

Pentafluorophenyl Acacen Complexes of Cobalt(III)

P. Royo* and J. Sancho

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Summary

The pentacoordinate $C_6F_5Co(acacen)$ complex was prepared by the Grignard reaction involving $BrCo(acacen)PPh_3$ and by oxidative addition of $BrTi(C_6F_5)_2$ to $Co(acacen)$. The addition of bases to solutions of $C_6F_5Co(acacen)$ permits isolation of the neutral mononuclear octahedral $C_6F_5Co(acacen)L$ complexes where $L = H_2O, NH_3, pyridine (py), benzylamine (ba)$ and piperidine (pip), in addition to the binuclear complex $[C_6F_5Co(acacen)]_2en$ and impure samples of the binuclear anionic complex $\{[C_6F_5Co(acacen)]_2CN\}K$. The new complexes were studied by i.r., visible-u.v. and n.m.r. spectroscopy.

Introduction

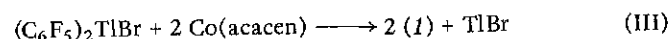
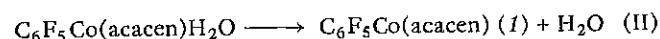
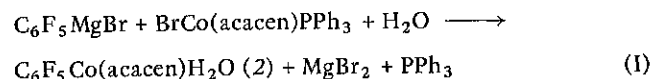
There have been numerous contributions to the chemistry of organometallic complexes of cobalt containing Schiff bases⁽¹⁻³⁾, which constitute simple models of the vitamin B_{12} coenzyme.

In relation to research projects carried out in our laboratory on the study of organometallic derivatives of transition elements containing C_6F_5 ligands, it was of interest to study the influence exercised by a tetradentate ligand of the type indicated on the $Co-C_6F_5$ bond. With this aim in mind we have prepared a series of cobalt(III) complexes containing the N,N' -ethylenebis(acetylacetonate iminate) ligand (acacen). While this manuscript was being written Deacon *et al.* reported the preparation of the pentacoordinate $(C_6F_5)Co(acacen)^{(4)}$ complex using the same reaction with $BrTi(C_6F_5)_2$ as oxidant.

Results and Discussion

Preparative Results

In accord with the following equations (I), (II) and (III), complex (2) has been prepared in good yield by the Grignard reaction, after eliminating the excess of the Grignard reagent by acid hydrolysis.



Complex (1) can be prepared in two different ways. The aquo complex (2) readily liberates water when dried in the presence of P_2O_5 and when subsequently heated *in vacuo* at $80-90^\circ$. On the other hand the same complex (1) can be obtained also in high yield by oxidation of $Co^{II}(acacen)$ with bromobis(pentafluorophenyl)thallium(III), a reagent extensively used by us to insert the C_6F_5 group into various transition metal atoms through oxidative additions⁽⁵⁻⁷⁾.

The second method offers the advantage of better yields in a much simpler way but is inconvenient because a thallium reagent must be used.

From complex (1) it is possible to obtain hexacoordinate complexes by addition of the desired base using the conditions appropriate in each case.

As a general pattern, the solutions containing the pentacoordinate species are green in nondonor solvents which turn red upon addition of a Lewis base, characterizing the formation of the hexacoordinate species. The colour change enables us to qualitatively assess the formation of the hexacoordinate complex.

Thus, by passage of dry ammonia gas through solutions of (1) in ether and subsequent cooling, complex (3) crystallizes. The saturated ammonia solution cannot be evaporated because the colour then changes and a green solution is obtained, from which the initial complex (1) crystallizes. Therefore, as with the aquocomplex, the ammonia complex readily liberates ammonia.

Addition of pyridine, benzylamine or piperidine in excess to solutions of (1) in ethanol leads to the formation of complexes (4), (5) and (6) all of which crystallize by cooling the solution in the presence of an excess of base. The addition of a minimum quantity of base at once produces a colour change. Likewise, the addition of ethylenediamine leads to the formation of complex (7).

All the complexes (1-7) are nonconductors in methanol and their analytical compositions correspond to the stoichiometries formulated in Table 1.

