

THE USE OF BIS(PENTACHLOROPHENYL)THALLIUM(III) CHLORIDE AS ARYLATING REAGENT

P. ROYO and R. SERRANO

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad, Murcia (Spain)

(Received July 18th, 1977)

Summary

Bis(pentachlorophenyl)thallium(III) chloride has been used as an arylating reagent for several transition metal complexes in low oxidation states. The pentachlorophenyl-transition metal complexes thus prepared have been studied by visible-UV and IR spectroscopy.

Introduction

Pentachlorophenyl-transition metal complexes are usually prepared by treating the corresponding metal halides with pentachlorophenyllithium or bromopentachlorophenylmagnesium. Much difficulty was experienced with these reactions when attempts were made to involve two C_6Cl_5 groups [1–4], and only four complexes containing two of such groups are known [5–7]. The successful use of $BrTl(C_6F_5)_2$ as an arylating reagent [8–10] prompted us to examine the oxidizing properties of $ClTl(C_6Cl_5)_2$ [11].

Results and discussion

Table 1 shows the transition metal complexes used and the corresponding reaction products. Thallous chloride was obtained in all cases.

The reaction of an excess of Hg_2Cl_2 leads to the isolation of $(C_6Cl_5)_2Hg$, which has been previously prepared [12,13]. From $Ni(CO)_2(dpe)$ [dpe = bis-(1,2-diphenylphosphino)ethane] in equimolar quantities, the new $(C_6Cl_5)_2Ni(dpe)$ is obtained with elimination of the two CO groups; it is noteworthy that this compound could not be prepared by Grignard method [3]. The reaction with $ClNi(PPh_3)_3$ in a molar ratio of 1/2 gives $Cl(C_6Cl_5)Ni(PPh_3)_2$ [1]. Again, elimination of PPh_3 , which can be recovered from the residual solution, preserves the four coordination at the metal atom. With *trans*- $ClRh(CO)(PPh_3)_2$, *trans*- $(C_6Cl_5)Rh(CO)(PPh_3)_2$ is obtained, but other rhodium derivatives are also detected. Thus, when the insoluble thallous chloride was filtered off and the

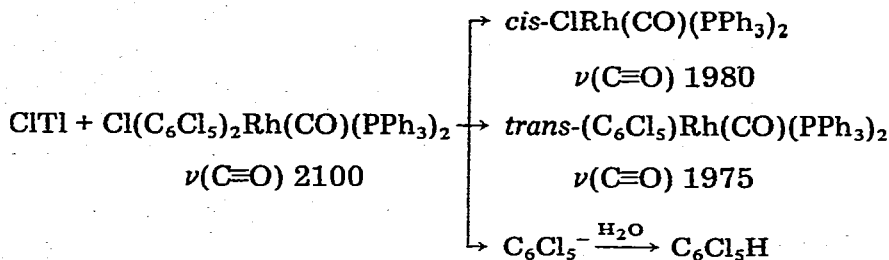
TABLE I
REACTIONS OF $(C_6Cl_5)_2TiCl$ WITH TRANSITION METAL COMPLEXES

Complex	Molar ratio Ti/complex	Reaction product
Hg_2Cl_2	excess Hg_2Cl_2	$(C_6Cl_5)_2Hg$
$Ni(CO)_2(dpe)$	1/1	$(C_6Cl_5)_2Ni(dpe)$
$ClNi(PPh_3)_3$	1/2	$Cl(C_6Cl_5)Ni(PPh_3)_2$
<i>trans</i> - $ClRh(CO)(PPh_3)_2$	1/1	<i>trans</i> - $(C_6Cl_5)Rh(CO)(PPh_3)_2$
$ClAuPPh_3$	1/1	$Cl(C_6Cl_5)_2AuPPh_3 + (C_6Cl_5)AuPPh_3$

solution evaporated, a crystalline fraction was obtained. Its IR spectrum showed only PPh_3 bands and two $\nu(C\equiv O)$ absorptions at 1960 and 1980 cm^{-1} . When we try to separate this mixture by crystallization from chloroform/ethanol the only product isolated was *trans*- $ClRh(CO)(PPh_3)_2$. This can be explained by assuming that the initial crystalline solid is a mixture of *cis*- and *trans*- $ClRh(CO)(PPh_3)_2$, and in recrystallization the *cis* form is converted into the *trans* form, which is the only form known until now. When shorter reaction times are used (about 2 h) the IR spectrum of the solid residue obtained by evaporation shows, along with PPh_3 and C_6Cl_5 bands, an additional peak of medium intensity at 2100 cm^{-1} assigned to an organorhodium(III) complex, which could not be isolated; C_6Cl_5H was recovered by sublimation of this residue. The overall reaction appears to be:

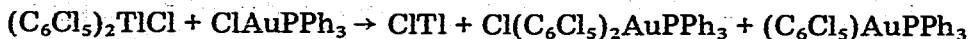


$\nu(C\equiv O)$ 1960



It seems clear that the *cis*- $ClRh(CO)(PPh_3)_2$ comes from the reductive elimination of the intermediate rhodium(III) complex and is recovered together with an excess of the initial *trans* complex, since isomerization of the *trans* compound must be excluded [14].

The red *trans*- $(C_6Cl_5)Rh(CO)(PPh_3)_2$ isomerizes to the *cis* form by boiling in ethanol or by slow evaporation of its solutions in organic solvents. Reaction with $ClAuPPh_3$ produces $Cl(C_6Cl_5)_2AuPPh_3$ as the major product. This complex decomposes slowly in boiling benzene and so small amounts of $(C_6Cl_5)AuPPh_3$ [15] are also formed.



All the reactions described are analogous to those observed when $(C_6F_5)_2TiBr$

TABLE 2
ANALYTICAL DATA FOR PENTACHLOROPHENYLMETAL COMPLEXES

Complex	Analyses (found ((calcd.) (%))		
	C	H	Cl
(C ₆ Cl ₅) ₂ Ni(dpe)	49.23 (47.75)	2.89 (2.53)	36.23 (37.09)
<i>trans</i> -(C ₆ Cl ₅)Rh(CO)(PPh ₃) ₂	55.75 (56.21)	3.70 (3.29)	18.91 (19.29)
<i>cis</i> -(C ₆ Cl ₅)Rh(CO)(PPh ₃) ₂	56.48 (56.21)	3.80 (3.29)	19.53 (19.29)
Cl(C ₆ Cl ₅) ₂ Au(PPh ₃)	37.21 (36.27)	1.63 (1.52)	39.86 (39.26)

TABLE 3
PHYSICAL DATA AND CONDUCTIVITY OF PENTACHLOROPHENYL COMPLEXES

Complex	Color	M.p. (°C)	Λ (ohm ⁻¹ cm ² mol ⁻¹) ^a (c × 10 ⁻⁴ mol l ⁻¹)
(C ₆ Cl ₅) ₂ Ni(dpe)	orange	244 (dec.)	0.75 (4.9)
<i>trans</i> -(C ₆ Cl ₅)Rh(CO)(PPh ₃) ₂	red	173 (dec.)	1.56 (5.0)
<i>cis</i> -(C ₆ Cl ₅)Rh(CO)(PPh ₃) ₂	yellow	189 (dec.)	0.73 (4.8)
Cl(C ₆ Cl ₅) ₂ Au(PPh ₃)	white	194	1.49 (4.7)

^a In acetone

TABLE 4
RELEVANT IR ABSORPTIONS (cm⁻¹) OF THE NEW PENTACHLOROPHENYL COMPLEXES

(C ₆ Cl ₅)Rh(CO)(PPh ₃) ₂		Assignment
<i>trans</i>	<i>cis</i>	
1975vs	1975vs	ν (C=O)
1322vs	1326s	
1312vs	1315vs	C ₆ Cl ₅
1297s	1299s	
1287s	1289s	
840w	850w	
665m	665m	δ (Rh—CO)
600m	600m	
450vw	445vw	ν (Rh—P)
	435vw	
(C ₆ Cl ₅) ₂ Ni(dpe)		Cl(C ₆ Cl ₅) ₂ Au(PPh ₃)
1323s	1335s	C ₆ Cl ₅
1313vs	1320vs	
	1292vs	
1283s	1286vs	
	850w	
	840w	ν (Au—Cl)
	670w	
	323m	

TABLE 5
ELECTRONIC SOLUTION SPECTRA OF THE NEW PENTACHLOROPHENYLMETAL COMPLEXES

Complex	λ_{\max} (nm) (ϵ) ($l \text{ mol}^{-1} \text{ cm}^{-1}$)
$(\text{C}_6\text{Cl}_5)_2\text{Ni}(\text{dpe})^b$	426(2300), 325(5000), 295(8400)
<i>trans</i> - $(\text{C}_6\text{Cl}_5)\text{Rh}(\text{CO})(\text{PPh}_3)_2^a$	533(200), 394(1800), 291(7600)
<i>cis</i> - $(\text{C}_6\text{Cl}_5)\text{Rh}(\text{CO})(\text{PPh}_3)_2^a$	530sh(40), 399(2400), 296(9700)
$\text{Cl}(\text{C}_6\text{Cl}_5)_2\text{Au}(\text{PPh}_3)^a$	300(7800)

