ON THE STRUCTURE OF TETRACOORDINATED ORGANOCOBALT COMPLEXES OF THE TYPE [CoR$_2$L$_2$]

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Summary

A series of square-planar organocobalt complexes of the type [CoR$_2$L$_2$] (R = 2,3,4,6-C$_6$HCl$_4$ and 2,3,6-C$_6$H$_2$Cl$_3$, L = PEtPh$_2$, PEt$_2$Ph, and PEt$_3$; R = 2,3,5,6-C$_6$HCl$_4$, and 2,6-C$_6$H$_3$Cl$_2$, L = PEt$_2$Ph, PEt$_3$, and $\frac{1}{2}$dpe) have been prepared in which the electronegativities of the ligand R vary progressively. The reaction of *o*-C$_6$H$_4$ClMgBr with [CoCl$_2$L$_2$] (L = PEtPh$_2$, PEt$_2$Ph, γ-pic or $\frac{1}{2}$bipy) did not give air stable compounds at room temperature, but the solutions obtained at −78°C appear to contain square-planar species for L = PEtPh$_2$, PEt$_2$Ph, and γ-pic, and tetrahedral for L$_2$ = bipy. The tendency towards square-planar or tetrahedral structures for the compounds [CoR$_2$L$_2$] depends on the following factors in order of importance: (i) when the neutral ligand is a phosphine a square-planar structure is adopted; (ii) when L is an aromatic amine, bulky *ortho* substituents on R favour a square-planar structure; and (iii) a tetrahedral geometry is favoured by bidentate amine ligands. The electronegativity of the organic group R seems to be less important.

Introduction

Organocobalt complexes of the type [CoR$_2$L$_2$] have been known for a number of years but the factors which determine their structure and stability are still far from being well understood. Until 1983 all the known tetracoordinate organometallic cobalt(II) complexes were described as having square-planar geometry. This year Klabunde et al. reported the preparation and isolation of blue complexes of the type [Co(C$_6$F$_5$)$_2$L$_2$] (L = py, bipy, THF, THT) having a tetrahedral geometry [1]. The similarity of these complexes to those we had previously reported of the type [CoR$_2$L$_2$], R = C$_6$Cl$_5$ or 2,4,6-C$_6$H$_2$Cl$_3$; L = PEtPh$_2$, PEt$_2$Ph, PEt$_3$, $\frac{1}{2}$dpe, py, 3,5-lut, $\frac{1}{2}$bipy, which are yellow or dark red (L = bipy) and had been assigned a square-planar geometry [2,3], prompted us to undertake a more thorough study of this type of compound.

In order to study the effect of the electronegativity and steric requirements of the organic ligand and of the nature and bulk of the neutral ligand on the structure of the complex, new organocobalt(II) complexes to complete the series of compounds of the type $[CoR_2L_2]$ (L = PEtPh$_2$, PEt$_2$Ph, PEt$_3$, $\frac{1}{2}$dpe; and R = polychlorophenyl group with the two *orto* chlorine atoms) were prepared, and the reactions of the Grignard reagent o-C$_6$H$_4$ClMgBr with the complexes $[CoCl_2L_2]$ for L = PEtPh$_2$, PEt$_2$Ph, γ-pic, $\frac{1}{2}$bipy were studied. Our results show that in organocobalt(II) complexes *ortho*-substituents in the organic ligand kinetically stabilize the product, that square-planar structures are favoured by phosphorus stabilizing ligands, by increased steric requirements in the organic ligand, and by the possibility that the complex can adopt a *trans* configuration.

Results and discussion

Preparation and characterization

The reaction of a Grignard reagent RMgX with the complexes $[CoCl_2L_2]$ (L = PEtPh$_2$, PEt$_2$Ph, and PEt$_3$) gave isolable compounds of the type $[CoR_2L_2]$ for R = 2,3,5,6-C$_6$HCl$_4$, 2,3,4,6-C$_6$HCl$_4$, 2,3,6-C$_6$H$_2$Cl$_3$, and 2,6-C$_6$H$_3$Cl$_2$. We had previously used Tamborski's method to prepare organocobalt(II) complexes of the type $[Co(C_6Cl_5)_2L_2]$ L = py, β-pic, γ-pic, 3,5-Lut, $\frac{1}{2}$dpe and $\frac{1}{2}$bipy [2]. We have extended this method to other polychlorophenyl groups (R). Thus, the addition of a stabilizing ligand L (L = PEtPh$_2$) to a solution of "CoR$_2$" prepared from anhydrous CoBr$_2$ and the corresponding Grignard reagent RMgX led to the isolation of the complexes $[CoR_2L_2]$, R = 2,3,5,6-C$_6$HCl$_4$ and 2,4,6-C$_6$H$_2$Cl$_3$.

