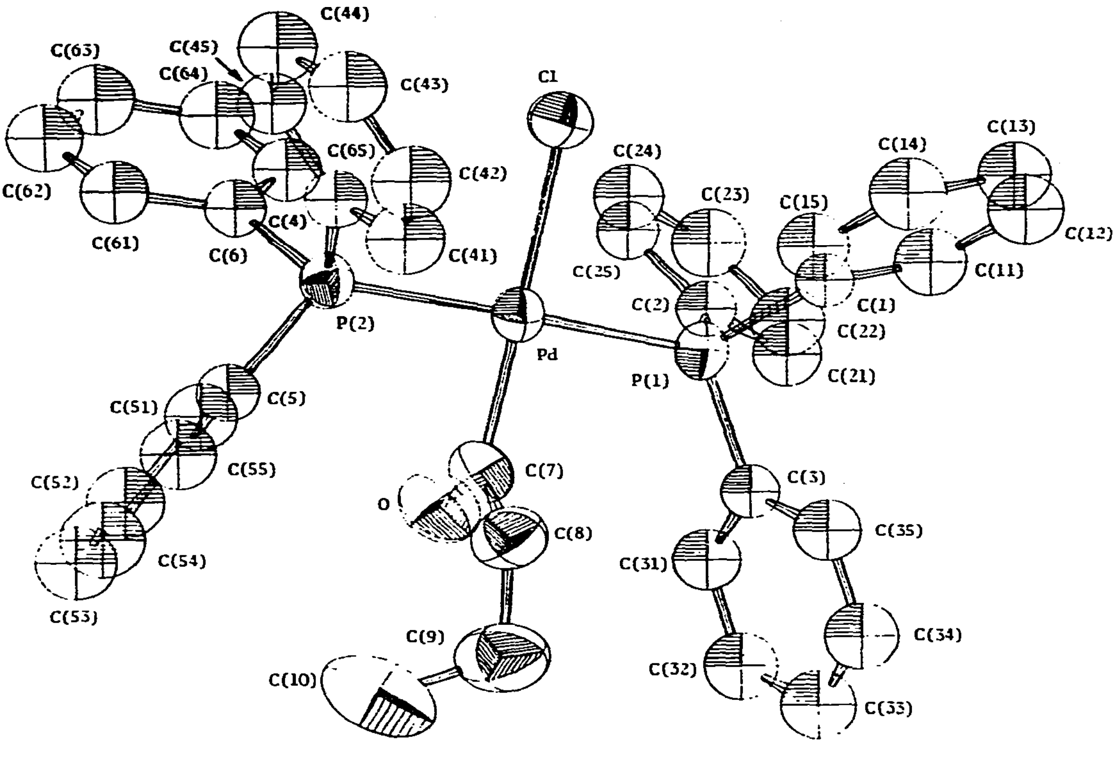
In both complexes a square plane about the metal atom M (M = Pt, (I); M = Pd, (III)) is defined by the phosphorus atoms of two triphenylphosphine ligands, one chlorine atom and the donor C sp^2 atom of the propionyl ligand. Deviations from ideal square planar coordination of the metal atoms are small, but significant. In III individual atoms are displaced by <0.03 Å from the coordination plane of the Pd atom (Table 5). In I distances of atoms to the coordination plane of the Pt atom are less than 0.05 Å (Table 5).

In the phosphine ligands of I and III corresponding bond lengths, valency angles, as well as orientations and conformations, agree well. The interbond angles at the phosphorus atoms show the usual departures from the ideal tetrahedral value. In many compounds containing coordinated PPh_3 groups [25] it has been found that the plane of one of the phenyl rings essentially contains the metal—phosphorus vector, another phenyl ring is twisted ca. 90° about its



(I)

Fig. 1. Molecular structure of *trans*-[Pt(COPr-n)(Cl(PPh$_3$)] (I).



(III)

Fig. 2. Molecular structure of *trans*-[Pd(COPr-n)Cl(PPh$_3$)$_2$] (III).

