

DECOMPOSITION REACTIONS OF SQUARE-PLANAR BIS-ARYL-COBALT(II) COMPLEXES

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Summary

The organocobalt complexes $[\text{CoR}_2\text{L}_2]$, with (a) $\text{L} = \text{PEtPh}_2$ and $\text{R} = 2,3,5,6\text{-C}_6\text{HCl}_4$, $2,4,6\text{-C}_6\text{H}_2\text{Cl}_3$ and $2,6\text{-C}_6\text{H}_3\text{Cl}_2$; and (b) $\text{R} = 2,4,6\text{-C}_6\text{H}_2\text{Cl}_3$ and $\text{L} = \text{PEt}_3$, PEt_2Ph , $\frac{1}{2}\text{dpe}$, $3,5\text{-lut}$ and $\frac{1}{2}\text{bipy}$, have been obtained by reaction of RMgX with $[\text{CoCl}_2\text{L}_2]$ or by ligand exchange from $[\text{CoR}_2(\text{PEtPh}_2)_2]$. The decompositions in benzene and carbon tetrachloride, and under oxidative conditions have been studied. In benzene solutions, the stability decreases with decrease in the number of chlorine atoms in R . A mixture of R-H and R-R is obtained in a ratio which depends on the nature of L , the configuration of the complex, and the presence of oxidants. The thermal decomposition takes place through a tricoordinate intermediate " CoR_2L ", when $\text{L} = \text{phosphine}$, or directly from $[\text{CoR}_2\text{L}_2]$ when $\text{L} = \text{amine}$. The oxidatively induced decomposition takes place through a cobalt(III) intermediate, which gives R-R when $\text{L} = \text{phosphine}$ or R-X ($\text{X} = \text{H}, \text{Br}$) when $\text{L} = \text{amine}$. The process is intramolecular in all cases.

Introduction

A study of the decompositions of the complexes $[\text{Co}(\text{C}_6\text{Cl}_5)_2\text{L}_2]$ [1] has shown the importance of the nature of the neutral ligands on the decomposition mechanisms. Thus when the decomposition of the complexes $[\text{Co}(\text{C}_6\text{Cl}_5)_2\text{L}_2]$ in which L is a tertiary phosphine is carried out in the presence of added bromine, the major product is the coupled species $(\text{C}_6\text{Cl}_5)_2$, while for $\text{L} = \text{aromatic amine}$ the decomposition products mainly arise from homolytic cleavage of the $\text{Co-C}_6\text{Cl}_5$ bond. Loss of chlorine atoms of the aromatic ring was also observed in the same study. These losses are thought to occur because of the steric compression in the ligand C_6Cl_5 and give rise to the appearance of substantial quantities of $\text{C}_6\text{H}_2\text{Cl}_3$, $\text{C}_{12}\text{HCl}_9$ and $\text{C}_{12}\text{H}_2\text{Cl}_8$.

Several new complexes $[\text{CoR}_2(\text{PEtPh}_2)_2]$ ($\text{R} = 2,3,5,6\text{-C}_6\text{HCl}_4$, $2,4,6\text{-C}_6\text{H}_2\text{Cl}_3$ and $2,6\text{-C}_6\text{H}_3\text{Cl}_2$) and $[\text{Co}(2,4,6\text{-C}_6\text{H}_2\text{Cl}_3)_2\text{L}_2]$ ($\text{L} = \text{PEt}_3$, PEt_2Ph , $\frac{1}{2}\text{dpe}$, $3,5\text{-lut}$ and $\frac{1}{2}\text{bipy}$) have been prepared, and the decompositions in solution studied in

order to determine the effect of the electronegativity of the organic group on the stability of the organocobalt complexes, and on the ratio of decomposition products ($R-H$ and $R-R$), and also to show that the decomposition pathways (which depend on L) do not depend on the electronegativity of the organic group R , and to rule out any possible effect of the loss of chlorine atoms on the decomposition process.