Earlier studies on the substitution of neutral ligands on the complexes $[CoR_2L_2]$ showed that L = PEtPh$_2$ is readily displaced by any other smaller and more basic phosphine [2]. This method was used to prepare novel organocobalt(II) complexes [3], and we have now used it to prepare new compound of the type $[CoR_2dpe]$ and to improve the yields of some of the products which can be prepared in low yield by the two methods described above. In accordance with our earlier results [2] we were also able to prepare a complex containing two different neutral ligands, [Co(2,4,6-C$_6$H$_2$Cl$_3$)$_2$(PEt$_3$)(PMe$_2$Ph)], by replacement of a PEt$_3$ ligand of the complex [Co(2,4,6-C$_6$H$_2$Cl$_3$)$_2$(PEt$_3$)$_2$] by PMe$_2$Ph.

All the new compounds are air stable yellow crystalline solids. Analytical results and magnetic moments are listed in Table 1. The magnetic moments are similar to those reported for analogous square-planar complexes having one unpaired electron [4,5]. The infrared spectra show the bands due to all the coordinated ligands [6,7]. The compounds containing a monodentate phosphine have been assigned a *trans* geometry by analogy with the complexes [Co(C$_6$Cl$_5$)$_2$(PEt$_2$Ph)$_2$] [4] and [Co(mesityl)$_2$(PEt$_2$Ph)$_2$] [8], which have been shown to have *trans* geometry.

The electronic spectra of benzene solutions of the complexes show a band of medium intensity between 350 and 450 nm, which in the light of the energy level diagram indicated by the ESR study of analogous complexes [9], can be assigned to a $d_{z^2} \rightarrow d_{x^2-y^2}$ transition (Table 2). In the complexes $[CoR_2(PEt_3)_2]$ this band is masked by the more intense charge-transfer bands and appears as a shoulder. The increase of the basicity of the phosphine and, to a lesser degree, the decrease of the electronegativity of the organic group, cause this band to move to shorter wavelength. This can be attributed to an increase of the σ-donor character of the ligand,

TABLE 1

ANALYTICAL AND MAGNETIC DATA

Compound	Analysis (found(calcd.) (%))			M.p.($^{\circ}$C)	μ(BM)
	C	H	Cl		
$[Co(2,3,4,6\text{-}C_6HCl_4)(PEtPh_2)_2]$	52.2 (52.38)	3.5 (3.52)	31.1 (30.92)	150–153	2.60
$[Co(2,3,6\text{-}C_6H_2Cl_3)_2(PEtPh_2)_2]$	56.2 (56.63)	4.1 (4.04)	24.8 (25.08)	239–143	2.63
$[Co(2,3,5,6\text{-}C_6HCl_4)_2(PEt_2Ph)_2]$	46.8 (46.81)	3.8 (3.93)	34.0 (34.54)	195–199	2.53
$[Co(2,3,4,6\text{-}C_6HCl_4)_2(PEt_2Ph)_2]$	46.9 (46.81)	3.9 (3.93)	34.3 (34.54)	189–192	2.38
$[Co(2,3,6\text{-}C_6H_2Cl_3)_2(PEt_2Ph)_2]$	51.2 (51.10)	4.6 (4.56)	27.7 (28.28)	156–160	2.66
$[Co(2,6\text{-}C_6H_3Cl_2)_2(PEt_2Ph)_2]$	56.4 (56.25)	5.2 (5.31)	20.6 (20.75)	151–153	2.17
$[Co(2,3,5,6\text{-}C_6HCl_4)_2(PEt_3)_2]$	39.4 (39.76)	4.3 (4.45)	39.3 (39.12)	196–198	2.38
$[Co(2,3,4,6\text{-}C_6HCl_4)_2(PEt_3)_2]$	39.6 (39.76)	4.4 (4.45)	39.0 (39.12)	192–194	2.40
$[Co(2,3,6\text{-}C_6H_2Cl_3)_2(PEt_3)_2]$	43.8 (43.93)	5.3 (5.22)	32.1 (32.42)	155–158	2.13
$[Co(2,6\text{-}C_6H_3Cl_2)_2(PEt_3)_2]$	48.8 (49.09)	6.1 (6.18)	23.9 (24.15)	172–176	2.35
$[Co(2,3,5,6\text{-}C_6HCl_4)_2dpe]$	51.7 (51.45)	3.0 (2.95)	31.3 (31.97)	209–212	2.17
$[Co(2,6\text{-}C_6H_3Cl_2)_2dpe)$	60.5 (60.91)	4.0 (4.04)	18.9 (18.93)	199–201	2.24

