EXCHANGE REACTIONS AND DECOMPOSITION PATHWAYS OF ORGANOCOBALT(II) SQUARE-PLANAR COMPLEXES

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(Received August 10th, 1981)

Summary

A number of compounds of the type $[Co(C_6Cl_5)_2L_2]$ (L = $PEtPh_2$, PEt_2Ph, PEt_3, py, β-pic, γ-pic, 3,5-lut, or L_2 = dpe and bipy) have been prepared by reacting C_6Cl_5MgX with $[CoCl_2L_2]$ or by adding the stabilizing ligand to a solution of "$Co(C_6Cl_5)_2$". Ligand exchange reactions show that a more basic displaces a less basic ligand. The compounds with L = PEt_2Ph, PEt_3, dpe, and bipy remain unaltered in boiling benzene, but when L = $PEtPh_2$ and 3,5-lut, partial decomposition occurs. The decompositions give only C_6HCl_5 when L = py, β-pic, γ-pic, and 3,5-lut, but a mixture of $C_6H_{1+n}Cl_{5-n}$ and $C_{12}H_nCl_{10-n}$ is obtained when L = $PEtPh_2$; the coupling occurs after the dissociation of the ligand. Decomposition in benzene in the presence of bromine gives C_6BrCl_5 when L is an amine, but $C_{12}H_nCl_{10-n}$ when L is a phosphine.

Introduction

The number of cobalt(II) square-planar organometallic compounds of the type $[CoXRL_2]$ or $[CoR_2L_2]$ is small compared to that of the Ni, Pd and Pt analogues. This may be due to the difficulty of isolating the presumably tetrahedral species $[CoXRL_2]$ [1]. The only solid compound of this type is the unstable $[CoBrMes(PPh_3)_2]$ [2]. The organocobalt complexes are stable when a second organic group R is attached to give $[CoR_2L_2]$ species. The stability of these complexes seems to be due to kinetic factors; and compounds with *ortho*-substituted aryl groups, viz. R = C_6F_5 [3], mesityl and C_6Cl_5 [4], are the most stable.

We describe in this paper the preparation, ligand exchange reactions, and thermal decompositions of pentachlorophenylcobalt(II) derivatives containing phosphines or substituted pyridine ligands, in order to compare their behaviour with that of the more intensively studied nickel complexes.

Results and discussion

Preparation and characterization

The compounds $[Co(C_6Cl_5)_2L_2]$ are prepared either by action of an excess of C_6Cl_5MgX in THF on the corresponding $[CoCl_2L_2]$ (L = $PEtPh_2$, PEt_2Ph, and PEt_3), or by Tamborski's method [5], in which $CoBr_2$ is treated with C_6Cl_5MgX and then the stabilizing ligand L is added (L = dpe, bipy, py, β-pic, γ-pic, and 3,5-lut). The organometallic is precipitated in both cases by adding methanol. We were unable to prepare the compounds with L = PPh_3 or α-methylpyridines by either method, and all attempts to prepare compounds of the type $[CoXRL_2]$, either by the action of the Grignard reagents in stoichiometric amounts on $[CoCl_2L_2]$ or by attack of HCl on $[CoR_2L_2]$, were unsuccessful.

All the new compounds are yellow-brown crystalline solids except for the bipyridine derivative which is dark red. They are stable as solids except for the compound containing pyridine, which decomposes rapidly even under nitrogen. Their solubility is low in the usual nonpolar solvents and diminishes with increasing basicity of the ligands. The compounds containing pyridine, and β- and γ-picoline decompose slowly in solvents such as benzene or ether and rapidly in chlorinated solvents. Analytical results and magnetic moments are listed in Table 1. The observed magnetic moments are similar to those reported for analogous square-planar complexes with one unpaired electron [4]. The infrared spectra show the bands due to the stabilizing ligands and C_6Cl_5 [6]. The compounds containing monodentate phosphines are assigned a *trans* geometry by analogy with $[Co(C_6Cl_5)_2(PEt_2Ph)_2]$ [4]; the compounds containing aromatic amines are assigned the same structure following Braunstein's arguments [7].