Results and discussion

Preparation and characterization

The complexes $[CoR_2(P\text{EtPh}_2)_2]$ $R = 2,6\text{-C}_6\text{H}_3\text{Cl}_2$, $2,4,6\text{-C}_6\text{H}_2\text{Cl}_3$ and $2,3,5,6\text{-C}_6\text{HCl}_4$; $[Co(2,4,6\text{-C}_6\text{H}_2\text{Cl}_3)_2L_2]$ for $L = P\text{Et}_3$ and $P\text{Et}_2\text{Ph}$ were prepared by reaction of $RMgX$ in THF with solid $[CoCl_2L_2]$. The solutions of the Grignard reagents were obtained either by treating $2,6\text{-C}_6\text{H}_3\text{Cl}_2\text{I}$ with magnesium or by metallation of the polychlorobenzenes $1,3,5\text{-C}_6\text{H}_3\text{Cl}_3$ or $1,2,4,5\text{-C}_6\text{H}_2\text{Cl}_4$ with benzylmagnesium chloride or ethylmagnesium bromide [2]. Taking advantage of the high lability of the $P\text{EtPh}_2$ ligand [1], the other complexes $[Co(2,4,6\text{-C}_6\text{H}_2\text{Cl}_3)_2L_2]$ ($L = \frac{1}{2}\text{dpe}$, $\frac{1}{2}\text{bipy}$ and $3,5\text{-lut}$) were prepared by ligand exchange in benzene solution. The mixed complex $[Co(C_6Cl_5)(2,4,6\text{-C}_6\text{H}_2\text{Cl}_3)(P\text{Et}_3)_2]$ was prepared by successive addition of the stoichiometric amount of C_6Cl_5MgCl and $2,4,6\text{-C}_6\text{H}_2\text{Cl}_3MgCl$ to $[CoCl_2(P\text{Et}_3)_2]$. The formation of these organocobalt complexes is possible only when R contains two chlorine atoms in *ortho* position.

All the new compounds are yellow-brown crystalline solids except for the bipyridine derivative which is dark red. They are air stable, but some decomposition of the complex $[Co(2,6\text{-C}_6\text{H}_3\text{Cl}_2)_2(P\text{EtPh}_2)_2]$ is observed during storage for a few months. 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 [3,4]. The infrared spectra show the bands due to all the coordinated ligands [2]. The low solubility of the complexes precluded the determination of the dipolar moments, but the compounds containing monodentate ligands can be assigned *trans* geometry by analogy with the complexes $[Co(C_6Cl_5)_2(P\text{Et}_2\text{Ph})_2]$ [3] and $[Co(\text{mesityl})_2(P\text{Et}_2\text{Ph})_2]$ [5], whose geometry has been shown to be *trans*.

The electronic spectra in benzene solution show a band of low intensity between 350 and 450 nm, which in terms of the energy level diagram inducted by the ESR study of analogous complexes [6], can be assigned to a $d_{z^2} \rightarrow d_{x^2-y^2}$ transition (Table 1). Some of the shoulders observed in this region have been taken to indicate the existence of *cis-trans* isomers of the C_6F_5 analogues [4]. This possibility can be ruled out in our case by the observation of the same absorptions in the electronic spectra of the $[Co(C_6Cl_5)_2(P\text{Et}_2\text{Ph})_2]$, to which a *trans* configuration has been confirmed beyond doubt by the dipole moments [3]; this is supported by the study of the near-infrared region of the electronic spectra, where a single, well resolved band is observed. This band, according to the energy level diagram previously reported [6], can be assigned to a transition between the states $[d_{z^2}]^1$ and $[d_{xy}]^1$, and should be sensitive to a change of symmetry of the complex.

TABLE 1
ANALYTICAL, MAGNETIC AND SPECTRAL DATA

Compound	Analytical data (found (calcd.) (%))				Dec. temp. (°C)	Magnetic moments (BM)	Visible and near infrared spectra nm (ε)
	C	H	Cl	N			
[Co(2,6-C ₆ H ₃ Cl ₂) ₂ (PEtPh ₂) ₂]	61.9 (61.64)	4.6 (4.66)	18.1 (18.19)		138-139	2.16	425(210)
[Co(2,4,6-C ₆ H ₂ Cl ₃) ₂ (PEtPh ₂) ₂]	56.5 (56.63)	4.0 (4.04)	25.0 (25.08)		159-162	2.44	428(210), 1005(9)
[Co(2,3,5,6-C ₆ HCl ₄) ₂ (PEtPh ₂) ₂]	51.3 (52.38)	3.5 (3.52)	31.2 (30.92)		173-176	2.54	
[Co(2,4,6-C ₆ H ₂ Cl ₃) ₂ (PEt ₂ Ph) ₂]	50.7 (51.10)	4.4 (4.56)	28.3 (28.28)		172-175	2.36	407(220), 983(6)
[Co(2,4,6-C ₆ H ₂ Cl ₃) ₂ (PEt ₃) ₂]	44.1 (43.93)	5.1 (5.22)	32.6 (32.42)		186-188	2.55	400(sh), 985(5)
[Co(2,4,6-C ₆ H ₂ Cl ₃) ₂ dpe]	54.5 (55.78)	3.4 (3.45)	26.1 (26.00)		220-222	2.39	410(620), 1005(29)
[Co(2,4,6-C ₆ H ₂ Cl ₃) ₂ bipy]	45.9 (45.88)	2.2 (2.10)	36.6 (36.93)	5.1 (4.86)	148-152	2.55	575(2600)
[Co(2,4,6-C ₆ H ₂ Cl ₃) ₂ (3,5-lut) ₂]	51.1 (49.24)	3.7 (3.50)	33.0 (33.54)	4.2 (4.42)	95-97	2.73	
[Co(C ₆ Cl ₅)(2,4,6-C ₆ H ₂ Cl ₃)(PEt ₃) ₂]	39.2 (39.76)	4.3 (4.45)	38.6 (39.12)		190-193	2.47	400(sh)