^a In cyclohexane. ^b In chloroform.

was employed [8,10,19], although $(\text{C}_6\text{Cl}_5)_2\text{TiCl}$ is a less effective oxidant. The yields are lower, probably because the pentachlorophenylthallium(III) chloride is much less soluble. The known compounds were characterized by analysis and by comparing their spectral and physical properties with literature values. Analytical and physical data for the new complexes are given in Tables 2 and 3.

Conductivity

All these compounds are shown to be non-electrolytes by the conductivities are listed in Table 3.

Electronic and IR spectra

The IR spectra of the new complexes show the characteristic bands of the neutral ligand (PPh_3 or dpe) and the C_6Cl_5 group. The most relevant absorptions which are listed in Table 4 require little comment. The very weak bands near 450 cm^{-1} in the rhodium complexes must be assigned to $\nu(\text{Rh}-\text{P})$ and they enable the *cis* and *trans* isomers to be distinguished [16].

The visible-UV absorption bands of the isolated complexes in chloroform and cyclohexane are shown in Table 5. The band at 426 nm in the spectrum of the nickel(II) complex must be assigned to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition in a square planar environment [17], while the two remaining, more intense bands must involve charge transfer processes. The spectrum of both rhodium complexes are identical, and the similarity to the spectrum of $[\text{Ir}(\text{dpe})_2]\text{Cl}$, whose planar structure has been confirmed by X-ray analysis [18], suggests an analogous structure for this compound. The spectrum of the gold complex does not show any band above 300 nm, as is usual for square planar gold complexes [17].

Experimental

IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer (in the range $4000-250 \text{ cm}^{-1}$) using Nujol mulls between CsI plates. Electronic solution spectra were recorded on a Perkin-Elmer 124 spectrophotometer (over the range $800-270 \text{ nm}$). Conductivities were measured with a Phillips 9501/01 conductimeter. C, H, N analyses were carried out on a Perkin-Elmer 240 micro-analyzer. Chlorine was determined according to [20].

All the reactions were carried out in refluxing benzene. Except for the reaction with Hg_2Cl_2 , the precipitated TiCl was filtered off and the solution evaporated to dryness under reduced pressure. Subsequent treatment of the solid residue was different in each case, as described below.

Reaction with Hg₂Cl₂

A mixture of (C₆Cl₅)₂TiCl and excess of Hg₂Cl₂ was refluxed for 6 h and then evaporated to dryness. (C₆Cl₅)₂Hg was extracted with hot nitrobenzene and crystallized by evaporation. Yield ca. 50%.

Reaction with Ni(CO)₂(dpe)

Equimolar amounts were refluxed in benzene for 10 h. A solution of the yellow residue in benzene was chromatographed on a silica column with benzene/ethanol (10/1) as eluent. The complex was crystallized by evaporation. Yield 25–30%.

Reaction with ClNi(PPh₃)₃

A molar ratio Ni/Ti 2/1 is stirred in benzene at room temperature for 24 h. The yellow residue obtained by evaporation to dryness was recrystallized twice from chloroform/ethanol. Yield 35%.

Reaction with trans-ClRh(CO)(PPh₃)₂

Equimolar amounts are refluxed for 7 h. C₆Cl₅H was sublimed from the red residue obtained by evaporation to dryness (100°C, 10⁻³ mm), and the remaining residue was extracted with warm cyclohexane. The extract was filtered and (C₆Cl₅)Rh(CO)(PPh₃)₂ was precipitated from the filtrate by adding hexane. It was recrystallized from chloroform/ethanol. Yield ca. 25%.

Reaction with ClAuPPh₃

Equimolar amounts are refluxed for 6 h. The residue was treated with warm cyclohexane and filtered. The filtrate was evaporated to give a first crystalline fraction of (C₆Cl₅)AuPPh₃ which was filtered off. Cl(C₆Cl₅)₂AuPPh₃ was obtained as the second crystalline fraction on evaporation and addition of hexane. Yield ca. 30%.

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