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REDUCTIVE CARBONYLATION OF COBALT(II) COMPLEXES WITH PHOSPHORUS–SULFUR BIDENTATE LIGANDS

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Summary

The synthesis of the low-spin cationic complexes $[Co(P–SR)_2](BF_4)_2$ ($P–SR = Ph_2PCH_2CH_2SR$) and its reaction with CO to form the cobalt(I) carbonyl complexes $[Co(CO)_2(P–SR)_2]BF_4$ are described. The chemical and spectroscopic properties of the complexes are presented and the stoichiometry and mechanism of the carbonylation reaction discussed.

Introduction

We are investigating the coordination chemistry of transition metal complexes containing various phosphorus-sulfur bidentate ligands [1–4]. A general feature of these compounds is their ability to undergo dissociation of the sulfur end of the chelate to generate in solution coordinatively-unsaturated species that could be of interest in homogeneous catalysis. We describe here the synthesis of some square-planar cobalt(II) derivatives containing the ligands $PPh_2CH_2CH_2SR$ (P-SMe, $R = CH_3$; P-SEt, $R = C_2H_5$; P-SPh, $R = C_6H_5$) together with an investigation of their reductive carbonylation to cobalt(I) carbonyl complexes $[Co(CO)_2(P–SR)_2]^+$.

This work is an extension of our previous studies on the reductive carbonylation of salts and complexes of cobalt(II) in the presence of phosphorus ligands [5,6].

Experimental

The ligands 1-(thioethyl)-2-(diphenylphosphino)ethane (P–SEt), 1-(thiomethyl)-2-(diphenylphosphino)ethane (P–SMe), and 1-(thiphenyl)-2-(diphenylphosphino)ethane (P–SPh) were prepared by addition of the appropriate chloro derivative $RSCH_2CH_2Cl$ to sodium diphenylphosphide in liquid ammonia [7].

Infrared spectra were obtained on a Jasco DS702G spectrophotometer calibrated with polystyrene. Visible spectra were recorded with a Perkin–Elmer 576 spectrophotometer. The $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker WP 80 SY

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TABLE 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE COMPLEXES

Compound	Color	$\mu_{eff.}$ [a] (BM)	Λ_M [b] ($cm^2\ ohm^{-1}\ mol^{-1}$)	Analysis (Found (calc)(%)) C	H
$[Co(P-SMe)_2](BF_4)_2$	orange	1.87	184	47.87 (47.84)	4.72 (4.55)
$[Co(P-SEt)_2](BF_4)_2$	orange	2.19	168	48.85 (49.19)	4.91 (4.90)
$[Co(CO)_2(P-SMe)_2]BF_4$	yellow		69	53.14 (53.20)	4.72 (4.74)
$[Co(CO)_2(P-SEt)_2]BF_4$	yellow		92	54.18 (54.42)	4.98 (5.10)
$[Co(CO)_2(P-SPh)_2]BPh_4$	yellow		46	73.47 (73.47)	5.39 (5.42)

[a] At 25°C. [b] In nitromethane at 25°C, for approximately 10^{-3} *M* solutions.

Fourier transform spectrometer equipped with a variable temperature probe. NMR spectra were recorded with CH_2Cl_2 solutions relative to an external acetone-d_6 lock, and chemical shifts were referenced to 85% H_3PO_4.

Conductance data were obtained with a Radiometer CDM-3 conductivity bridge. Magnetic moments were determined by the Gouy method and the observed values are corrected for the diamagnetism of the ligands.

Absorption of CO at constant pressure was monitored with a standard apparatus containing a thermostatted gas-burette.

Preparation of the complexes

Some properties and analytical data are reported in Tables 1 and 2.

$[Co(P-SR)_2](BF_4)_2$ (R = Me, Et). A mixture of the appropriate P-SR ligand (2.0 mmol), $Co(BF_4)_2 \cdot 6H_2O$ (1.0 mmol) and 2-propanol (20 ml) was heated under nitrogen at 60°C until a clear red solution formed. The mixture was then stirred at room temperature for 12 h. The orange-red precipitate was recrystallized from dichloromethane-2-propanol.

$[Co(CO)_2(P-SR)_2]BF_4$ (R = Me, Et). A stirred mixture of $Co(BF_4)_2 \cdot 6H_2O$ (2.0 mmol) and P-SR (6.0 mmol) in 2-propanol (50 ml) was gently warmed under

TABLE 2

SPECTROSCOPIC DATA FOR THE COBALT COMPLEXES

Complex	Electronic spectra λ_{max} [a] (nm)	IR $\nu(CO)$ [b] (cm^{-1})	$^{31}P\{^1H\}$ NMR [a] δ (ppm)	$J(P-P')$ (Hz)
$[Co(P-SMe)_2](BF_4)_2$	384			
$[Co(P-SEt)_2](BF_4)_2$	371			
$[Co(CO)_2(P-SMe)_2]BF_4$		2010, 1926	48.4(d), 81.4(d)	118
$[Co(CO)_2(P-SEt)_2]BF_4$		1999, 1932	49.4(d), 80.9(d)	110
$[Co(CO)_2(P-SPh)_2]BPh_4$		2003, 1954	46.4(d), 78.5(d)	117

[a] In CH_2Cl_2. [b] In Nujol mulls.

nitrogen to give a red solution. The reaction vessel was then filled with carbon monoxide and the yellow product which slowly separated was filtered off, washed with 2-propanol, and recrystallized twice from dichloromethane-2-propanol.

