Journal of Organometallic Chemistry, 205 (1981) 223—228
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CARBONYL-ORGANOCOBALT(I) AND -(II) COMPLEXES

P. ROYO and A. VAZQUEZ

Departamento de Química Inorgánica, Facultad die Ciencias, Universidad de Alcalá de Henares, Madrid (Spain)

(Received July 18th, 1980)

Summary

Passage of CO through solutions of complexes $(C_6F_5)_2CoL_2$ gives carbonyl derivatives $(C_6F_5)_2CoL_2(CO)$ (L_2 = 2 PEt_3, 2 P-n-Bu_3, 2 PPh_3, $Ph_2PCH_2CH_2PPh_2$). The properties of these compounds are described.

The compounds are also produced by treating solutions of $(C_6F_5)_2Co(dioxane)_2$ with CO, but a simultaneous reduction to $(C_6F_5)Co(CO)_4$ takes place. Treatment of the latter complex with monodentate ligands gives substitution products $(C_6F_5)Co(CO)_3L$ (L = PEt_3, P-n-Bu_3, PPh_3) all of which are monomeric, whereas the addition of $Ph_2PCH_2CH_2PPh_2$ gives the dimer $(C_6F_5)(CO)_2CoL$—$LCo(CO)_2(C_6F_5)$. The properties of these compounds are discussed.

Introduction

Several carbonyl-cobalt(II) complexes such as $X_2Co(CO)L_2$ (X = Cl, Br, I; L = PEt_3, P-n-Bu_3, PPh_2Me, P-$PhMe_2$ and X = Cl; L = PEt_3, P-n-Bu_3) have been isolated [1—2]]. The study of reversible addition of CO to tertiary phosphine complexes of cobalt(II) reveals [3] that the formation of the pentacoordinate carbonyl complex is generally followed by the reduction of cobalt to give the pentacoordinate carbonyl-cobalt(I) derivative, and the cobalt(II) compound usually cannot be recovered. It has also been observed that the reaction of CO with $Br(mesityl)Co(PPh_3)_2$ gives $BrCo(CO)_2(PPh_3)_2$ [4], but no other reactions of σ-organocobalt(II) complexes with CO have been described.

Results and discussion

The organocobalt(II) complexes $(C_6F_5)_2CoL_2$ (L_2 = 2 PEt_3, 2 P-n-Bu_3, 2 PPh_3, dpe) react with carbon monoxide to form pentacoordinate carbonyl-cobalt(II) complexes

$$(C_6F_5)_2CoL_2 + CO \rightleftharpoons (C_6F_5)_2CoL_2(CO) \qquad (1)$$

(I, $L_2 = 2\ PEt_3$; II, $L_2 = 2$ P-n-Bu_3; III, $L_2 = 2\ PPh_3$; IV, $L_2 = Ph_2PCH_2{-}CH_2PPh_2$

Analytical data are shown in Table 1.

The reaction takes place in benzene solution and also in the solid state at room temperature and ordinary pressure. Complex III cannot be isolated in solution as the passage of CO produces decomposition with elimination of C_6F_5 to give $[Co(CO)_3(PPh_3)]_2$. The reaction has to be carried out with a suspension of $(C_6F_5)_2Co(PPh_3)_2$ in petroleum ether.

All the compounds are indefinitely stable under nitrogen but evolve CO in the air at room temperature. This decomposition is not complete for complex I even after several weeks, whereas complexes II and IV decompose completely in this time to give $(C_6F_5)_2CoL_2$, the colour going from green to yellow. Complex III decomposes rapidly giving a green residue which does not contain C_6F_5 or CO. The same decomposition occurs much more rapidly upon heating the solids, and is complete at 110—120° C for all complexes.

The yellowish-green complex IV becomes yellow if exposed to a vacuum, upon heating, upon exposure to IR radiation, or simply on storing for several days under nitrogen. The change is accompanied by an increase of a weak IR ν(CO) band at 1990 cm^{-1}. This transformation does not take place in solution, which always shows only a ν(CO) band. Even solutions of the yellow complex with two ν(CO) bands in the solid give only one band.