TABLE 2

VISIBLE SPECTRA OF $[CoR_2L_2]$ [a]

Compound	ε (nm)
$[Co(C_6Cl_5)_2(PEtPh_2)_2]$	440 (240)
$[Co(2,3,5,6\text{-}C_6HCl_4)_2(PEtPh_2)_2]$	433 (210)
$[Co(2,3,4,6\text{-}C_6HCl_4)_2(PEtPh_2)_2]$	435 (220)
$[Co(2,4,6\text{-}C_6H_2Cl_3)_2(PEtPh_2)_2]$	428 (210) [b]
$[Co(2,3,6\text{-}C_6H_2Cl_3)_2(PEtPh_2)_2]$	425 (240)
$[Co(2,6\text{-}C_6H_3Cl_2)_2(PEtPh_2)_2]$	425 (210) [b]
$[Co(C_6Cl_5)_2(PEt_2Ph)_2]$	415 (245)
$[Co(2,3,5,6\text{-}C_6HCl_4)_2(PEt_2Ph)_2]$	413 (210)
$[Co(2,3,4,6\text{-}C_6HCl_4)_2(PEt_2Ph)_2]$	410 (210)
$[Co(2,4,6\text{-}C_6H_2Cl_3)_2(PEt_2Ph)_2]$	407 (220) [b]
$[Co(2,3,6\text{-}C_6H_2Cl_3)_2(PEt_2Ph)_2]$	408 (210)
$[Co(2,6\text{-}C_6H_3Cl_2)_2(PEt_2Ph)_2]$	405 (sh)
$[Co(C_6Cl_5)_2dpe]$	423 (700)
$[Co(2,3,5,6\text{-}C_6HCl_4)_2dpe]$	417 (590)
$[Co(2,4,6\text{-}C_6H_2Cl_3)_2dpe]$	410 (620) [b]
$[Co(2,6\text{-}C_6H_3Cl_2)_2dpe]$	408 (sh)
$[CoR_2(PEt_3)_2]$ [c]	< 400
$[Co(C_6Cl_5)_2bipy]$	555 (1400) 525 (sh)
$[Co(2,4,6\text{-}C_6H_2Cl_3)_2bipy]$	605 (3500) 565 (sh) 375 (4250)
$[Co(2,4,6\text{-}C_6H_2Cl_3)_2bipy]$ [d]	575 (2600) 350 (4000)

[a] Spectra were obtained in benzene except when indicated otherwise. [b] Ref. [3]. [c] R = C_6Cl_5; 2,3,5,6-C_6HCl_4; 2,3,4,6-C_6HCl_4; 2,3,6-$C_6H_2Cl_3$; 2,4,6-$C_6H_2Cl_3$; and 2,6-$C_6H_3Cl_2$. [d] In methanol.

which causes a larger destabilization of the antibonding $d_{x^2-y^2}$ orbital with respect to the antibonding d_{z^2} orbital.

The electronic spectra of the square-planar complexes [CoR$_2$bipy] (R = C$_6$Cl$_5$ and 2,4,6-C$_6$H$_2$Cl$_3$) were reexamined. It was found that for R = C$_6$Cl$_5$ the electronic spectrum is not dependent on the solvent, the same spectra being obtained for the solid state as for solutions. However, for R = 2,4,6-C$_6$H$_2$Cl$_3$ the electronic spectra is very dependent on the solvent, red solutions analogous to those observed for R = C$_6$Cl$_5$ being obtained in MeOH but a blue solution in C$_6$H$_6$ (see Table 2). Even though the electronic spectra in the two solvents cannot be unambiguously assigned, we think that the colour change could be due to a distortion of the square-planar arrangement of ligands present in the solid state or in MeOH towards a tetrahedral geometry in benzene solution.

Structural behaviour

When a solution of a Grignard reagent RMgX (R = polychlorophenyl group with two *ortho* chlorine atoms) is added to the complexes [CoCl$_2$L$_2$] a deep green solution is first formed. According to Matsuzaki et al. [10] this solution must contain the monosubstituted tetrahedral complex [CoClRL$_2$]. When more RMgX is added, the solution turns yellow-brown or red for L$_2$ = bipy, and according to the same authors [10] this is due to the formation of the disubstituted square-planar compound [CoR$_2$L$_2$]; these complexes were isolated by the addition of MeOH to the yellow-brown solution.