$[Co(CO)_2(P\text{–}SPh)_2]BPh_4$. A solution of P–SPh (6.0 mmol) in CH_2Cl_2 (20 ml) was added to a solution of $Co(BF_4)_2 \cdot 6H_2O$ (2.0 mmol) in ethanol (20 ml) and the mixture was stirred in a carbon monoxide atmosphere until a yellow solution formed (3 days). The dichloromethane was removed under reduced pressure and the residual oil was washed with ethanol. The yellow mass so formed was taken up in CH_2Cl_2 (5 ml) and a solution of sodium tetraphenylborate (2.0 mmol) in ethanol (20 ml) was added. Slow evaporation of dichloromethane gave a yellow product, which was recrystallized twice from dichloromethane/ethanol.

Results and discussion

The ligands P–SMe and P–SEt react with $Co(BF_4)_2 \cdot 6H_2O$ in 2-propanol to produce orange compounds of the composition $[Co(P\text{-}SR)_2](BF_4)_2$. Attempts to prepare a ditetrafluoroborate complex with P–SPh was unsuccessful; reaction apparently occurred in solution but no solid product could be obtained.

The $[Co(P\text{–}SR)_2](BF_4)_2$ complexes contain the planar $[Co(P\text{–}SR)_2]^{2+}$ cations, as evidenced by infrared spectra, which exhibit the bands of ionic BF_4 groups, and by the conductivities of their nitromethane solutions which are typical of 2/1 electrolytes. Moreover, the room temperature magnetic moments of the complexes lie in the range 1.9–2.2 BM, which is rather low for planar cobalt(II) complexes, but comparable with the values reported for other planar $[Co(L\text{–}L)_2](ClO_4)_2$ derivatives (L–L = diphosphine, diarsine [8,9]).

The visible spectra of the two $[Co(P\text{-}SR)_2](BF_4)_2$ complexes closely resemble each other, both in the solid state and in solution, and display a band at ca. 380 nm with a weaker absorption (or absorptions) in the nm range 480–530. The spectra resemble those of planar $[Co(diphosphine)_2]^{2+}$ [10].

The $[Co(P\text{–}SR)_2](BF_4)_2$ derivatives react with carbon monoxide under ambient conditions to give carbonyl complexes of cobalt(I) of the type $[Co(CO)_2(P\text{–}SR)_2]BF_4$. The compounds can be obtained more simply by treating $Co(BF_4)_2 \cdot 6H_2O$ in alcohol with carbon monoxide in the presence of an excess of the appropriate P–SR ligand. When this route is used the P–SPh ligand also yields the biscarbonyl adduct.

The yellow $[Co(CO)_2(P\text{–}SR)_2]Y$ ($Y = BF_4$, BPh_4) complexes were characterized by elemental analysis and found to be 1/1 electrolytes in nitromethane. Their IR spectra show in the 2010–1930 cm^{-1} region two CO stretching vibrations which are consistent with a *cis* arrangement of the carbonyl groups. The $^{31}P\text{-}\{^1H\}$ NMR spectra of the $[Co(CO)_2(P\text{–}SR)_2]^+$ cation, which are stereochemically rigid at room temperature, show two doublets at 46.4–48.4 and 78.5–81.4 ppm. The doublet with the largest downfield shift (Δ 95 ppm) is associated with the phosphorus atom involved in a five-membered chelate ring, while the doublet at higher field (Δ 65 ppm) can be assigned to a P–SR group bonded to the cobalt through the phosphorus atom only [11].

The $[Co(CO)_2(P\text{–}SR)_2]^+$ cations probably possess a distorted trigonal bipyramidal geometry, with the chelate P–SR ligands spanning axial and equatorial positions and with two axial phosphorus atoms. That this structure is preferred is indicated by the large J(P–P) value, ca. 115 Hz, which is consistent with an axial P–P coupling constant [12].