Decomposition reactions

The relative stabilities in solution and the decomposition products from the organocobalt complexes have been examined for reactions in boiling benzene and carbon tetrachloride as well as in benzene with added bromine. These decompositions were carried out in the air and under nitrogen and some differences were observed (see results in Tables 2, 3, 4 and 5).

Benzene solutions. When the complexes $[\text{CoR}_2(\text{PEtPh}_2)_2]$ were refluxed in benzene for 6 h, a decrease in the stability of the complex was observed on decreasing the electronegativity of the organic group; thus some unchanged starting material was recovered for $\text{R} = 2,3,5,6\text{-C}_6\text{HCl}_4$, but complete decomposition was observed for $\text{R} = 2,4,6\text{-C}_6\text{H}_2\text{Cl}_3$ and $2,6\text{-C}_6\text{H}_3\text{Cl}_2$ (Table 2). Thermal decomposition of the organometallics in benzene led to coupling and reduction products (R-R and R-H , respectively), with an increase in the yield of the coupling product on decreasing the number of chlorine atoms on the aromatic ring, mainly in the reactions carried out in the air.

The decompositions of the complexes $[\text{Co}(2,4,6\text{-C}_6\text{H}_2\text{Cl}_3)_2\text{L}_2]$ (Table 3) follow a similar pattern to that observed for the analogous complexes with C_6Cl_5 [1]. There is a strong dependence of the products on the nature of the neutral ligand; when $\text{L} =$ tertiary phosphine the complexes are recovered unchanged except when L is PEtPh_2 , in which case the complex is completely decomposed to a mixture of R-H and R-R ; nevertheless when $\text{L} =$ aromatic amine the decomposition is complete when $\text{L} = 3,5\text{-lut}$ but only partial when $\text{L} = \frac{1}{2}$ bipy. In both cases the major product is R-H .

It is important to note the sensitivity of these decomposition reactions to oxygen. When oxygen is present (air or pure oxygen) the reaction is accelerated and the ratio of the decomposition products RH/R-R varies, the yield of R-R being higher when the neutral ligand is a tertiary phosphine and that of R-H higher for $\text{L} =$ amine. The sensitivity towards oxygen also depends on the electronegativity of the organic ligands, being greater for the trichlorophenyl than in the tetrachlorophenyl derivatives (Table 2).

It has been proposed that the reductive elimination process observed in the decomposition of the complexes $[\text{Ni}(\text{aryl})\text{CH}_3(\text{PET}_3)_2]$ takes place via an inter-

TABLE 2
DECOMPOSITION OF $[\text{CoR}_2(\text{PEtPh}_2)_2]$ IN BENZENE SOLUTION (6 h reflux)

R	Unchanged complex, yield (%)	Atmosphere	% R-H ^a		% R-R ^a	
C_6Cl_5 ^b	80	Air	73	C_6HCl_5	7	$\text{C}_{12}\text{Cl}_{10}$
			12	$\text{C}_6\text{H}_2\text{Cl}_4$ ^c	8	$\text{C}_{12}\text{HCl}_9$ ^d
2,3,5,6- C_6HCl_4	30	N ₂	88			12
	30	Air	79			21
2,4,6- $\text{C}_6\text{H}_2\text{Cl}_3$	—	N ₂	60			40
	—	Air	18			82
2,6- $\text{C}_6\text{H}_3\text{Cl}_2$	—	Air	10			90
Mesityl ^e	25		18			82
(L = PEt_2Ph)						

^a Weight %. ^b Ref. 1. ^c 1,2,4,5- $\text{C}_6\text{H}_2\text{Cl}_4$. ^d Mixture of isomers. ^e 30°C, 3 h, ref. 10.

