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COBALT COMPLEXES OF 2,2'-BIPYRIDINE AND 1,10-PHENANTHROLINE
I. REACTION WITH ALKYL HALIDES AND π-ACIDS

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SUMMARY

New series of stable σ- and π-allylic cobalt dimetallo-organic complexes with 2,2'-bipyridine and 1,10-phenanthroline as ligands have been prepared. PMR spectra are reported. A mechanism of formation, involving hydridic intermediates, is proposed and discussed.

INTRODUCTION

Coordinatively unsaturated complexes which include "soft ligands" and have d^8 or d^{10} electronic configurations coordinate and activate small molecules and undergo oxidative addition and insertion reactions into *e.g.* the metal–carbon or metal–hydrogen bonds[1]. Such reactions play a very important role in homogeneous catalysis. In particular, Co^I, stabilized by several tetradentate conjugate chelating systems having nitrogen or nitrogen and oxygen as donor atoms, behaves as a powerful nucleophilic species, and undergoes oxidative addition and formal insertion reactions[2]. From these reactions, complexes with a stable Co^{III}–C σ-bond can be obtained. The Co^{III}–H bond is very unstable and easily undergoes homolytic cleavage[2e].

In this paper we report similar behaviour for Co^I derivatives with bidentate chelating ligands such as 2,2'-bipyridine (Bipy) and 1,10-phenanthroline (Phen)[3]. These complexes should be of particular interest in the field of homogeneous catalysis, as they have one free coordination site when the metal/chelate ratio is 2/1, and three such sites when the metal/chelate ratio is 1/1.

RESULTS AND DISCUSSION

We have carried out reductions of Co^{II} and Co^I Bipy or Phen complexes in the presence of alkyl halides or π-acids such as butadiene, carbon monoxide, acetylene, phenylacetylene. Analytical data for the isolated complexes are reported in Table 1.

(*a*). Sodium borohydride reduction of a methanolic solution of a Co^{II} complex with Bipy or Phen in a ratio Co/L 1/2 in the presence of alkyl halides gave stable cationic derivatives (I) having two organic groups σ-bonded to cobalt. The corre-

TABLE 1

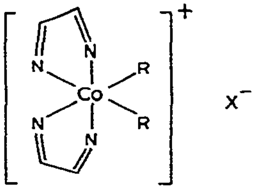
ANALYTICAL DATA FOR THE ISOLATED COMPLEXES

Compound		Analysis found (calcd.) (%)			PMR data	
Number	Formula	C	H	N	Group	Chemical shift (τ)
(I)	$[(C_7H_7)_2Co(Bipy)_2]I$	59.92 (60.01)	4.42 (4.44)	8.23 (8.23)		
(II)	$[(C_7H_7)_2Co(Bipy)_2]ClO_4$	62.20 (62.53)	4.57 (4.63)	8.50 (8.58)	CH_2	6.55 (center of *AB* quartet)[a]
(III)	$[(C_7H_7)_2Co(Bipy)_2]PF_6$	58.31 (58.46)	4.33 (4.32)	7.98 (8.02)		
(IV)	$[(CH_3)_2Co(Bipy)_2]ClO_4$	51.74 (51.56)	4.39 (4.43)	11.21 (11.19)	CH_3	9.2 sharp singlet[b]
(V)	$[(C_2H_5)_2Co(Bipy)_2]ClO_4$	55.0 (54.50)	5.28 (4.95)	10.50 (10.60)	CH_3 CH_2	10.0 (center of triplet)[b] 8.2 (center of multiplet)
(VI)	$[(C_7H_7)_2Co(Phen)_2]I$	62.30 (62.65)	3.95 (4.15)	7.59 (7.69)		
(VII)	$[Co(Bipy)(C_4H_7)_2]ClO_4$	50.71 (50.89)	5.15 (5.22)	6.47 (6.59)		
(VIII)	$[Co(Bipy)(C_4H_7)_2]PF_6$	46.14 (45.97)	4.65 (4.72)	5.81 (5.96)		
(IX)	$[Co(Phen)(C_4H_7)_2]ClO_4$	53.48 (53.52)	4.95 (4.94)	6.33 (6.24)		
(X)	$[Co(Phen)(C_4H_7)_2]PF_6$	48.33 (48.59)	4.57 (4.47)	5.58 (5.67)		
(XI)	$[Co(Bipy)(CO)_2]_2$	52.74 (53.16)	2.79 (2.97)	10.10 (10.33)		