Some physical properties are summarized in Table 2.

The reaction of a suspension of the blue $(C_6F_5)_2Co(dioxane)_2$ in hexane with CO initially gives a green solid and a green yellowish solution. After two hours at room temperature the suspended solid is blue and the solution is yellow. The intermediate green solid cannot be isolated but its formation is favoured at lower temperatures (—78° C).

TABLE 1

ANALYTICAL DATA FOR CARBONYLORGANOCOBALT(I) AND -(II) COMPLEXES

Complex		Analysis found(calcd.)(%)		
		C	H	Co
I	$(C_6F_5)_2Co(PEt_3)_2(CO)$	45.63 (45.68)	4.47 (4.60)	8.73 (8.96)
II	$(C_6F_5)_2Co$(P-n-$Bu_3)_2(CO)$	53.68 (53.82)	6.58 (6.59)	6.84 (7.14)
III	$(C_6F_5)_2Co(PPh_3)_2(CO)$	62.40 (62.24)	3.16 (3.35)	6.05 (6.20)
IV	$(C_6F_5)_2Co$ dpe(CO)	57.34 (57.16)	2.77 (2.95)	6.90 (7.19)
VI	$(C_6F_5)Co(PEt_3)(CO)_3$	42.41 (42.08)	4.02 (3.53)	13.30 (13.76)
VII	$(C_6F_5)Co$(P-n-$Bu_3)(CO)_3$	48.79 (49.23)	5.10 (5.31)	11.06 (11.50)
VIII	$(C_6F_5)Co(PPh_3)(CO)_3$	56.43 (56.66)	2.56 (2.64)	10.00 (10.29)
IX	$[(C_6F_5)Co(CO)_3]_2$ dpe	51.53 (51.89)	2.45 (2.37)	11.37 (11.57)

TABLE 2

PHYSICAL PROPERTIES, CONDUCTIVITIES AND MAGNETIC DATA OF CARBONYLORGANOCOBALT(I) AND -(II) COMPLEXES

Complex	Colour	M.p. (°C)	Λ (ohm^{-1} cm^2 mol^{-1}) [a] ($c = 10^{-4}$ mol l^{-1})	$10^6\chi_M$	μ_{eff}(BM) (T 298°K)
I	green	117(d)	0.2	2099	2.24
II	green	130(d)	0.2	2314	2.35
III	brown	78(d)	—	1786	2.07
IV	yellowish-green	155—170(d)	0.2	2195	2.28
VI	dark yellow	46— 50	0.2	—	diamagnetic
VII	dark yellow	48— 50	0.2	—	diamagnetic
VIII	pale yellow	120—155(d)	0.2	—	diamagnetic
IX	pale yellow	130—140(d)	0.2	—	diamagnetic

[a] = in acetone.

The blue insoluble solid decomposes immediately in air and rapidly under nitrogen to give an intractable residue which does not contain CO. The observed IR spectrum, chemical behaviour and analytical data (of impure samples) suggest that it must be formulated as "$(C_6F_5)_2Co(CO)_3$". Evaporation of the yellow solution gives $(C_6F_5)Co(CO)_4$ [5]. When the same reaction is carried out in THF or benzene only a solution is obtained, which contains a mixture of Co^I and Co^{II} organocarbonyls.

The reaction can be represented by eq. 2.

$$(C_6F_5)_2Co(dioxane)_2 \xrightarrow{CO} \underset{(V)}{"(C_6F_5)_2Co(CO)_3"} \xrightarrow{CO} (C_6F_5)Co(CO)_4 \qquad (2)$$

The dioxane is displaced by carbon monoxide and at the same time reduction occurs to give complex V.