TABLE 3

THERMAL DECOMPOSITION OF $[\text{Co}(\text{2,4,6-Cl}_3\text{C}_6\text{H}_2)_2\text{L}_2]$ IN BENZENE (6 h reflux)

Ligand + additive	Unchanged complex, yield (%)	Atmosphere	Relative yields of polychlorophenyl products ^a	
			1,3,5- $\text{C}_6\text{H}_3\text{Cl}_3$	2,4,6,2',4',6'- $\text{C}_{12}\text{H}_4\text{Cl}_6$
PEt_3 , PEt_2Ph , dpe	95	Air, N_2	—	—
PEtPh_2	—	N_2	60	40
$\text{PEtPh}_2 + \text{PEtPh}_2$	<i>b</i>	N_2	55	45
$\text{PEtPh}_2 + \text{CoBr}_2$	<i>c</i>	N_2	70	30
PEtPh_2	—	Air	18	82
$\text{PEtPh}_2 + \text{CoBr}_2$	<i>c</i>	Air	13	87
PEtPh_2	—	O_2	12	88
3,5-lut	—	Air	92	8
bipy	~60	N_2	80	20
bipy	~40	Air	85	15
bipy	—	O_2	95	5
bipy + bipy	<i>d</i>	N_2	~100	—
dpe + AgClO_4 ^e	—	N_2	60	40
$\text{PEt}_2\text{Ph} + \text{AgClO}_4$ ^e	—	N_2	91	9
$\text{PEtPh}_2 + \text{AgClO}_4$ ^e	—	N_2	90	10
$\text{PEt}_2\text{Ph} + \text{AgClO}_4$ ^e	—	Air	79	21

^a Average results, reproducibility $\pm 3\%$ except for the PEtPh_2 compounds under N_2 ($\pm 5\%$). ^b Total decomposition 32 h (80% of the starting product is recovered after 6 h). ^c 4 h. ^d 30 h. ^e 1 h at room temperature $\text{Co}^{2+}/\text{Ag}^+ 1/2$.

mediate formed by dissociation of a phosphine group [7]. Free phosphine or anhydrous CoBr_2 are added to the solution of $[\text{Co}(\text{2,4,6-Cl}_3\text{C}_6\text{H}_2)_2(\text{PEtPh}_2)_2]$, the rate of decomposition is retarded and accelerated, respectively, but there are no significant changes in the ratios of the decomposition products (Table 3), suggesting that the decomposition takes place by initial release of a phosphine ligand, and that the formation of the decomposition products occurs via the same intermediate:

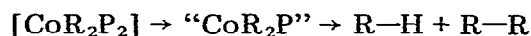


TABLE 4

DECOMPOSITION OF $[\text{Co}(\text{2,4,6-Cl}_3\text{C}_6\text{H}_2)_2\text{L}_2]$ IN THE PRESENCE OF BROMINE (2 h reflux in benzene, $\text{Co/Br } 1/5$)

L + additive	Weight % of polychlorohalophenyl products ^a	
	RBr	R-R
PEt_3		~100
PEt_2Ph		~100
PEtPh_2	22	78
$\text{PEtPh}_2/\text{CoBr}_2$ (10/1)		~100
dpe	5	95
3,5-lut	97	3
bipy	96	4

^a Reproducibility $\pm 2\%$.

TABLE 5

DECOMPOSITION OF $[\text{Co}(\text{2,4,6-}\text{C}_6\text{H}_2\text{Cl}_3)_2\text{L}_2]$ IN CARBON TETRACHLORIDE

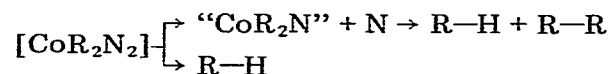
L (8 h reflux)	Atmosphere	Weight % of polychlorophenyl products ^a	
		$\text{C}_6\text{H}_3\text{Cl}_3$	$\text{C}_{12}\text{H}_4\text{Cl}_6$
PEt_3	Air	5	95
PEt_2Ph	Air	14	86
PEtPh_2	Air	68	32
PEtPh_2	N_2	66	34
dpe ^b	Air	6	94
bipy	Air	16	84
3,5-lut	Air	17	83

^a Reproducibility $\pm 3\%$. ^b 85% recovery of unchanged complex.