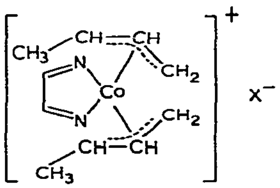
[a] In $CDCl_3$ at −20°. [b] In CD_3COCD_3 at 23°.

sponding benzyl derivative was also isolated from the $[Co^I(Bipy)_3]^+$ complex in the presence of benzyl chloride.

Co^{II} Bipy or Phen complexes, reacted with 2-butenyl bromide, give π-allyl derivatives (II) in low yields. Good yields of di-2-butenyl derivatives (II) were obtained, however, when the reduction of a Co^{II} salt with Bipy or Phen in a Co/L ratio 1/2 or[4] 1/1 of an anhydrous methanolic solution of $[Co(Bipy)_3]^+$ was carried out in presence of an excess of butadiene. Under the same conditions, in the presence of butadiene, $Co(DPE)_2Br_2$ gave the known[5] $[Co(DPE)_2H]^0$ complex*.



(I)



(II)

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* DPE = 1,2-bis(diphenylphosphino)ethane.

Complexes of type (I) are red, diamagnetic and crystalline, and decompose slowly in the air. They catalyze the polymerization of acrylonitrile and methyl acrylate, probably by acting as radical sources. As expected, the $[Et_2Co(Bipy)_2]^+ClO_4^-$ is less reactive than the corresponding Co^{II} complex[6b].

Inspection of molecular models suggests that, because of a marked steric hindrance, the *trans* cations, should be less stable than the *cis* isomers. In agreement with this, the PMR spectra (Fig. 1) show a non bipyridine equivalence of the hydrogen atoms in the 6 and 6' positions of the groups. There is a high-field shift for the 6' proton, which lies close to and above the plane of a pyridine ring of the second ligand group, whereas the resonance of the 6 proton, which does not feel the pyridine ring current effect, appears at lower fields.

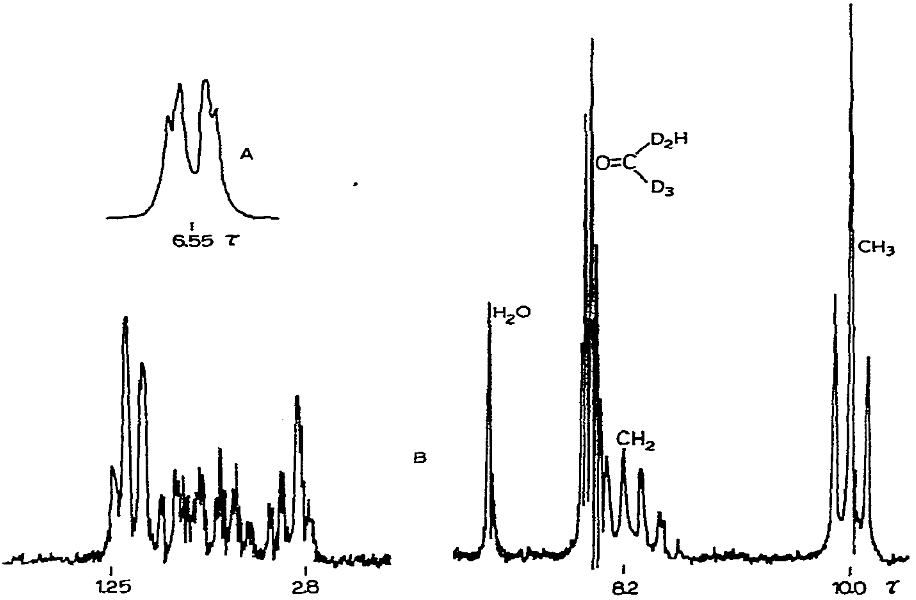


Fig. 1. 60 MHz PMR spectra of A. $[(C_7H_7)_2Co(Bipy)_2]ClO_4$ at −20° in $CDCl_3$ (*AB* quartet). B. $[(C_2H_5)_2$-$Co(Bipy)_2]ClO_4$ at 23° in CD_3COCD_3.