P—C bond with respect to the first ring, while the third phenyl ring assumes an intermediate orientation. Complexes I and III conforms only approximately to this stereochemistry. Of the phenyl groups attached to P(1), the ring C(3)—C(35) lies roughly at right angles to the plane M,P(1), C(3), while the other two rings C(1)—C(15) and C(2)—C(25) are both at angles of ca. 23° with respect to their corresponding M P C planes. For P(2), however, while the ring C(6)—C(65) is only slightly twisted from the plane M, P(2), C(6) the ring C(5)—C(55) lies roughly at right angles to the plane M, P(2), C(5). The third ring C(4)—C(45) is in an intermediate position with respect to the plane M, P(2), C(4).

Within each complex the mutually *trans* M—P bonds are equal in length [2.314(4) and 2.320(4) in I and 2.340(1) and 2.342(1) Å in III]. The mean of I, 2.317(4), is shorter than that of III, 2.341(1), but the difference is slight and of little energetic significance. All M—P bond lengths in the compounds examined are significantly greater than the weighted average, 2.302(1) Å, for Pt(II)—P bond lengths in 22 complexes containing mutually *trans*-tertiary phosphines of the type PR_nPh_{3-n} (R = alkyl; n = 0—3) [26]. Nevertheless, it is significant that in both complexes the M—P bond length does not reach the sum of the single bond covalent radii, 2.41 Å (Pt^{II} and Pd^{II} probably have equal covalent radii in their planar derivatives, i.e., 1.31 Å; 1.10 is the covalent radius of phosphorus [27]). This shortening has been used as evidence for a M—P double bond, i.e.,

TABLE 5

SOME MEAN PLANES, AND TWIST, DIHEDRAL AND TORSIONAL ANGLES OF COMPLEXES I AND III

1) *Complex I*
   - a) Some mean planes with the distances (Å) of the atoms to the plane:
     - Plane 1: $0.9183X + 0.1395Y + 0.3706Z = 2.8038$
       - Pt 0.025 Cl 0.030
       - P(1) —0.045 C(7) 0.035
       - P(2) —0.045
     - Plane 2: $-0.3348X + 0.1735Y + 0.9262Z = 0.0608$
       - Pt, C(7), C(8), O
     - Plane 3: $0.6093X + 0.7822Y + 0.1304Z = 4.1850$
       - Pt, P(1), C(1)
     - Plane 4: $-0.2803X + 0.9070Y - 0.3142Z = 2.3011$
       - Pt, P(1), C(2)
     - Plane 5: $0.8875X - 0.1249Y + 0.4436Z = 1.8781$
       - Pt, P(1), C(3)
     - Plane 6: $0.5474X + 0.8364Y + 0.0281Z = 4.1870$
       - Pt, P(2), C(4)
     - Plane 7: $0.9269X - 0.0123Y + 0.3752Z = 2.3359$
       - Pt, P(2), C(5)
     - Plane 8: $-0.3627X + 0.8659Y - 0.3443Z = 1.9512$
       - Pt, P(2), C(6)
   - b) Twist angle (°) between the phenyl ring and corresponding Pt—P—C plane.
     - Pt—P(1)—C(1) and C(1)—C(15) = 22.8
     - Pt—P(1)—C(2) and C(2)—C(25) = 23.8
     - Pt—P(1)—C(3) and C(3)—C(35) = 82.3
     - Pt—P(2)—C(4) and C(4)—C(45) = 53.1
     - Pt—P(2)—C(5) and C(5)—C(55) = 71.0
     - Pt—P(2)—C(6) and C(6)—C(65) = 8.7
   - c) Dihedral angles (°) between the phenyl rings.
     - C(1)—C(15) and C(2)—C(25) = 70.7
     - C(1)—C(15) and C(3)—C(35) = 84.7
     - C(2)—C(25) and C(3)—C(35) = 56.3
     - C(4)—C(45) and C(5)—C(55) = 75.1
     - C(4)—C(45) and C(6)—C(65) = 61.8
     - C(5)—C(55) and C(6)—C(65) = 68.9
   - d) Some torsion angles (°).
     - Pt—C(7)—C(8)—C(9) = —170.6
     - C(7)—C(8)—C(9)—C(10) = —75.7