The organometallics containing dpe or PEt_2Ph are mainly recovered unchanged (90–85%) even after refluxing in benzene with anhydrous CoBr_2 under N_2 for 6 h; the decomposition products $\text{C}_6\text{H}_3\text{Cl}_3$ and $\text{C}_{12}\text{H}_4\text{Cl}_6$ are present in 1/1 ratio for the dpe and 3/1 ratio for the PEt_2Ph complexes. When the complexes $[\text{Co}(\text{2,4,6-}\text{C}_6\text{H}_2\text{Cl}_3)_2\text{P}_2]$ are stirred in benzene with a better phosphine trap like Ag^+ , total decomposition occurs readily even at room temperature; these reactions clearly show the effect of the configuration of the starting product on the ratio of decomposition products. The addition of duroquinone to the reaction solution of $[\text{Co}(\text{2,4,6-}\text{C}_6\text{H}_2\text{Cl}_3)_2(\text{PEtPh}_2)_2]$ in the air or N_2 , has no effect on the rate of decomposition or on the ratio of decomposition products.

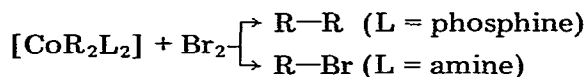
After refluxing an equimolecular mixture of $[\text{Co}(\text{2,4,6-}\text{C}_6\text{H}_2\text{Cl}_3)_2\text{L}_2]$ and $[\text{Co}(\text{C}_6\text{Cl}_5)_2\text{L}_2]$ ($\text{L} = \text{PEtPh}_2$) in benzene in the air for 6 h, 30% of the C_6Cl_5 -containing complex was recovered unchanged. Analysis of the remaining solution shows the presence of the corresponding R-H , R-R and also a small amount (5%) of the cross-coupling product $\text{C}_6\text{Cl}_5\text{-C}_6\text{H}_2\text{Cl}_3$. These results are consistent with an intramolecular decomposition process.

Among the complexes containing aromatic amines (bipy and 3,5-lut) the coupling product also seems to be favoured by the *cis* configuration of the starting organocobalt (Table 3), but in this case the presence of oxygen directs the reaction towards the formation of the reduction products R-H . The addition of free ligand leads to exclusive formation of R-H , a result which is consistent with the existence of two parallel decomposition pathways.



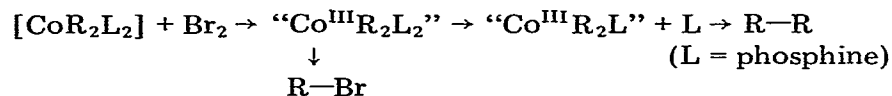
Benzene solutions with added bromine. Boiling the benzene solutions of $[\text{Co}(\text{2,4,6-}\text{C}_6\text{H}_2\text{Cl}_3)_2\text{L}_2]$ containing bromine resulted in total decomposition of all the organometallic compounds (Table 4) giving R-Br and/or coupling product R-R , depending on the neutral ligand (aromatic amine or tertiary

phosphine).



A mixture of R—Br and R—R is obtained when L = PEtPh₂, but if CoBr₂ is also added, the only product obtained is R—R.

The dependence of the Co/Br₂ ratio on the amount of BrR, suggests that the coupling product is formed after a dissociative step.



(L = bipy, 3,5-lut, PEtPh₂)

In the reductive elimination mechanism the initial dissociation of the phosphine should be favoured by its oxidation. The formation of RBr seems to proceed by homolytic cleavage of the Co—R bond in the intermediate "Co^{III}R₂L₂" (L = 3,5-lut, bipy and PEtPh₂), a species less stable than those with L = PEt₃, PEt₂Ph or dpe. The decomposition of the organocobalt must occur through a cobalt(III) intermediate formed by the oxidation of the cobalt(II); this intermediate has been proposed in similar decomposition of analogous compounds [8] and the proposal is in accord with observations during electrochemical decompositions.

The electrochemical oxidation of the complexes [Co(2,4,6-C₆H₂Cl₃)₂L₂] in acetonitrile at room temperature under nitrogen at 1.6 V, gives only the coupling product R—R for L = PEtPh₂ or PEt₂Ph, but 92% of RH and 8% of R—R are obtained for L₂ = bipy. During the decomposition a change corresponding to the transfer of one electron per molecule is observed for L₂ = bipy, while for the phosphines a greater change is observed, probably due to some oxidation of the phosphine.