The PMR spectra also show that there is restricted rotation about the Co–C bond in ethyl and benzyl derivatives. The non-equivalence of methylenic protons arising from this effect, has previously been reported (see *e.g.* ref. 7). In the Bipy complexes of type (I), the methylenic protons give a multiplet for the ethyl derivative, due to $J(A-B)$, $J(CH_3-A)$ and $J(CH_3-B)$ couplings, and a pattern very near to an *AB* quartet for the di-benzyl derivative. In the Phen di-benzyl complex the CH_2 signal is also split in an *AB* quartet.

Integrations confirm the presence of a R/L ratio of 1/1.

The IR spectra, as frequently found for other series of Bipy or Phen complexes[8], show a very similar pattern for all the compounds. The more intensive bands are those characteristic of coordinated ligands and ionic ClO_4^-. A splitting of the symmetric out-of-plane bending of the ring hydrogens, was suggested by Martin *et al.*[3], as evidence for a *cis*-configuration. Such a splitting is clearly visible at about 765 cm^{-1}

for the benzyl derivatives, but it should be noted that the spectra were recorded in solid state.

The complexes of type (II) are orange and diamagnetic, and are uni-univalent electrolytes. PMR measurements at −20° in $CDCl_3$ indicate that a mixture of *syn* and *anti* isomers is present. The spectrum of the Phen derivative (Fig. 2) is very similar to that reported by McClellan *et al.*[9] and Bertrand *et al.*[10] for the 2-butenylcobalt tricarbonyl complex and was interpreted in the same way, some peaks remaining however unassigned. The *syn* and *anti* isomers seem to be present in a ratio of about 3/1. A poor PMR spectrum was obtained for the Bipy derivative, owing to its high reactivity towards the solvent, but roughly the same conclusions can be inferred.

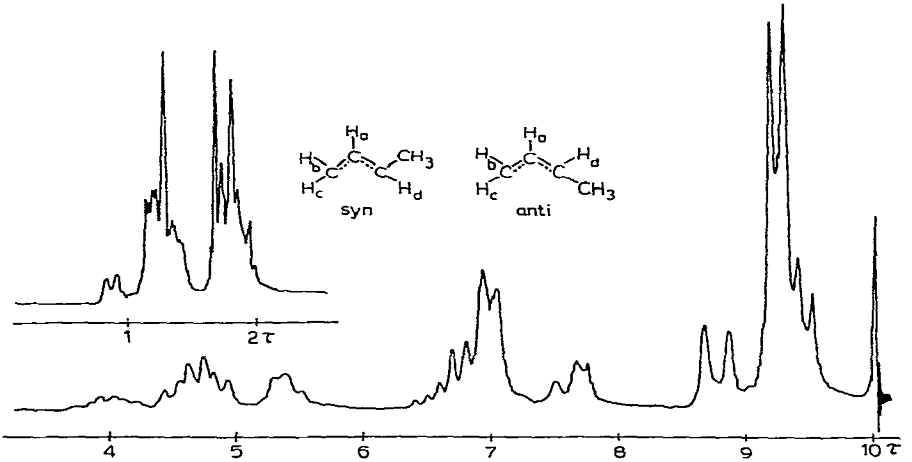


Fig. 2. 60 MHz PMR spectrum of $[Co(Phen)(C_4H_7)_2]ClO_4$ at −20° in $CDCl_3$.

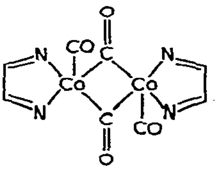
On thermal decomposition in ethylene glycol, the 2-butenyl derivatives yielded 1-butene (78%), *cis*-2-butene (16%) and *trans*-2-butene (3%).