TABLE 1

ANALYTICAL DATA, DECOMPOSITION POINTS AND MAGNETIC MOMENTS OF $[Co(C_6Cl_5)_2L_2]$ [a]

L	Analysis found (calcd.) (%)				Dec. point (°C)	μ (BM)	Yield (%)
	C	H	N	Cl			
PEt$_3$	36.7 (36.33)	3.9 (3.80)		44.7 (44.64)	212—14	2.6	40
PEtPh$_2$	48.7 (48.72)	3.1 (3.07)		35.3 (35.95)	155—60	2.47	75
dpe	47.5 (47.74)	2.5 (2.53)		36.8 (37.09)	218—22	2.34	65
py	36.8 (36.69)	1.5 (1.41)	3.9 (3.91)		142—44	[b]	60
β-pic	38.4 (38.75)	2.1 (1.90)	3.5 (3.77)		143—45	2.17	65
γ-pic	39.0 (38.75)	2.1 (1.90)	3.6 (3.77)		156—58	1.84	45
3,5-lut	40.5 (40.45)	2.5 (2.35)	3.5 (3.63)		162—64	2.01	75
bipy	37.1 (37.02)	1.3 (1.13)	3.7 (3.92)		210—12	1.73	75

[a] $[Co(C_6Cl_5)_2(PEt_2Ph)_2]$ was characterized by Chatt and Shaw [4]. [b] These figures are difficult to reproduce because of the unstability of the product.

The electronic spectra in all cases show a band of low intensity between 405 and 410 nm when L is a monodentate amine, and at 415—440 nm when L is a phosphine. In $[Co(C_6Cl_5)_2(PEt_3)_2]$ this band is masked by the more intense charge-transfer bands. The compound containing bipyridine shows an intense band ($\epsilon = 1.4 \times 10^3$) at 555 nm. The order of these maxima (subst. py $<$ PEt$_3$Ph $<$ dpe $<$ PEtPh$_2$ $<$ bipy) is the opposite of that observed for the compounds $[NiCl(C_6Cl_5)L_2]$(bipy $<$ dpe $<$ PEt$_3$ $<$ PPh$_3$ $<$ subst. py).

Substitution reactions

Ligand exchange reactions were examined in order to compare the variations in stability upon variation of the ligand. Benzene was used as a solvent since this is the solvent in which the complexes are most stable. The temperature used was determined by the stability of the corresponding organometallic complexes. The ligand exchanges between amine ligands (py, β-pic, γ-pic, 3,5-lut, bipy) result in displacement only when the entering ligand is more basic than the leaving ligand. For example, 3,5-lut (pK_a 6.15) replaces β-pic (pK_a 5.68), but not vice versa.

Bipyridine replaces any monodentate amine, probably because of the chelate effect, but can itself be displaced by 3,5-lut, a stronger base as reflected in reactions 1 and 2 (Table 2).

For exchanges between the phosphines PEtPh$_2$, PEt$_2$Ph, PEt$_3$ and dpe, the criterion that a phosphine with the smaller cone angle displaces one with a larger angle [8] holds only as long as the basicity of the phosphine increases as its size decreases. All the other phosphines displace PEtPh$_2$ (pK_a^- 9.41) totally and irreversibly, but equilibria are set up for the exchange with dpe ligand (reactions 3—6, Table 2). If the entering phosphine is smaller but less basic than the leaving phosphine, substitution is not complete. Thus, the reaction of PMe$_2$Ph (pK_a 6.25) with the complex containing PEt$_3$ (pK_a 8.69) gives $[Co(C_6Cl_5)_2(PEt_3)$-$(PMe_2Ph)]$, regardless of the conditions (reactions 7 and 8).

Exchanges between phosphines (PEt$_3$, PEt$_2$Ph, PEtPh$_2$, dpe) and amines (3,5-lut and bipy) show that except for PEtPh$_2$, the phosphines completely replace the amines in accord with the relative basicity and the greater stability of the