Addition of L = PEt_3, $P\text{-}n\text{-}Bu_3$, PPh_3 and dpe to THF solutions of the mixture of Co^I and Co^{II} complexes gives a mixture of substituted derivatives which can be resolved into the components, the $(C_6F_5)_2CoL_2(CO)$ previously described and $(C_6F_5)CoL(CO)_3$ (VI, L = PEt_3; VII, L = $P\text{-}n\text{-}Bu_3$; VIII, L = PPh_3).

An easier and cleaner way of obtaining the substituted organocarbonylcobalt(I) complexes consist of adding ligands to the previously mentioned hexane solutions of $(C_6F_5)Co(CO)_4$. Complexes VI—IX (IX = $[(C_6F_5)(CO)_2Co]_2$dpe) were isolated in this way. Analytical data are summarized in Table 1.

"$(C_6F_5)_2Co(CO)_3$" is thermally unstable even at low temperatures (—78°C) and under nitrogen. Its decomposition gives a gray residue which does not contain CO or C_6F_5. It was not possible to obtain samples pure enough for a study of its behaviour and analytical composition. Complexes V—IX are indefinitely stable under nitrogen. Several of their properties are listed in Table 2.

Structural studies

All the compounds are monomeric in benzene with the exception of complex IX which was shown to be a dimer by molecular weight measurements (Table 3).

TABLE 3

MOLECULAR WEIGHT MEASUREMENTS ON CARBONYL-ORGANOCOBALT(I) AND -(II) COMPLEXES

Complex		Molecular weight (in benzene) found (calcd.)
I	$(C_6F_5)_2Co(PEt_3)_2(CO)$	640.2 (657.37)
II	$(C_6F_5)_2Co(P\text{-}n\text{-}Bu_3)_2(CO)$	780.1 (825.70)
III	$(C_6F_5)_2Co(PPh_3)_2(CO)$	— (945.64) (decomposes)
IV	$(C_6F_5)_2Codpe(CO)$	800.0 (919.48)
VI	$(C_6F_5)Co(PEt_3)(CO)_3$	400.2 (428.18)
VII	$(C_6F_5)Co(P\text{-}n\text{-}Bu_3)(CO)_3$	488.0 (512.34)
VIII	$(C_6F_5)Co(PPh_3)(CO)_3$	565.9 (572.31)
IX	$[(C_6F_5)Co(CO)_3]_2dpe$	1006.1 (1018.47)

The organocarbonylcobalt(I) complexes are diamagnetic whereas cobalt(II) complexes I—IV (d^7) are paramagnetic with μ_{eff} = 2.0—2.3 BM at room temperature.

The electronic spectra observed for the cobalt(II) carbonyl complexes (Table 4) show two *d—d* absorption bands at ca. 650—700 and 400—500 mμ, which could be assigned to expected transitions for a trigonal bipyramidal geometry. No *d—d* absorption bands were observed for the cobalt(I) carbonyl complexes.

All the isolated compounds show IR absorptions characteristic of the C_6F_5 group [6—7]. The monocarbonyl-cobalt(II) complexes show an IR ν(CO) band between 1995 and 2020 cm^{-1} (Table 5). The wave number of this band is higher than in the corresponding halo derivatives and increases in the order $PEt_3 < P\text{-}n\text{-}Bu_3 < dpe < PPh_3$. The new band which is present for complex IV (dpe) in the solid must be due to the transformation to one of its isomers, although it is not possible to identify this transformation. The IR spectrum observed for complex IV is in agreement with a C_s or C_{2v} trigonal bipyramidal geometry.

Complexes VI—VII show three absorptions due to ν(CO) stretching frequencies in agreement with a C_s trigonal bipyramidal geometry, whereas complex VIII shows only two bands suggesting a C_{3v} trigonal bipyramidal structure. The IR spectrum of the dimer IX shows three bands, suggesting a dinuclear structure with both (C_6F_5) groups in *trans* positions with respect to the equatorial planes or both located in the equatorial plane.