It should also be noted that the effect of oxygen on the thermal decomposition of the organocobalts in benzene is parallel to the effect of added bromine, if the appearance of RBr is regarded as equivalent to the appearance of RH in the former.

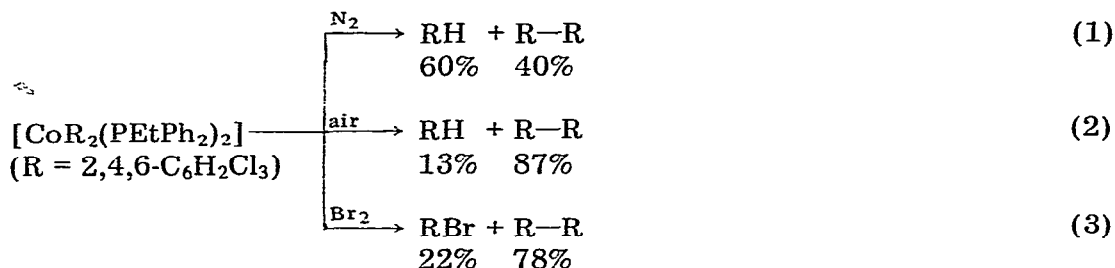
Carbon tetrachloride solution. In this solvent, decomposition occurs for all the complexes [CoR₂L₂] (R = C₆Cl₅) except those with L₂ = dpe or bipy [1]. Under the same conditions, the complex with R = 2,4,6-C₆H₂Cl₃ and L₂ = dpe is recovered unchanged in 85% yield (Table 5). The decompositions in this solvent are not sensitive to oxygen, and high yields of the coupling products are obtained even for the complexes containing amines.

In the decomposition of an equimolar mixture of [Co(2,4,6-C₆H₂Cl₃)₂L₂] and [Co(C₆Cl₅)₂L₂] (L = PEtPh₂ or $\frac{1}{2}$ bipy), only a small amount (~4%) of the cross-coupling product is obtained and some of the [Co(C₆Cl₅)₂bipy] is recovered unchanged. The decomposition of the compound [Co(C₆Cl₅)(2,4,6-C₆H₂Cl₃)(PEt₃)₂] mainly gives the coupling product C₆Cl₅ · 2,4,6-C₆H₂Cl₃, consistent with an intramolecular decomposition process. It has been suggested that in halocarbon solvents decomposition can take place through the oxidative addition of the solvent itself to give an intermediate which rapidly decomposes

[9]. Although it has not been possible to detect any product incorporating a fragment of the solvent, a free radical mechanism cannot be ruled out.

Conclusions

The decrease of the electronegativity of the organic group R in $[\text{CoR}_2\text{L}_2]$ compounds is accompanied by a decrease in the stability of the organocobalt. The decomposition processes depend upon the reaction conditions and routes for the phosphine complexes in benzene can be summarized as follows:



The phosphine-containing compounds decompose thermally by dissociation of a phosphine group prior to the cleavage of the Co—R bond. It has been observed that reaction 2 is only slightly sensitive to changes in the concentration of oxygen (air or pure oxygen) while reaction 1 is very sensitive to the presence of traces of oxygen. The decomposition in presence of added bromine (reaction 3), gives a RBr/R—R ratio very similar to that obtained in the oxygen-induced reaction 2; the formation of R—R in this manner also seems to involve an initial dissociative step. The electrochemical oxidation shows the formation of a cobalt(III) intermediate during the decomposition.

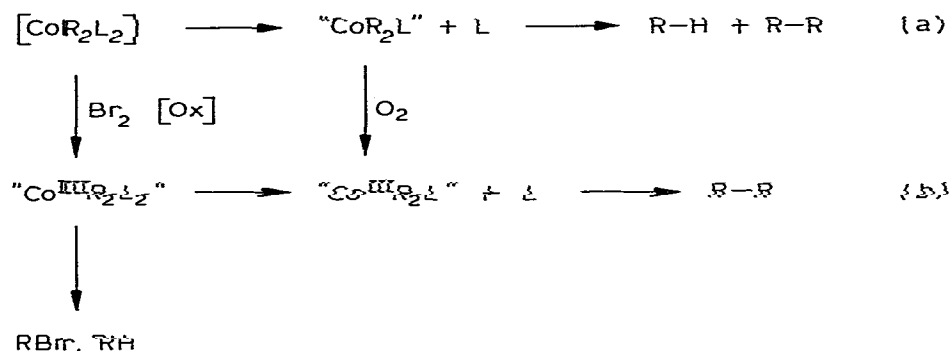
When the decompositions are carried out under oxygen an increase in the yield of coupling product is observed, analogous to that observed in the decomposition induced electrochemically or by added bromine; this suggests that oxygen also oxidatively induces the reductive coupling process. Added bromine causes the decomposition of all the organocobalt complexes studied, while under oxygen the only complexes which undergo decomposition are those which are also thermally decomposed. This suggests that oxygen acts on the intermediate formed by elimination of a phosphine. Nevertheless a lower reactivity towards oxygen of four-coordinate compounds due to electronic factors cannot be ruled out.