2) *Complex III*
   - a) Some mean planes with the distances (Å) of the atoms to the plane.
     - Plane 1: $0.9194X + 0.1494Y + 0.3639Z = 2.8472$
       - Pd 0.035 Cl 0.012
       - P(1) —0.031 C(7) 0.016
       - P(2) —0.031
     - Plane 2: $-0.3546X + 0.1665Y + 0.9200Z = -0.0096$
       - Pd, C(7), C(8), O
     - Plane 3: $0.6270X + 0.7696Y + 0.1209Z = 4.1408$
       - Pd, P(1), C(1)
     - Plane 4: $-0.2774X + 0.9020Y - 0.3308Z = 2.2027$
       - Pd, P(1), C(2)
     - Plane 5: $0.8900X - 0.1153Y + 0.4411Z = 1.9653$
       - Pd, P(1), C(3)
     - Plane 6: $0.5491X + 0.8343Y + 0.0489Z = 4.1399$
       - Pd, P(2), C(4)
     - Plane 7: $0.9286X - 0.0197Y + 0.3706Z = 2.3447$
       - Pd, P(2), C(5)
     - Plane 8: $-0.3734X + 0.8698Y - 0.3225Z = 1.8619$
       - Pd, P(2), C(6)
   - b) Twist angle (°) between the phenyl ring and corresponding Pd—P—C plane.
     - Pd—P(1)—C(1) and C(1)—C(15) = 23.1
     - Pd—P(1)—C(2) and C(2)—C(25) = 22.4
     - Pd—P(1)—C(3) and C(3)—C(35) = 81.4
     - Pd—P(2)—C(4) and C(4)—C(45) = 54.7

TABLE 5 (continued)

Pd—P(2)—C(5) and C(5)—C(55) = 71.7
Pd—P(2)—C(6) and C(6)—C(65) = 7.8

c) Dihedral angles (°) between the phenyl rings

C(1)—C(15) and C(2)—C(25) = 70.4
C(1)—C(15) and C(3)—C(35) = 83.2
C(2)—C(25) and C(3)—C(35) = 56.6
C(4)—C(45) and C(5)—C(55) = 73.6
C(4)—C(45) and C(6)—C(65) = 62.8
C(5)—C(55) and C(6)—C(65) = 69.0

d) Some torsion angles (°).

Pd—C(7)—C(8)—C(9) = −169.9
C(7)—C(8)—C(9)—C(10) = −70.7

d_π—d_π bonding from the nonbonding *d* orbitals on metal to the empty phosphorus *d* orbitals [28]. The present results support this hypothesis.

Both metal—acyl linkages (2.00(2) Å, (I) and 1.996(6) Å, (III)) are slightly shorter than the sum, 2.05 Å, of the σ covalent radii (Pt^{II} and Pd^{II} probably have equal covalent radii in their planar derivatives: i.e., 1.31 Å; 0.74 Å is the covalent radius of C(sp^2) [27]). This would indicate the formation of a strong bond between the M^{II} ion and the acyl carbon. In addition it seems that the short M—C(acyl) bonds noted in the present study possess partial double-bond character, arising from "back-donation" of *d* electrons from the metal into the empty π-antibonding orbital of the acyl group. The large *trans* influence of σ-bonded carbon is well established [29]. The consequence of this in the present structures is that the M—Cl bonds *trans* to M—C(acyl) are among the longest M—Cl bonds known, with observed bond lengths of 2.446(1) Å, (III), and 2.450(4) Å, (I). The only other cases which come close to matching the extremely long M—Cl bond lengths observed here also involve a chloro ligand *trans* to σ-bonded carbon of acyl groups [30]. The very long M—Cl bond lengths observed in the present study are thus a consequence of the short and strong M—C(acyl) bond in the *trans* position.