Of all the compounds of this kind isolated so far, only the non air stable complexes reported by Klabunde [1] have a tetrahedral geometry, while all the others [2–5], which are much more air stable, have a square-planar geometry according to their magnetic moments.

When an organic group with only one *ortho*-chlorine substituent was used no organometallic compound could be isolated, but the change of colour of the solution is noteworthy. When the Grignard reagent o-C$_6$H$_4$ClMgBr is added to the starting material [CoCl$_2$L$_2$] at $-78°$C initially deep green and then yellow-brown solutions are obtained for L = PEtPh$_2$, PEt$_2$Ph or γ-pic.

These solutions are completely analogous to those mentioned above which gave isolable compounds, but the products slowly decompose during the work-up. When L$_2$ = bipy, even with a large excess of the Grignard reagent a green solution and a green precipitate were obtained, but no organocobalt(II) complex was isolated at room temperature. The green colour is probably due to the disubstituted tetrahedral complex, by analogy with the complexes prepared by Klabunde [1].

Conclusions

Phosphorus ligands favour a square-planar geometry independent of the electronegativity and steric requirements of the organic ligand and irrespective of whether the phosphine is mono- or bi-dentate (in the latter case a *cis* configuration must necessarily be adopted). All the phosphine complexes of the type [CoR$_2$L$_2$] [2–5] (this work) are square-planar, and even in the case of the compounds not isolated (R = p-C$_6$H$_4$X [11] or o-C$_6$H$_4$Cl (this work)) the presence of the disubstituted square-planar complexes can reasonably be assumed. The stabilization of a square-planar geometry by phosphorus ligands can be related to Chatt's arguments and

Matsuzaki's results: Chatt proposed [12] that back donation of metal d-electrons into the $3d$ orbitals of the trivalent phosphorus ligands is more important for square-planar than for tetrahedral geometry. The greater the metal–ligand π-interaction the larger the difference between the LUMO and the HOMO orbitals, and the more favoured the square-planar over the tetrahedral geometry. Matsuzaki et al. [11] have shown by ESR that in square-planar complexes of the type $[CoR_2L_2]$ (L = tertiary phosphine) there are π-interactions between the cobalt and the phosphine, presumably through a $P(d\pi)\ldots Co(d\pi)$ overlap.

When the neutral ligand is an aromatic amine the stabilization of the square-planar geometry by π-interactions between the metal d-orbitals and the π-orbitals of the aromatic amine is much less important. In this case the geometry of the compound is strongly dependent on the organic group. The complexes $[CoR_2L_2]$ (L = py or $\frac{1}{2}$bipy) are tetrahedral for $R = C_6F_5$ [1] and square-planar for $R = C_6Cl_5$ [2] or $2,4,6-C_6H_2Cl_3$ [3]. Another factor which affects the geometry of this type of complex is the mono- or bi-dentate character of the amine. A monodentate amine allows a *trans* configuration, so favouring a square-planar geometry, while a bidentate amine forces a *cis* configuration and favours a tetrahedral geometry. This is shown in the reaction of $o\text{-}C_6H_4ClMgBr$ with the complexes $[CoCl_2L_2]$, for L = γ-pic a yellow solution presumed to contain the disubstituted square-planar complex, while for L_2 = bipy a green solution and a green precipitate, probably of the disubstituted tetrahedral compound, are formed. The structure of the tetracoordinate complex also depends on the nature of the organic ligand R.