When an excess of CN^- is added to a solution of (1) in methanol, cleavage of the C_6F_5-Co bond takes place and, upon evaporation of the solvent, a substance crystallizes which is identified as $CNCo(acacen)H_2O$. If the $CN^-/complex (1)$ ratio is 1:1 a solid is isolated, the analytical composition of which is halfway between that of the anionic mononuclear complex $[C_6F_5Co(acacen)CN]K$ and that of the binuclear complex (8). Its i.r. spectrum shows two $\nu(C\equiv N)$ absorption bands which indicate the presence of both components. However, the mixture cannot be resolved by repeated recrystallization.

If the $CN^-/complex (1)$ ratio is 1:2 the solid obtained is predominantly the dinuclear complex since the $\nu(C\equiv N)$ vibration situated at higher wave numbers intensifies, whereas the vibration at lower wave numbers becomes very weak. Nevertheless, the mixture still cannot be resolved

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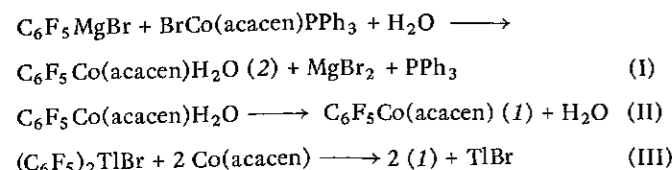
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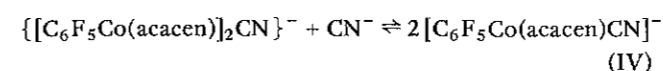
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Table 1. Analytical results for $C_6F_5Co(acacen)L$ complexes.

Complex	Analysis Found (Calcd.) %				
	C	H	N	Co	
1 $C_6F_5Co(acacen)$	48.2 (48.2)	4.1 (4.8)	5.9 (6.2)	12.8 (13.2)	
2 $C_6F_5Co(acacen)H_2O$	47.05 (46.3)	4.8 (4.7)	5.8 (6.1)	12.9 (12.6)	
3 $C_6F_5Co(acacen)NH_3$	46.6 (46.6)	5.1 (4.5)	9.3 (8.5)	12.9 (12.7)	
4 $C_6F_5Co(acacen)py$	52.15 (52.6)	4.9 (4.9)	8.0 (7.9)	11.8 (11.2)	
5 $C_6F_5Co(acacen)ba$	53.9 (54.1)	5.2 (5.9)	7.5 (7.6)	10.75 (10.6)	
6 $C_6F_5Co(acacen)pip$	51.9 (51.8)	5.5 (5.9)	8.05 (7.9)	10.9 (11.05)	
7 $[C_6F_5Co(acacen)]_2en$	48.1 (47.8)	5.05 (4.6)	8.7 (8.8)	12.55 (12.3)	
8 $\{[C_6F_5Co(acacen)]_2CN\}K$	45.6 (47.2)	4.2 (3.85)	7.9 (7.4)	12.6 (12.25)	

and analysis of the obtained product reveals the presence of a small amount of the mononuclear complex.

The solution always contains species possibly in equilibrium, *viz*:



which cannot be displaced at will because the presence of an excess of CN^- causes cleavage of the C_6F_5-Co bond.

The addition of an excess of tributylphosphine to the solution of (1) in ethanol leads to the formation of $C_6F_5Co(acacen)PBu_3$ which is identified in solution but cannot be isolated in the solid state. The addition of triphenylphosphine, triphenylarsine and their oxides to the solutions of (1) in ethanol does not produce any reaction.

Infrared Spectra

All the complexes show i.r. spectra which reveal the presence of the C_6F_5 group, of the tetradentate ligand and the corresponding axial base. The C_6F_5 group displays bands at $1600-1635m, 1490-1510vs, 1050-1070vs, 950-960vs,$ and $610m cm^{-1}$ ⁽⁸⁾. The acacen ligand in all its complexes displays bands at $1570-1590vs, 1500-1520vs, 770s,$ and $740m cm^{-1}$ ⁽⁹⁾. Consequently all the isolated complexes show, in addition to other less intense bands, the following absorptions:

1. A broad intense band between 1570 and $1630 cm^{-1}$ which is the result of the superposition of the absorptions due to the stretching vibrations of the $C=C$ conjugated system of the acacen ligand and the C_6F_5 group.
2. A broad intense band between 1490 and $1520 cm^{-1}$ which is the result of the superposition of the absorptions due to the stretching vibrations of the conjugated system of the C_6F_5 group, of the acacen ligand and also the $\nu(C\equiv N)$ stretching vibration of the said ligand.
3. Three intense bands at $1050, 1010$ and $960 cm^{-1}$ due to the C_6F_5 group.
4. Two intense bands at 740 and $770 cm^{-1}$ due to the acacen ligand.
5. A group of medium intensity bands with absorption peaks at $685-690, 650-655, 630-635, 600-615$ and $475-495 cm^{-1}$ characteristic of the chelate system and difficult to assign.

Besides these bands, each complex shows those which are characteristic of the axial base. The mixture obtained when complex (1) is treated with CN^- in 1:1 molar ratio displays two bands at 2170 and $2120 cm^{-1}$. The second of

these peaks almost disappears whereas the first intensifies when the complex (1)/ CN^- ratio is 1:2. The first band at $2170 cm^{-1}$ must be assigned to the stretching vibration of a CN bridge group whereas that at $2120 cm^{-1}$ must be assigned to the $\nu(C\equiv N)$ stretching vibration of a CN terminal group. The separation between the two is small but is in accord with other observations made in complexes of this type⁽¹⁾.

Visible-u.v. Spectra

The visible-u.v. spectra of various organometallic complexes of cobalt(III) with acacen have been reported by Costa *et al.*⁽¹⁰⁾

In agreement with their results, in the visible region, the hexacoordinate complexes exhibit three bands lying in the regions $19900-21400, 23100-25300$ and $27000-27600 cm^{-1}$ which have been assigned to d-d transitions corresponding to complexes of cobalt(III) with tetragonal distortion⁽¹¹⁾.

The visible-u.v. spectral data for the isolated complexes together with those for the $C_6F_5Co(acacen)PBu_3$ complex, only identified in solution, are given in Table 2.

The pentacoordinate complex exhibits a visible spectrum similar to that of the octahedral complex, a notable shift however being observed of the first band towards a region of lower wave numbers, $15700 cm^{-1}$, in accord with observations made⁽¹⁰⁾ about this type of complex.

The diffuse reflectance spectra are the same as those obtained in solution, so we can anticipate the structure of the complex being the same in solid state as in solution.

The Gaussian analysis of the visible-u.v. spectrum of the

Table 2. Near u.v. and visible absorption frequencies and intensities of $C_6F_5Co(acacen)L$ complexes.

Complex	Solvent	Frequencies/ $10^3 cm^{-1}$ ($\log \epsilon_{max}$)		
		$\nu_{IR}(^1A_1 \rightarrow ^1E^a)$	$\nu_{IA}(^1A_1 \rightarrow ^1A_2)$	$\nu_{II}(^1A_1 \rightarrow ^1B_2, ^1E^b)$
1	$CHCl_3$	15.7 (2.53)	22.7 (3.37)	27.4 (3.57)
3	$EtOH^b$	20.2 (2.44)	23.1sh ^a	27.0sh
4	$EtOH$	20.0 (2.52)	23.1sh	27.0sh
5	$EtOH$	19.9 (2.50)	23.1sh	27.0sh
6	$EtOH$	20.0 (2.51)	23.1sh	27.0sh
7	$EtOH$	20.0 (2.48)	23.1sh	27.0sh
PBu_3	$EtOH$	21.4 (3.66)	25.3 (3.51)	27.6 (3.70)

a) Frequencies of absorption bands revealed as shoulders are estimated; intensities are given for the absorptions at the cited frequency.

b) All spectra of octahedral complexes were recorded in the presence of an excess of the ligand.