TABLE 2

SELECTED EXCHANGE REACTIONS

$[Co(C_6Cl_5)_2L_2] + 2L' \xrightarrow{\text{Benzene}} [Co(C_6Cl_5)_2L_2'']$
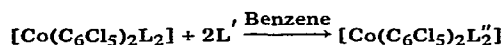
	L	L' (L'/Co)	Conditions	L'' (Yield, %)
1	3.5-lut	bipy (2/1)	room temp., 3 h	bipy (>95%)
2	bipy	3,5-lut (10/1)	room temp., 12 h	bipy (80%) + 3,5-lut (10%)
3	PEt$_2$Ph	dpe (1/1)	reflux, 6 h	dpe (35%) + PEt$_2$Ph (55%)
4	dpe	PEt$_2$Ph (4/1)	reflux, 6 h	dpe (30%) + PEt$_2$Ph (65%)
5	dpe	PEt$_3$ (4/1)	reflux, 6 h	PEt$_3$ (85%)
6	PEt$_3$	dpe (1/1)	reflux, 6 h	PEt$_3$ (55%) + dpe (35%)
7	PEt$_3$	PMe$_2$Ph (2/1)	reflux, 6 h	(PEt$_3$)(PMe$_2$Ph) (85%)
8	PEt$_3$	PMe$_2$Ph (4/1)	reflux, 20 h	(PEt$_3$)(PMe$_2$Ph) (80%)
9	PEtPh$_2$	3,5-lut (2/1)	room temp., 3 h	3,5-lut (47%) + PEtPh$_2$ (43%)
10	PEtPh$_2$	bipy (1/1)	reflux, 3 h	bipy (>95%)

Co—P bond. The amines replace only PEtPh$_2$ (reactions 9 and 10). This substitution may be due to the more basic character of the nitrogen-containing ligand, but may be steric in origin, the complex with PEtPh$_2$ being less stable than the others, as shown by the decomposition reactions.

The results indicate that, leaving aside [Co(C$_6$Cl$_5$)$_2$(PEtPh$_2$)$_2$] which may be exceptional because of the larger volume of the phosphine, the exchanges can be interpreted in terms of the basicity of the ligands involved.
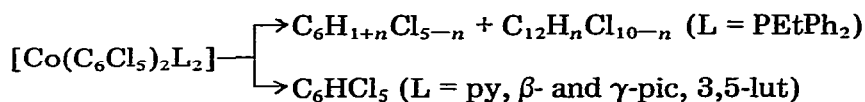
Decomposition reactions

The stabilities of the organocobalt compounds have been examined in boiling benzene and carbon tetrachloride, and in some cases in the solid state. The reactions in solution were carried out in the air, except for those with added free phosphines which were carried out under nitrogen.

The results for benzene solutions (data collected in Table 3), show the relative stability of the compounds studied. The compounds containing bipy, dpe, PEt$_3$, and PEt$_2$Ph are recovered unchanged but partial decomposition occurs for those containing PEtPh$_2$ and 3,5-lut in the times used. The other compounds, containing monodentate amines, are rapidly decomposed.

The decompositions of the analogous nickel compounds [NiAr(CH$_3$)(PEt$_3$)$_2$] [9] and [NiAr$_2$(PEt$_3$)$_2$] [10] in benzene are complete and give better than 90% yields of the coupling products. The reactions are assumed to have an intermolecular mechanism with a dissociative step, [MR$_2$L$_2$] → "[MR$_2$L]" + L, preceding the coupling.

The decomposition of [Co(C$_6$Cl$_5$)$_2$L$_2$] in the same solvent involves two modes of decomposition, one giving biaryl and the other producing polychlorobenzene; both paths seem to be accompanied by halogen loss from C$_6$Cl$_5$. The relative contributions of these modes depend on the nature of the stabilizing ligand:

$$[Co(C_6Cl_5)_2L_2] \begin{cases} \rightarrow C_6H_{1+n}Cl_{5-n} + C_{12}H_nCl_{10-n} \ (L = PEtPh_2) \\ \rightarrow C_6HCl_5 \ (L = py,\ \beta\text{- and } \gamma\text{-pic, 3,5-lut}) \end{cases}$$

We attempted to prove the existence of an initial dissociative step in the mechanism of decomposition of this compound and examined the effect of added CoBr$_2$, which might function as a phosphine scavenger with [Co(C$_6$Cl$_5$)$_2$-(PEtPh$_2$)$_2$] in benzene. Total decomposition occurred, and the products were the same as those obtained without added CoBr$_2$. Addition of free phosphine practically suppresses the decomposition of the organometallic within the times used.

The results are consistent with the existence of a common species "[CoR$_2$L]", which disappears by one of the two pathways. The amount of C$_6$HCl$_5$ or C$_6$H$_2$Cl$_4$ obtained can be taken to reflect the instability of the complex, which will be greater in the intermediate containing only one coordinated phosphine. The organometallic compounds containing amines as stabilizing ligands are far less stable. The Co—C$_6$Cl$_5$ bond cleavage and the subsequent abstraction of hydrogen atoms do not seem to involve an initial dissociative step, as indicated by the low sensitivity of the reaction to the addition of free ligand or CoBr$_2$ in the case of the β-pic derivative.