The electronegativity of the organic groups, as determined by the number of chlorine atoms on the aromatic ring, seems not to be an important factor in the stabilization of one structure relative to the other. Thus, the complexes $[CoR_2L_2]$ where L = tertiary phosphine and $R = C_6Cl_5$ [5], 2,3,5,6- and 2,3,4,6-C_6HCl_4, 2,4,6-$C_6H_2Cl_3$ [3], 2,3,6-$C_6H_2Cl_3$, and 2,6-$C_6H_3Cl_2$ are square-planar, and even for $R = o\text{-}C_6H_4Cl$ a solution of the square-planar species is obtained. When the neutral ligand is a monodentate aromatic amine, a square-planar complex is isolated for $R = C_6Cl_5$ [2] or $2,4,6-C_6H_2Cl_3$ [3] or obtained in solution when $R = o\text{-}C_6H_4Cl$. On the other hand, the complexes $[CoR_2bipy]$ in which the neutral ligand is bidentate, so forcing a *cis* arrangement, are dark red and square-planar in the solid state for $R = C_6Cl_5$ and $2,4,6-C_6H_2Cl_3$, while the green solution obtained for $R = o\text{-}C_6H_4Cl$ is likely to contain the tetrahedral complex. The dependence of the electronic spectra of $[Co(2,4,6-C_6H_2Cl_3)_2bipy]$ on the solvent is probably due to a change from a square-planar geometry in the solid state or in methanol solution to a tetrahedral geometry in benzene. If this is the case, it would be and indication of some dependence of the geometry on the electronegativity of the organic group. For $R = C_6Cl_5$ the complex $[CoR_2bipy]$ is square-planar in the solid state and no change in the electronic spectrum is observed in solution, while for $R = 2,4,6-C_6H_2Cl_3$ a transition from a square-planar to tetrahedral geometry seems to take place as the solvent is varied.

Large variations are observed for the complexes $[Co(C_6F_5)_2L_2]$; when L = tertiary phosphine the compounds are square-planar [5] while for L = py or $\frac{1}{2}$bipy the complexes are tetrahedral [1]. The ligands C_6Cl_5 and C_6F_5 stabilize different geometries even though they have almost the same electronegativity [13]. This shows that the steric requirements of the organic groups are the most important factors favouring one geometry over the other for amine complexes. Thus, the complexes

[CoR$_2$bipy] and [CoR$_2$py$_2$] are square-planar for R = C$_6$Cl$_5$ but tetrahedral for R = C$_6$F$_5$. Furthermore, the complexes [Co(2,4,6-C$_6$H$_2$Cl$_3$)$_2$L$_2$] (L = γ-pic or $\frac{1}{2}$bipy) are also square-planar, while the complex [Co(o-C$_6$H$_4$Cl)$_2$bipy] is tetrahedral, showing that the less sterically demanding ligand o-C$_6$H$_4$Cl cannot enforce a square-planar geometry for bidentate amine complexes. In this case the different electronegativity of the organic groups may also be of some importance in determining the geometry of the complex.

It can be concluded that the structure of the organometallic species [CoR$_2$L$_2$] depends primarily on the nature of the ancillary ligand L not on its bulk; phosphine ligands stabilize square-planar species while for aromatic amines it is the organic ligand which determines the geometry. The most important characteristic of the organic ligand is its bulk, and organic groups with bulky *ortho* substituents enforce a square-planar geometry. The third factor, though a less important one, which favours square-planar over tetrahedral geometry is the monodentate nature of the aromatic amine which allows a *trans* configuration.

The effect of the electronegativity of R on the molecular geometry is negligible. The role of the organic ligands is thus limited to the saturation of a coordination site, and when there are bulky *ortho* substituents on the organic ring they block the axial coordination sites and so protect the square-planar species towards oxygen and other reagents.

Experimental

Chemical analyses were carried out at the "Instituto de Química Bio-Orgánica del CSIC de Barcelona". Magnetic susceptibilities were measured by the Faraday method on an Oxford electromagnet (11 kgauss) connected to a Cahn 2000 microbalance. Elelctronic spectra were recorded on a Beckman UV 5230 spectrophotometer.

Preparative methods

All the reactions were carried out under nitrogen. The compounds [CoCl$_2$L$_2$] (L = PEtPh$_2$, PEt$_2$Ph, and PEt$_3$) were prepared by published methods [4].

Grignard reagents. 2,3,5,6-C$_6$HCl$_4$MgX, 2,3,4,6-C$_6$HCl$_4$MgX, 2,4,6-C$_6$H$_2$Cl$_3$MgX were obtained by refluxing a solution of benzylmagnesium chloride in THF with 1,2,4,5-C$_6$H$_2$Cl$_4$, 1,2,3,5-C$_6$H$_2$Cl$_4$, 1,3,5-C$_6$H$_3$Cl$_3$ or 1,2,4-C$_6$H$_3$Cl$_3$ (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-C$_6$H$_3$Cl$_2$MgI and o-C$_6$H$_4$ClMgBr were prepared by refluxing a mixture of Mg (0.60 g, 20 mmol) and 2,6-C$_6$H$_3$Cl$_2$I or o-C$_6$H$_4$BrCl (12 mmol) in THF (20 ml) for 30–40 min. The solutions were allowed to cool to room temperature and used immediately.