$C_6F_5Co(acacen)py$ complex reveals the existence of four bands as a result of the asymmetry of the first band, which contains two components at 18700 and 20100 cm^{-1} . This splitting is a consequence of the lowering of the symmetry from C_{4v} , accepted as a first approximation by Costa, and arises from the disappearance of the degeneracy of the $^1E^a$ state. This behaviour reveals that the orientation of the C_6F_5 ring in the axial direction leads to inequivalence of the d_{xz} and d_{yz} orbitals, revealing the presence of a C_6F_5-Co π bond interaction. Such interactions have been suggested already on other occasions⁽¹²⁾ to explain the greater stability of the pentafluorophenyl derivatives.

1H n.m.r. Spectra

The 1H n.m.r. spectra of $RCo(acacen)L$ complexes have been studied by Hill *et al.*⁽¹³⁾. These authors found that the =CH protons are very sensitive to the changes in the axial ligands R and L.

We have studied the spectra of the pentacoordinate and the hexacoordinate complex with pyridine. When pyridine is added to a chloroform solution of the pentacoordinate species, the =CH and $-CH_3$ chemical shifts are displaced to higher field until, in the presence of an excess of base, the said values remain constant and correspond to the totally formed hexacoordinate species.

Table 3 shows the values which correspond to the pentacoordinate complex and the totally formed hexacoordinate complex together with those values known for other octahedral complexes containing other organic radicals.

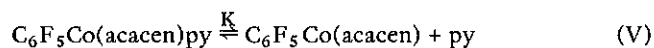
The displacement of the chemical shifts to lower field presumes a growing acceptor capacity by the organic ligand, withdrawing electronic charge from the metal atom.

In accord with the data in Table 3 the organic radicals can be arranged according to their acceptor capacity, *viz.*: $C_6F_5 > Ph > Et > Me > allyl$. When the axial base is absent, the acceptor capacity of the organic radical increases.

Table 3. 1H n.m.r. τ values for $C_6F_5Co(acacen)$ and $RCo(acacen)py$ complexes in $CDCl_3$.

	=CH—	OC-CH ₃	NC-CH ₃	Ref.
MeCo(acacen)py	5.20	8.07	8.10	(13)
EtCo(acacen)py	5.23	8.07	8.11	(13)
AllylCo(acacen)py	5.15	8.06	8.07	(13)
PhCo(acacen)py	5.26	8.06	8.09	(13)
$C_6F_5Co(acacen)py$	5.39	8.20	8.28	—
$C_6F_5Co(acacen)$	4.63	7.76	7.96	—

The variation in chemical shift upon addition of pyridine enables one to calculate the stability constant for the said complex using the method described by Hill *et al.*⁽¹⁴⁾. Thus, for the equilibrium:



we calculate $K = 148$. Again this value is greater than those values found for other complexes containing organic radicals⁽¹⁵⁾, thus confirming that an increase in the acceptor capacity of the organic radical, and consequently a decrease in the electron density at the metal atom, stabilizes the Co-base axial bond.

Experimental

Spectroscopic Measurements

The i.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer using KBr pellets.

Visible-u.v. solution spectra were recorded on a Perkin-Elmer 124 spectrophotometer. Ethanol was used as solvent for the $RCo(acacen)L$ complexes in the presence of an excess of the ligand. The green $RCo(acacen)$ complex was examined in chloroform solution.

The diffuse reflectance spectra of the solids were recorded on a Cary 14 spectrophotometer.

1H n.m.r. spectra were recorded on Perkin-Elmer RI 60 Hz and Bruker-Spectrospin 90 Hz instruments. The shifts were measured from TMS as an internal standard.

The C, H and N analyses were made with a Perkin-Elmer 240 microanalyzer.

Materials

$Co^{II}(acacen)^{(16)}$, $BrCo(acacen)PPh_3^{(17)}$ and $(C_6F_5)_2TiBr^{(18)}$ compounds were prepared by literature methods.

Grignard reagents were freshly prepared in anhydrous THF just before use and reactions were carried out in an inert atmosphere of dry nitrogen.

Synthesis of the complexes

$C_6F_5Co(acacen) (1)$

The pentacoordinate complex was prepared by drying (2) *in vacuo* over P_2O_5 and afterwards by heating it at 100–110° *in vacuo*. The green powder was not recrystallized. The yield was quantitative.