Boiling solutions in benzene containing bromine resulted in total decomposi-

TABLE 3

THERMAL DECOMPOSITION OF [Co(C6Cl5)2L2] IN SOLUTION

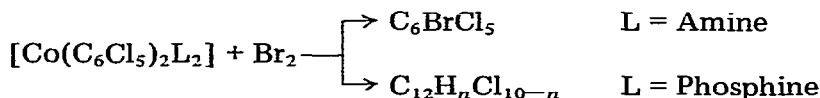| Ligand + additive	Unaltered complex (Yield, %)	Relative yields of polychlorophenyl products (%)					
		$C_6H_2Cl_4$	C_6HCl_5	C_6Cl_6	$C_{12}H_2Cl_8$ [b]	$C_{12}HCl_9$ [b]	$C_{12}Cl_{10}$
Benzene (reflux, 6 h)							
PEt3, PEt2Ph, dpe, bipy	[Co(C6Cl5)2L2] (95)						
PEtPh2	[Co(C6Cl5)2(PEtPh2)2] (80)	12	73			8	7
py, β-pic, γ-pic		~3	~92			~2	~3
3,5-lut	[Co(C6Cl5)2(3,5-lut)2] (35)	7	87		1	4	1
PEtPh2 + CoBr2		8	83			4	5
Carbon tetrachloride (reflux, 8 h)							
PEtPh2			33		2	14	51
PEt2Ph		4	9		7	31	49
PEt3		2	10		4	27	57
dpe	[Co(C6Cl5)2dpe] (95)						
β-pic		3	68			9	10
3,5-lut		4	68			8	20
bipy	[Co(C6Cl5)2bipy) (90)	a	47	11		14	39
PEtPh2 + PEtPh2			4			15	81
PEt2Ph + CoBr2			15			24	45
β-pic + β-pic		5	90			3	2
β-pic + CoBr2		4	90			3	3

[a] C6BrCl5, 5%. [b] Mixture of isomers.

TABLE 4

DECOMPOSITION OF [Co(C_6Cl_5)$_2$L$_2$] IN PRESENCE OF BROMINE (4 h REFLUX IN BENZENE)

L	Relative yields of polychlorophenyl products (%)			
	C_6HCl_5	C_6BrCl_5	$C_{12}HCl_9$	$C_{12}Cl_{10}$
PEtPh$_2$	1	20	14	65
PEt$_2$Ph		1	24	75
PEt$_3$		3	18	79
dpe		3	16	81
py, β-pic, γ-pic, 3.5-lut, bipy		~100		

tion of all the organometallic compounds (Table 4). The compounds containing amines give only C_6BrCl_5. The formation of biaryl in yields greater than 95% is favoured when the organometallic contains phosphine ligands, except for L = PEtPh$_2$, for which a 79% yield is observed. The greater ease of decomposition and almost selective formation of coupled products in the case of compounds containing phosphine ligands may be related to the mechanism proposed by Kochi for the decomposition of organonickel complexes [11] catalyzed by oxidants and involving Ni^{III} species. These intermediates seem to be insufficiently stabilized by nitrogen ligands to allow the coupling reaction to proceed.

$$[Co(C_6Cl_5)_2L_2] + Br_2 \longrightarrow \begin{cases} C_6BrCl_5 & L = Amine \\ C_{12}H_nCl_{10-n} & L = Phosphine \end{cases}$$

In CCl$_4$, decomposition occurs for all the compounds except that containing dpe, and is incomplete with [Co(C_6Cl_5)$_2$bipy]. There is a greater proportion of biaryl product even when the starting organometallics contain stabilizing amines (Table 3). The effects of added reagents in this solvent are puzzling. Thus CoBr$_2$ seems not to accelerate the decomposition and the phosphine seems not to slow it. At the same time CoBr$_2$ directs the reaction towards C_6HCl_5, but addition of the phosphine directs it towards the coupled product in the case of the phosphine-containing complexes. On the other hand, addition of free amines or CoBr$_2$ directs the decomposition reaction to the formation of C_6HCl_5 for the amine-containing compounds. Some contribution from a radical mechanism cannot be ruled out in this type of solvent. Similar results were observed with CH$_2$Cl$_2$ or CHCl$_3$ as solvent.