The reaction scheme 1 can thus be suggested for phosphine compounds. The thermal decomposition (path a) mainly gives R—H, while when decompositions are oxidatively induced (path b) the major product is the coupled species R—R.

In the thermal decomposition, the higher yield of coupling product for $\text{L} = \frac{1}{2} \text{dpe}$ than for $\text{L} = \text{PEt}_2\text{Ph}$ or PEtPh_2 , in the reaction induced by Ag^+ , indicates that a configuration which places the two R groups together favours the coupling products.

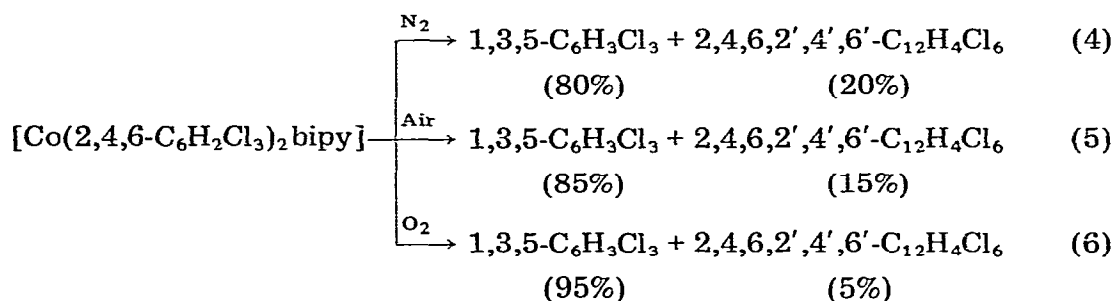
The variation of the electronegativity of the organic group R has little influence on the R—H/R—R ratio from the thermal decomposition. However, when oxygen is present, the amount of R—R markedly increases with the decrease of

SCHEME 1



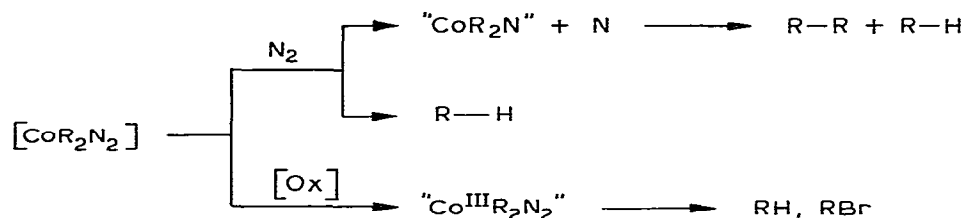
the electronegativity of R. This could be related to the higher reactivity of the intermediate "CoR₂L" towards oxygen, which is to be expected as a result of the decreasing electronegativity of the organic group.

The compounds stabilized by nitrogen-containing ligands show the following behaviour.



The reactions 4, 5 and 6 can be understood in the light of the results for the complexes with R = C₆H₂Cl₃ or C₆Cl₅ [1]. Thus, the reaction Scheme 2 is suggested:

SCHEME 2



The reaction in the presence of air (5) can be explained by the decomposition along the two parallel pathways. In this case oxidative induction does not detectably favour the coupling process.

Experimental

Chemical analyses were carried out at the "Instituto de Química Bío-Orgánica del C.S.I.C. de Barcelona". GLC analyses were performed on a Hewlett—Packard 5710A instrument with a 5% SE-30 on Chromosorb Q column (2 m) connected to a Hewlett—Packard 3390A integrator. Mass spectra were carried out on a H-P 5930A spectrometer. Magnetic susceptibilities were measured by the Faraday method on a Oxford electromagnet (11 kgauss) connected to a Cahn 2000 microbalance.