The same complex can also be obtained by heating a mixture of $Co(acacen)$ (0.65 g 2 mmol) and $(C_6F_5)_2TiBr$ (0.62 g 1 mmol) in benzene at the reflux temperature for 3h. The solid obtained by partial evaporation of the benzene was extracted with THF from which the desired complex crystallized in *ca.* 65% yield.

$C_6F_5Co(acacen)H_2O (2)$

A THF solution of C_6F_5MgBr was added slowly to a stirred suspension of $BrCo(acacen)PPh_3$ in THF at 0° and the mixture was set aside at room temperature for 4h. It was then poured into ice-cooled water and hydrolyzed with 1M HBr. The crude product which precipitated was washed with petroleum ether. From the ether washing, PPh_3 displaced from the complex was recovered in quantitative yield. Finally the crude solid was dissolved in 100:1 acetone: water and crystallized by slow evaporation. The resulting crystalline deep brown solid was obtained in 60% yield.

$C_6F_5Co(acacen)NH_3 (3)$

Ammonia was bubbled through a suspension of (1) (0.40 g) in ethyl ether (250 cm^3) for 0.5 h. The remaining solid was filtered off and the red solution, when cooled at 0°, resulted in a crystalline red solid (10% yield).

$C_6F_5Co(acacen)py$ (4)

This compound was prepared by dissolving (1) in the minimum amount of pyridine and adding ethyl ether. Upon cooling the solution, red crystalline needles were obtained which were filtered off, washed with anhydrous ethyl ether and dried *in vacuo* at room temperature (60% yield).

$C_6F_5Co(acacen)L$ ($L = ba, pip$) (5, 6)

Benzylamine or piperidine in excess (1 cm³) was added to a stirred solution of (1) (0.45 g 1mmol) in hot ethanol. After 0.5h the solution was cooled and corresponding complexes separated as red crystalline needles which were washed with a little cold ethanol, ethyl ether and dried *in vacuo* at room temperature (60% yield).

$[C_6F_5Co(acacen)]_2en$ (7)

This complex was obtained by heating an ethanolic solution of (1) with a slight excess of ethylenediamine. The orange red crystalline solid which separated on cooling was washed with ethanol and ethyl ether and dried *in vacuo* (70% yield).

$\{[C_6F_5Co(acacen)]_2CN\}K$ (8)

A. $C_6F_5Co(acacen)$ (0.44 g 1 mmol) dissolved in methanol was stirred for 4h at room temperature with KCN (0.13 g 2 mmol). The green solution turned red. It was evaporated to dryness and the residue was crystallized from chloroform to give a red solid identified as $CNCo(acacen)H_2O$.

B. To a solution of (1) (0.88 g 2 mmol) in chloroform was added KCN (0.06 g 1 mmol) dissolved in methanol and the mixture was stirred for 2h at room temperature. Using the

established work up procedure, a reddish brown solid crystallized from chloroform which was identified as the desired complex, slightly contaminated by $[C_6F_5Co(acacen)CN]K$.

Acknowledgements

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Carboxylatorhodiumbis(triphenylphosphine) Dihydrides: Preparation and Catalytic Activity in Homogeneous Hydrogenation

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Summary

Complexes of the type $RhH_2(PPh_3)_2(O_2CR)$ ($R = n-C_5H_{11}$, Ph, $PhCH=CH$ and $PhCH_2CH_2$) have been prepared and characterized. The compounds are active catalysts for the hydrogenation of olefinic substances. Analogous carboxylato complexes play a role in the hydrogenation of unsaturated carboxylic acids by rhodium-phosphine catalysts.

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Introduction

Several types of rhodium carboxylato complexes have been used already in the homogeneous catalytic hydrogenation of alkenes or alkynes, such as $Rh(PPh_3)_3(O_2CR)^{(1)}$, or precursors for the preparation of catalytically active solutions like $[Rh(OAc)_2]_2^{(2)}$ and $Rh(PPh_3)_3(OAc)^{(3)}$. Furthermore, rhodium carboxylato complexes are presumably the active species in the solutions obtained from $[Rh(PPh_3)_2(C_8H_{12})]^+[PF_6]^-$, Et_3N , H_2 and carboxylic acids⁽⁴⁾