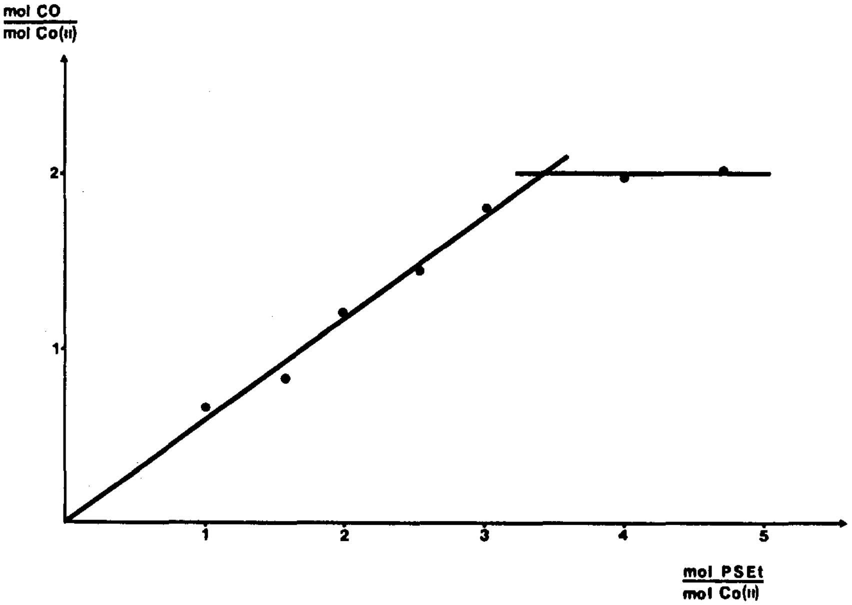

Fig. 1. Influence of P–SEt concentration on the ratio of mol of CO taken up to mol of $Co(BF_4)_2 \cdot 6H_2O$ in isopropanol. $[Co(BF_4)_2]$ is constant.

The dicarbonyl complexes are, however, far from being an ideal trigonal bipyramidal, because the OC–Co–CO angles calculated from the relative intensities of the symmetric and antisymmetric CO stretching vibrations [13], are about 135°. Information on the stoichiometry of the carbonylation reaction was obtained using $[Co(P\text{–}SEt)_2](BF_4)_2$ as the starting complex. In $C_2H_4Cl_2$ or CH_2Cl_2 the reaction of carbon monoxide with $[Co(P\text{–}SEt)_2](BF_4)_2$ results in a non-stoichiometric reduction of cobalt(II) to $[Co(CO)_2(P\text{–}SEt)_2]BF_4$, which is the only carbonyl derivative present in the reaction mixture. Indeed, quantitative IR analyses, using standard solutions of $[Co(CO)_2(P\text{–}SEt)_2]BF_4$, indicate that the cobalt(I) formed is equivalent to ca. 50% of the starting cobalt(II). In contrast, in the presence of excess of added P–SEt, the original cobalt(II) is quantitatively converted into the $[Co(CO)_2(P\text{–}SEt)_2]^+$ derivative, suggesting that P–SEt acts as the reducing agent.

The cobalt(I) complex was also formed in excellent yields by treating $Co(BF_4)_2 \cdot 6H_2O$ and P–SEt with carbon monoxide in 2-propanol. The quantitative aspects of this reaction were investigated (in a gas-burette apparatus) by measuring the CO uptake at constant pressure. Experiments were carried out at constant $Co(BF_4)_2$ concentration in the presence of varying amounts of P–SEt.

As can be seen from Fig. 1, an increase in the phosphine: cobalt ratio results in a parallel increase in the number of mol of carbon monoxide taken up per mol of cobalt(II). When the P–SEt/$Co(BF_4)_2$ ratio is > 3.5, 2 mol of CO per mol of $Co(BF_4)_2$ are absorbed, with quantitative formation of $[Co(CO)_2(P\text{–}SEt)_2]BF_4$ (indicating that no disproportionation of cobalt(II) occurred).

Moreover, the IR spectrum of the crude product obtained by evaporation of the reaction mixtures shows a band at 1180–1200 cm^{-1} which is attributed to the P=O stretching frequency. On the basis of the above observations, the following stoichiometry can be reasonably proposed for the reaction:

$$2Co^{2+} + 7P\text{–}SEt + 4CO + H_2O \rightarrow 2[Co(CO)_2(P\text{–}SEt)_2]^+ + OP\text{–}SEt + HP^+\text{–}SEt$$

The reductive carbonylation of $Co(BF_4)_2 \cdot 6H_2O$ probably involves the primary formation of a Co^{II}-bidentate ligand adduct, which then adds CO and is finally reduced to the cobalt(I) carbonyl derivative.

In this regard it is noteworthy that $Co(BF_4)_2 \cdot 6H_2O$ does not undergo reductive carbonylation in the presence of diphosphines of the types $Ph_2PCH_2CH_2PPh_2$ and *cis*-$Ph_2PCH{=}CHPPh_2$. The lack of reactivity of the Co^{II}-diphosphine systems must be due to the inability of the $[Co(diphosphine)_2]^{2+}$ intermediates to add carbon monoxide. In the case of P–SR ligands the steric constraints are less than with diphosphine ligands, and so the addition of CO to cobalt(II)-bis-chelated complexes could be facilitated. Moreover the possibility of dissociation of the thioether arm of the P–SR ligand may also allow direct formation of the dicarbonyl-cobalt(II) adduct which is most readily reduced to cobalt(I).

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