Preparative methods

All the reactions were carried out under nitrogen. The compounds $[\text{CoCl}_2\text{L}_2]$ ($\text{L} = \text{PEtPh}_2$, PEt_3 and PEt_2Ph) were prepared by published methods [3,11].

Grignard reagents. 2,4,6- $\text{C}_6\text{H}_2\text{Cl}_3\text{MgX}$ and 2,3,5,6- $\text{C}_6\text{HCl}_4\text{MgX}$ were obtained by refluxing solutions of benzylmagnesium chloride in THF and 1,3,5- $\text{C}_6\text{H}_3\text{Cl}_3$ or 1,2,4,5- $\text{C}_6\text{H}_2\text{Cl}_4$ (10 mmol) for 40 min. The resulting dark red solutions were allowed to cool to room temperature and used immediately. The solution of benzylmagnesium chloride was prepared by treating 0.60 g of Mg and 2.5 ml (20 mmol) of benzyl chloride in THF (20 ml) at room temperature for 30 min.

2,6- $\text{C}_6\text{H}_3\text{Cl}_2\text{MgI}$ was prepared by refluxing a mixture of Mg (0.60 g, 20 mmol) and 2,6- $\text{C}_6\text{H}_3\text{Cl}_2\text{I}$ (3.28 g, 12 mmol) in THF (20 ml) for 30–40 min. The pink suspension was allowed to cool to room temperature and used immediately.

Additions to $[\text{CoCl}_2\text{L}_2]$ ($\text{L} = \text{PEt}_3$, PEt_2Ph , PEtPh_2). The corresponding Grignard reagent was added to solid $[\text{CoCl}_2\text{L}_2]$ at room temperature. After 30 min methanol was added and the mixture left at -10°C for 24 h. The precipitate was washed with water, dilute HCl and methanol. The product may be recrystallized from benzene/methanol.

The relative amounts of $[\text{CoCl}_2\text{L}_2]$ /Grignard reagent are 1/5 for the magnesium reagents obtained by metallation and 1/4 for 2,6- $\text{C}_6\text{H}_3\text{Cl}_2\text{MgI}$. The yields were about 50–80%.

$[\text{Co}(\text{C}_6\text{Cl}_5)(2,4,6\text{-C}_6\text{H}_2\text{Cl}_3)(\text{PEt}_3)_2]$ was prepared by successive addition of the stoichiometric amount of $\text{C}_6\text{Cl}_5\text{MgCl}$ and an excess of 2,4,6- $\text{C}_6\text{H}_2\text{Cl}_3\text{MgCl}$ to solid $[\text{CoCl}_2(\text{PEt}_3)_2]$. The product obtained was recrystallized twice.

Replacement reactions by L ($\text{L} = \text{dpe}$; 3,5-lut; bipy). 2 mmol of L were added to a solution of 1 mmol (0.8 g) of $[\text{Co}(2,4,6\text{-C}_6\text{H}_2\text{Cl}_3)_2(\text{PEtPh}_2)_2]$ in 30 ml of benzene. The reaction was carried out at room temperature (10 h) for $\text{L} = 3,5\text{-lut}$ and bipy, and at reflux temperature (6 h) for $\text{L} = \text{dpe}$. The yields were about 75–85%.

Decomposition reactions

Thermal decompositions in solution were carried out by refluxing 0.1 g of complex in 30 ml of freshly distilled solvent under the atmosphere indicated for each experiment (the nitrogen used must be carefully deoxygenated). The amounts of CoBr_2 and duroquinone added were 0.01 g unless otherwise specified. Free PEtPh_2 was added in ratio Co/PEtPh_2 , 1/1.

The solution of the appropriate organocobalt complex was refluxed for the

indicated time and then treated with 1% aqueous HCl at room temperature. The benzene solution was decanted and evaporated almost to dryness. Any unchanged organocobalt complex (when present) was precipitated with ether or methanol and filtered in the cold. The remaining solution was concentrated, dried and chromatographed. Mass spectra were determined for samples from the reaction with Br₂. These samples were used as to give the retention times for use in the quantitative chromatographic analyses.

Electrolytic oxidations were carried out under nitrogen on a potentiostat Amel 555A and a coulometer Amel 721 with a working potential of 1.6 V. The three-compartment cell included a platinum sheet electrode, surrounded by a Pt spiral counter-electrode and a reference electrode of Hg/Hg₂SO₄/K₂SO₄ sat. The solvent was deoxygenated acetonitrile and the supporting electrolyte was tetra-*n*-butylammonium perchlorate (0.05 *M*).

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