TABLE 4

ELECTRONIC SOLUTION SPECTRA OF THE CARBONYL-ORGANOCOBALT(II) COMPLEXES

Complex		$\lambda_{max.}$ (mμ) (ε) ($l mol^{-1} cm^{-1}$) (in chloroform)
I	$(C_6F_5)_2Co(PEt_3)_2(CO)$	690(162), 450—417(sh), 304(6989), 246(15199)
II	$(C_6F_5)_2Co(P\text{-}n\text{-}Bu_3)_2(CO)$	690(57), 405—375(sh), 294(6826), 273(sh), 261(21420)
III	$(C_6F_5)_2Co(PPh_3)_2(CO)$	650, 425(sh). Decomposes in solution
IV	$(C_6F_5)_2Codpe(CO)$	768(158), 407(789), 323(sh), 285(sh), 242(21519)

TABLE 5

ν(C—O) STRETCHING FREQUENCIES OF ORGANOCOBALT(I) AND -(II) COMPLEXES

Complex		ν(C—O) cm^{-1} [a]
I	$(C_6F_5)_2Co(PEt_3)_2(CO)$	1995vs(N); 1990vs(b)
II	$(C_6F_5)_2Co(P\text{-}n\text{-}Bu_3)_2(CO)$	2000vs(N); 1995vs(b)
III	$(C_6F_5)_2Co(PPh_3)_2(CO)$	2020vs(N); 2020vs(b)
IV	$(C_6F_5)_2Codpe(CO)$	1990w-vs, 2019vs(N); 2019(b)
	"$(C_6F_5)_2Co(CO)_3$"	2065s, 2040m(sh), 2025s(N)
VI	$(C_6F_5)Co(PEt_3)(CO)_3$	2060m, 1990—1960vs, 1900vs(N); 2055m, 2000—1970vs, 1900vs(h)
VII	$(C_6F_5)Co(P\text{-}n\text{-}Bu_3)(CO)_3$	2050m, 1990—1970vs, 1900s(N); 2065s, 1990—1970s, 1900s(h).
VIII	$(C_6F_5)Co(PPh_3)(CO)_3$	1990—1970vs(N); 1995m, 1980s(t).
IX	$[(C_6F_5)Co(CO)_3]_2dpe$	2060m, 2000vs, 1970vs(N); 2060w, 1995s, 1975s(t)

[a] N = Nujol; b = benzene; h = hexane; t = toluene.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer at 4000—250 cm^{-1}. Near IR and Vis-UV spectra were recorded on a Perkin-Elmer 330 spectrophotometer at 186—2600 mμ. Conductivities were measured with a Philips PW 9501/01 conductimeter. Magnetic measurements were carried out by the Faraday method with a Bruker magnet system fitted with variable temperature control unit. Molecular weight measurements were carried out with a Knauer vapour pressure osmometer. C, H, N analyses were made with a Perkin-Elmer 204 B microanalyzer. Cobalt was determined according to ref. 8. Melting points were determined with a Reichert Thermopan microscope. The pentafluorophenylcobalt(II) complexes $(C_6F_5)_2CoL_2$ (L_2 = dioxane, phosphine), were prepared as previously described [9].

$(C_6F_5)_2CoL_2(CO)$ (L_2 = 2 PEt_3, 2 P-n-Bu_3, 2 PPh_3, dpe) (I—IV)

Carbon monoxide at 18°C/1 atm was slowly bubbled for 20—30 minutes through the yellow solutions of $(C_6F_5)_2CoL_2$ (L_2 = 2 PEt_3, 2 P-n-Bu_3, dpe) (ca. 1 g) in benzene (30 ml). The solutions rapidly became dark green. They were concentrated by evaporation and dark green crystals were formed on cooling. The solids were filtered off, washed with hexane, and dried under reduced pressure. Yield ca. 60%.

Similar treatment with $(C_6F_5)_2Co(PPh_3)_2$ caused precipitation of a dark green solid. This product was identified as $[Co(CO)_3PPh_3]_2$ from its analysis and IR spectrum.