On sodium borohydride reduction they furnished n-butane (40%), *cis*-2-butene (12%) and *trans*-2-butene (45%). The complexes, like diethyl(bipyridine)-nickel[6a], are good catalysts for acrylonitrile polymerization. They do not react with carbon monoxide or triphenylphosphine, but with alkylphosphines give red solutions in which the π-2-butenyl system has probably been converted into a σ-2-butenyl group, as found for the π-allylnickel bromide dimer[11].

(*b*). Reduction of the $Co(Bipy)_2X_2$ complex in the presence of carbon monoxide gives a blue-black compound. Analysis and ν(CO) data suggest that the compound (III), previously prepared in a different way by Behrens and Aquila[12], is formed. $[Co(Bipy)_2]^+$ does not react with carbon monoxide to give (III) in the absence of a reducing agent ($NaBH_4$).

(*c*). Reduction of Bipy and Phen complexes of Co^{II} in a ratio 1/1 or 1/2, under the same conditions but in the presence of phenylacetylene or acetylene, causes polymerization of these substrates.

A mechanism for the formation of the complexes obtained, involving the



(III)

unstable Co^I hydridic derivative (A), as shown in Fig. 3, is proposed. The decomposition of (A) could occur either by homolytic cleavage of the Co–H bond, to give a Co^0 derivative, or by oxidative addition of HX to give a dihydridic derivative, which decomposes yielding Co^I and H_2. The oxidative addition of RX, on the other hand, gives stable dimetallo-organic derivatives.

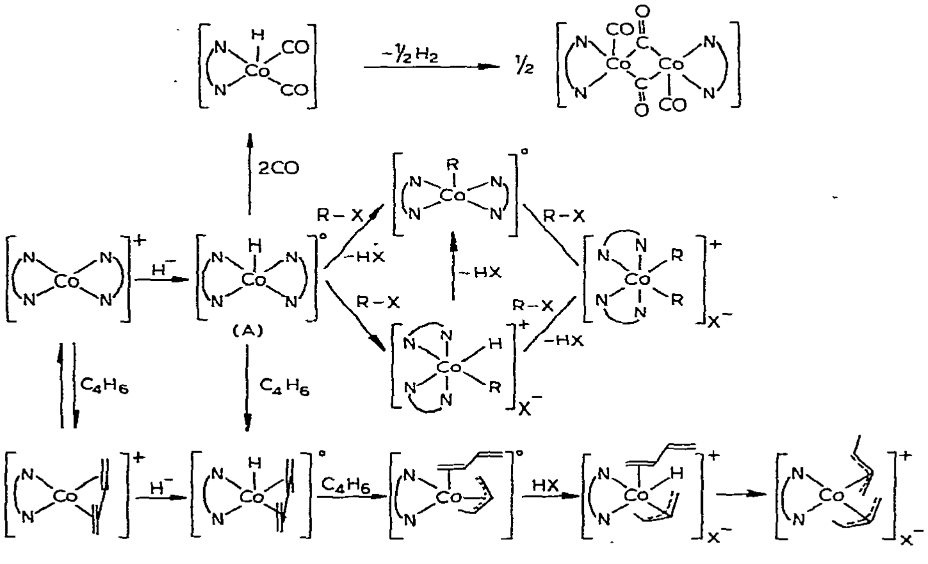


Fig. 3. Proposed mechanism for the formation of the isolated organometallic complexes.

It is interesting to compare the chemical behaviour of our complexes with that of the corresponding DPE derivatives. With the latter a stable hydridic derivative was formed, which underwent oxidative addition by $HClO_4$ to give a stable *cis*-dihydridic species[5], while with RX unstable organometallic intermediates were apparently formed[13]. By contrast, the Co^I Bipy or Phen derivatives can undergo facile replacement of a chelate molecule by π-acceptor ligands or chelates. Such reactions lead to production of (III), to the polymerization of unsaturated hydrocarbons and to the formation of 2-butenyl derivatives. These complexes can thus be regarded as coordinatively unsaturated complexes.

The formation of 2-butenyl derivatives requires π-coordination of butadiene, followed by its insertion into a Co–H bond. Coordination of butadiene is supported by the isolation[4] of [Co(phen) $(PBu_3)C_4H_6$] ClO_4. If the molecule acts as a chelate, an *anti*-2-butenyl derivative should be formed. The observed 3/1 *syn*/*anti* ratio implies that *anti–syn* isomerization occurs, as in the case of the 2-butenylcobalt tricarbonyl complex[10].