Conclusions

It is remarkable that even though complexes I and III are isostructural, and have essentially the same bond distances and angles, they show very different catalytic activities in solution. The palladium complex is an excellent catalyst (precursor) for the hydrocarboalkoxylation of olefins in solvents of any polarity, either in the presence of $SnCl_2$ or in its absence, but is not able to catalyze the hydroformylation. The platinum complex is highly active (and regioselective) only in combination with $SnCl_2$ and in nonpolar or moderately polar solvents in the hydroformylation, which is suppressed in solvents such as alcohols. Moreover, only with the platinum complex is the presence of a Pt—Sn bond essential for the catalytic activity. Thus it seems that the nature of the central metal atom plays a fundamental role in the later steps of the catalytic sequence.

Acknowledgements

The authors thank the Italian C.N.R. for financial support, the Montedison S.p.A. of P. to Marghera (Venice) (in the person of Dr. G. Patron) for supplying propene, and Mr. G. Biasioli for technical assistance.

References

1 G. Cavinato and L. Toniolo, J. Molec. Catal., 10 (1981) 161.
2 I. Wender and P. Pino, Organic Syntheses via Metal Carbonyls, Vol. II, Wiley, New York, pp. 43—296, and references therein.
3 J. Falbe, New Syntheses with Carbon Monoxide, Springler-Verlag, Berlin, pp. 1—225 and 243—308, and references therein.
4 J.F. Knifton, J. Org. Chem., 41 (1976) 2885.
5 G. Cavinato, L. Toniolo, S. Gladiali and C. Botteghi, J. Organometal. Chem., to be submitted.
6 J.F. Knifton, J. Org. Chem., 41 (1976) 793.
7 L.J. Kehoe and R.A. Schell, J. Org. Chem., 35 (1970) 2846.
8 I. Schwager and J.F. Knifton, J. Catal., 45 (1976) 256.
9 C.Y. Hsu and M. Orchin, J. Amer. Chem. Soc., 97 (1975) 3553.
10 Y. Kawabata, T. Hayashi and I. Ogata, J. Chem. Soc. Chem. Commun., (1979) 462.
11 R. Bardi, A. Del Pra, A.M. Piazzesi and L. Toniolo, Inorg. Chim. Acta, 35 (1979) L345.
12 G. Cavinato and L. Toniolo, Inorg. Chim. Acta, submitted.
13 R. Eisenberg and J.A. Ibers, Inorg. Chem., 4 (1965) 773.
14 International Tables for X-ray Crystallography, Vol. IV, 2nd ed., Kynoch Press, Birmingham 1974, 99.
15 International Tables for X-ray Crystallography, Vol. IV, 2nd ed., Kynoch Press, Birmingham 1974, 149.
16 G.M. Sheldrick, SHELX-76, Program for Crystal Structural Determination, University of Cambridge (1976).
17 D. Wright, J. Chem. Soc. Chem. Commun., (1966) 197.
18 E. Lodewijk and D. Wright, J. Chem. Soc. (A), (1968) 119.
19 J. Chatt and B.L. Shaw, J. Chem. Soc., (1962) 5075.
20 R.D. Gillard and M.F. Pilbrow, J. Chem. Soc. Dalton, (1974) 2320.
21 J.V. Kingston and G.R. Scollary, J. Chem. Soc. (A), (1971) 3765.
22 G.W. Parshall, Inorg. Chem., 11 (1972), 433.
23 J.C. Bailar Jr. and H. Itatani, J. Amer. Chem. Soc., 89 (1967) 1592.
24 H.A. Tayin and J.C. Bailar Jr., J. Amer. Chem. Soc., 89 (1967) 3420.
25 V.G. Albano, P. Bellon and M. Sansoni, J. Chem. Soc. (A), (1971) 2420.
26 C.J. Cardin, D.J. Cardin, M.F. Lappert and K.W. Muir, J. Chem. Soc. Dalton, (1978) 46.
27 L. Pauling, The Nature of the Chemical Bond", 3rd ed., Cornell Press, Ithaca, 1960.
28 G.G. Messmer and E.L. Amma, Inorg. Chem., 5 (1966) 1775.
29 D.L. Weaver, Inorg. Chem., 9 (1970) 2250.
30 O.P. Anderson and A.B. Packard, Inrog. Chem., 17 (1978) 1333.