Additions to [CoCl$_2$L$_2$] (L = PEtPh$_2$, PEt$_2$Ph, and PEt$_3$). The appropriate Grignard reagent was added to solid [CoCl$_2$L$_2$] at room temperature. After 30 min the solution was cooled to −10°C, methanol was added, and the mixtrue was kept at −10°C for 24 h. The precipitate was washed with water, dilute hydrochloric acid and methanol. The product may be recrystallized form benzene/methanol. The relative amounts of [CoCl$_2$L$_2$]/Grignard reagent are 1/5 for the magnesium reagents obtained by metallation and 1/4 for 2,6-C$_6$H$_3$Cl$_2$MgI. The yields were about

40–80% for all the compounds except $[Co(2,3,5,6-C_6HCl_4)_2(PEt_3)_2]$ and $[Co(2,3,4,6-C_6HCl_4)_2L_2]$ (L = PEtPh$_2$, PEt$_2$Ph, and PEt$_3$) for which yields of 10–30% where obtained.

Addition of phosphine to "CoR$_2$".   The appropriate Grignard reagent was added to anhydrous CoBr$_2$ (1.08 g, 5 mmol). The mixture was stirred at room temperature until dissolution was complete, then 20 mmol (4.3 g) of PEtPh$_2$ were added and the stirring was continued for 20 min. Then 25–40 ml of methanol were added and the mixture was kept at $-10\,°C$ for several hours. The product was filtered off, washed with dilute HCl and with alkanes or cold benzene to remove any cobalt salt or polychlorobenzene. The complexes $[CoR_2(PEtPh_2)_2]$ (R = 2,3,5,6-C$_6$HCl$_4$, and 2,4,6-C$_6$H$_2$Cl$_3$) were obtained by this method in a 30% yield.

Substitution reactions.   A solution of 1 mmol of the complex $[CoR_2(PEtPh_2)_2]$ and 4 mmol (0.47 g) of PEt$_3$ or 1 mmol (0.4 g) of dpe in 30 ml of benzene was refluxed for 1 h. The volume of the solution was reduced to 10 ml, and methanol added to induce precipitation of the product. This method was used to prepare all the dpe compounds and $[Co(2,3,5,6-C_6HCl_4)_2(PEt_3)_2]$. The yields were about 85–90%.

Preparation of $[Co(2,4,6-C_6H_2Cl_3)_2(PEt_3)(PMe_2Ph)]$.   A solution of 1 mmol (0.66 g) of $[2,4,6-C_6H_2Cl_3)_2 (PEt_3)_2]$ and 2 mmol (0.28 g) of PMe$_2$Ph in 30 ml of benzene was refluxed for 5 h. The solution was worked up as above to give the product in 85% yield. Dec. temp. 165–167°C. Anal. Found: C, 46.34: H, 4.27; Cl, 31.53. $C_{26}H_{30}Cl_6Co_2P_2$ calcd.: C, 46.20; H, 4.47; Cl, 31.47%.

Reactions of o-C$_4$H$_4$ClMgBr with $[CoCl_2L_2]$ (L = PEtPh$_2$, PEt$_2$Ph, γ-pic, and $\frac{1}{2}$bipy).   The Grignard reagent prepared as above was slowly added to solid $[CoCl_2L_2]$ (2 mmol) either at room temperature or at $-78°C$. A green solution was initially obtained for L = PEtPh$_2$, PEt$_2$Ph, and γ-pic. When more o-C$_6$H$_4$ClMgBr was added the solution turned yellow-brown (deep green for L$_2$ = bipy). No product could be obtained from these solutions due to decomposition. When L = γ-pic the yellow-brown solution turned red and then grey-green when warmed to room temperature.

For the polychlorophenyl ligands IR bands are observed at: 1350, 1295, 1145, 1030, 835 and 650 cm^{-1} for 2,3,5,6-C$_6$HCl$_4$; 1370, 1290, 850, 790, and 620 cm^{-1} for 2,3,4,6-C$_6$HCl$_4$; 1515, 1370, 1345, 1245, 1150, 850, 790 and 770 cm^{-1} for 2,4,6-C$_6$H$_2$Cl$_3$; 1395, 1150, 1025, and 793 cm^{-1} for 2,3,6-C$_6$H$_2$Cl$_3$; 1540, 1405, 1375, 1260, 770, 760 and 750 cm^{-1} for 2,6-C$_6$H$_3$Cl$_2$.

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