The instability of the hydridic derivative (A) and the easy replacement of one of the chelated ligands, could be attributed to the considerable electronic density at the cobalt atom, produced by the strong σ-donating power of the nitrogen atoms and the moderate π-accepting power of π-antibonding orbitals of the ring system.

EXPERIMENTAL

$R_2Co(Bipy)_2X$ (*I–V*)

A deaerated solution of 1.5 g Bipy (10 mmoles) and 1.2 g $CoCl_2 \cdot 6\ H_2O$ (5 mmoles) in methanol (100 ml) was reduced by an excess of $NaBH_4$ in the presence of the appropriate alkyl halide. A red solution was rapidly formed. By adding an aqueous solution of the anion and evaporating the methanol, the complexes were obtained as red crystals. They were recrystallized from methanol/water or acetone/-water.

$(C_7H_7)_2Co(Phen)_2I$ (*VI*)

This compound was prepared, by the above procedure, using 10 mmoles of Phen.

$Co(Bipy)(C_4H_7)_2X$; $Co(Phen)(C_4H_7)_2X$ (*VII–X*)

(*a*). To 1.2 g $CoCl_2 \cdot 6\ H_2O$ (5 mmoles) in methanol (100 ml) 1.5 Bipy or 1.98 g $Phen \cdot H_2O$ (10 mmoles) were added. The deaerated solution was saturated at 0° with butadiene and reduced by $NaBH_4$. To the yellow-orange solution formed, an aqueous solution of the anion was added, and the solvent was evaporated. The complexes were obtained as orange crystals after repeated recrystallizations from acetone/water.

(*b*). The same products were more easily prepared using Co/Bipy or Co/Phen in a ratio of 1/1.

(*c*). A deaerated solution of 0.6 g $CoCl_2 \cdot 6\ H_2O$ and 1.2 g Bipy (7.5 mmoles) in 50 ml anhydrous methanol was reduced by $NaBH_4$. There was no colour change when the stable deep blue solution of $[Co(Bipy)_3]^+$ was saturated with butadiene for 30 min. When more $NaBH_4$ was added, the solution rapidly turned to green and then to orange. The di-2-butenyl derivative was isolated in low yield. A $[Co(Bipy)_3]^+$ solution, treated with benzyl chloride similarly afforded the di-benzyl derivative only after $NaBH_4$ addition.

Phenylacetylene or acetylene polymerization

0.6 g $CoCl_2 \cdot 6\ H_2O$ (2.5 mmoles) and 0.4 or 0.8 g Bipy (2.5–5 mmoles) were dissolved in 100 ml methanol. The deaerated solution was treated with 5 ml phenylacetylene and reduced by $NaBH_4$. The solution turned violet, and a yellow solid precipitated slowly. Recrystallization from CH_2Cl_2 and n-hexane gave a solid with a mol.wt. 1190 (1.2% w/w in benzene). (Found: C, 92.0; H, 6.22. $(C_8H_6)_n$ calcd.: C, 94.1; H, 5.92%.)

When the same reaction was carried out in the presence of acetylene, a black solid was obtained; this was not further investigated.

$[Co(Bipy)(CO)_2]_2$ (*XI*)

A methanolic solution (50 ml) containing 0.6 g $CoCl_2 \cdot 6\ H_2O$ (2.5 mmoles) and 0.8 g Bipy (5 mmoles) was saturated with CO and reduced with $NaBH_4$. The blue-black microcrystalline solid which immediately precipitated was filtered under nitrogen and dried in vacuum.

Techniques

PMR spectra were recorded at −20° with a Jeol JNM-C-60-HL spectrometer, using CD_3COCD_3 or $CDCl_3$ as solvents. IR spectra were recorded on Nujol and Hostaflon mulls, with a Perkin–Elmer 225 spectrophotometer. GLC was performed with a 2 m alumina column at 25°, with a Carlo Erba GT gaschromatograph. Reported data are average values of three runs.

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