The thermal decompositions of the compounds in the solid state under nitrogen were monitored by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Decompositions were also carried out in open and sealed tube at a fixed temperature to determine weight losses and collect the decomposition products. The results are listed in Table 5. The DSC experiments show an initial strongly exothermic peak which corresponds to a complex decomposition of the organometallic together with the oxidation of the phosphine ligand and loss of chlorine from the pentachlorophenyl group. The residues from the thermolysis at a fixed temperature in a sealed tube were extracted with benzene and the solutions analyzed by GLC. The products again show the existence of two decomposition pathways; [Co(C_6Cl_5)$_2$bipy] gives hardly any

TABLE 5

THERMAL DECOMPOSITION OF $[Co(C_6Cl_5)_2L_2]$ IN SEALED TUBE (1 h)

L	Temperature (°C)	Relative yields of polychlorophenyl products (%)				
		$C_6H_2Cl_4$ [a]	C_6HCl_5	$C_{12}H_2Cl_8$ [b]	$C_{12}HCl_9$ [b]	$C_{12}Cl_{10}$
PEt$_3$	240—245	8	26	19	42	5
dpe	260—265	3	41	5	19	32
bipy	240—245	4	85 [a]		2	4

[a] $1,2,4,5\text{-}C_6H_2Cl_4$. [b] Mixture of isomers. [c] C_6Cl_6 is also formed (5%).

coupling product, reflecting again the difference in stabilizing effects of dpe and bipy.

It is noteworthy that the ligands which give rise to *cis* configurations do not favour the reductive elimination reactions in any of the processes studied.

Experimental

Chemical analyses and TG-DSC experiments were carried out at the "Instituto de Química Bio-Organica del CSIC de Barcelona". GLC analysis was performed on a Perkin-Elmer 3720 instrument using a 2 m, 2.5% SE-30 on Chromosorb R column.

Preparative methods

All the reactions were carried out under nitrogen. The compounds $[CoCl_2L_2]$ (L = PEt$_3$, PEt$_2$Ph, PEtPh$_2$) were prepared according to the literature [4].

[Co(C$_6$Cl$_5$)$_2$L$_2$], L = PEt$_3$, PEt$_2$Ph, PEtPh$_2$. The magnesium reagent was prepared from C$_6$Cl$_6$ (5.7 g, 20 mmol) and Mg (0.60 g, 25 mmol) in THF (20 ml) using C$_2$H$_5$MgBr as initiator. The mixture was refluxed for 20 min and after cooling was added to 8 mmol of $[CoCl_2L_2]$. The brown solution was cooled to —10°C and treated with methanol. The solid which separated was filtered off, washed with 1% aqueous HCl, and recrystallized from benzene/methanol.

[Co(C$_6$Cl$_5$)$_2$L$_2$], L = py, β-pic, γ-pic, 3,5-lut; L$_2$ = dpe, bipy. Pentachlorophenylmagnesium chloride, prepared as above, was added to CoBr$_2$ (1.08 g, 5 mmol). The mixture was stirred at room temperature until dissolution was complete, then added to 50 mmol of the monodentate ligand or to 10 mmol of the bidentate ligand. The mixture was stirred at room temperature for 20 min, then 25—40 ml of methanol were added and the mixture was cooled to —10°C for several hours. The product was filtered off, washed with 1% aqueous HCl and with alkanes or cold benzene to eliminate any cobalt salt or polychlorobenzene.

The dpe, bipy, and 3,5-lut complexes were recrystallized from benzene/methanol.

Exchange reactions

The reactions were carried out in benzene, under dry nitrogen, at room temperature when the added ligand was a monodentate amine and under reflux when the ligand was bipy or a phosphine. 150 mmol of monodentate amine, 30 mmol of phosphine or 2,2'-bipyridine, or 15 mmol of 1,2-bis(diphenylphos-

phino)ethane were added to 15 mmol of $[Co(C_6Cl_5)_2L_2]$ in 30 ml of benzene and the mixture was stirred for 4 to 6 hours under the specified conditions. The solution was filtered and concentrated to dryness in a rotary evaporator. Both the precipitate and the residue were analyzed.

Decomposition reactions

Thermal decompositions in solution were carried out with 0.1 g of complex in 30 ml of solvent (benzene or carbon tetrachloride) under reflux for a maximum of 8 hours. After cooling, the solution was filtered and concentrated. Both the precipitate and the solution were investigated by Mass spectra, IR spectroscopy and GLC. The decomposition in presence of bromine were carried out as above using a 2.5/1 bromine/cobalt mol ratio.

Thermal decompositions in the solid state at constant temperature were carried out in both sealed and open tubes. After cooling, the solids were extracted with benzene and the solutions and residues examined.

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