Compound III was isolated by using a suspension of the organocobalt(II) complex (1 g) in petroleum ether or n-hexane (60 ml). This yellow suspension was shaken for 40 minutes under one atmosphere of carbon monoxide at room temperature, and turned green. The remaining insoluble residue was removed by filtration. The pale yellow filtrate gave III as brown crystals by concentration and cooling. Yield 55%.

When the same reactions were carried out in the solid state at room temperature and ordinary pressure, the yellow starting materials gave dark green crystals of complexes I, II and IV.

$(C_6F_5)Co(CO)_4$ and "$(C_6F_5)_2Co(CO)_3$"

Carbon monoxide was bubbled through a blue suspension of $(C_6F_5)_2Co(dioxane)_2$ (15.4 mmol) in hexane (200 ml). After treatment for 2 h at room temperature, the suspension turned green. A blue solid was filtered off, washed with hexane and dried under vacuum to give a residue formulated as "$(C_6F_5)_2Co(CO)_3$". The solution was filtered and evaporated to dryness and the yellow solid residue was sublimed under reduce pressure (20—25°C) to give pure V.

When carbon monoxide was bubbled through a blue solution of $(C_6F_5)_2Co(dioxane)_2$ (15.4 mmol) in THF (70 ml) only a yellowish-green solution was obtained. The IR spectrum (ν(CO) = 2025, 2060, 2120 cm^{-1}) suggests a mixture of "$(C_6F_5)_2Co(CO)_3$" and V. Addition of a dilute THF solutions of PEt_3 led to new ν(CO) absorptions at 1970—2000 and 1910 cm^{-1}. The reactions may generally be followed by the steady decrease of the ν(CO) absorptions of the starting mixture of carbonyls. After stirring at room temperature for a few minutes, the solution was evaporated to dryness. The yellowish-green residue was extracted with pentane to give a pale yellow solution and a dark green residue. The pale yellow solution produced VI upon concentration and cooling. The dark green residue was recrystallized from benzene/hexane to give I. The details of the treatment of the yellowish-green crude residue to give complexes $(C_6F_5)_2L_2(CO)$ (I, II, IV) and $(C_6F_5)CoL(CO)_3$ (VI, VII, IX) varied somewhat with the ligand L.

$(C_6F_5)Co(CO)_3L$ ($L = PEt_3$, P-n-Bu_3, PPh_3) (VI—VIII) and $[(C_6F_5)Co(CO)_3]_2dpe$ (IX)

PEt_3 (0.7 ml, 5.0 mmol) was added to a solution of V (1.69 g, 5 mmol) in hexane (50 ml). The solvent was removed under vacuum at 0°C to give yellow crystals of VI. Yield 60%.

Compound VII was similarly obtained.

Addition of an equimolar ratio of benzene PPh_3 or dpe solutions caused precipitation of a pale yellow solid. In each case the solid was filtered off and washed with hexane to give VIII or IX. Yields 75—80%.

Acknowledgement

We greatly appreciate the award of a Research Fellowship (to A.V.) by the Ministerio de Educación y Ciencia (Spain).

References

1 G. Booth and J. Chatt, J. Chem. Soc., (1962) 2099.
2 G. Aklan, Ch. Förster, E. Hergovich, G. Speier and L. Markó, Veszprémi Vegyip. Egyet. Közlem., 12 (1973) 131.
3 M. Bressan, B. Corain, P. Rigo and A. Turco, Inorg. Chem., 9 (1970) 1733.
4 A. Sacco, Gazett. Chim. Ital., 93 (1963) 542.
5 J.B. Wilford, A. Forster and F.G.A. Stone, J. Chem. Soc., (1965) 6519.
6 D.A. Long and D. Steele, Spectrochim. Acta, 19 (1963) 1955.
7 I.J. Iams, E.P. Lippincott and R.T. Bailey, Spectrochim. Acta, 22 (1966) 695.
8 A.M.G. MacDonald and P. Sirichanya, Microchem. J., 14 (1969) 199.
9 P. Royo and A. Vázquez, in press.