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Preliminary communication

$[Co^I(CO)(dppe\text{-}P,P')_2]_2\{Co_2^{II}[\mu\text{-}Ph_2P(O)CH_2CH_2P(O)Ph_2]\text{-}Cl_6\}$, a polynuclear cobalt carbonyl ion-pair complex

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Abstract

The compound $CoCl_2 \cdot 6H_2O$, in the presence of zinc powder, reacts with dppe and CO under mild conditions to form $Co^ICo^{II}(dppe)_2(CO)Cl_3$. This compound in CH_2Cl_2 solution auto-oxidizes in air to a polynuclear cobalt carbonyl ion-pair complex having mixed valence states, $[Co^I(CO)(dppe\text{-}P,P')_2]_2\{Co_2^{II}[\mu\text{-}Ph_2P(O)\text{-}CH_2CH_2P(O)Ph_2]Cl_6\}$. In the cation cobalt possesses a distorted trigonal bipyramidal, and in the anion it has tetrahedral configuration. The shortest distance between non-hydrogen atoms of the cation and anion is 3.561 Å.

The compound $CoCl_2 \cdot 6H_2O$ reacts with the bidentate ligand 2-(diphenylphosphino)pyridine (Ph_2Ppy) and carbon monoxide in the presence of zinc powder under mild conditions to give two binuclear cobalt carbonyl complexes having mixed valence states, $Co^ICo^{II}(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)_2Cl_3$ [1] and $Co^0Co^I(\mu\text{-}Ph_2Ppy)_2(\mu\text{-}CO)(CO)Cl$ [2]. When $Ph_2PCH_2CH_2PPh_2$ (dppe) was used instead of Ph_2Ppy we obtained a new binuclear cobalt carbonyl complex having mixed valence states, $Co^ICo^{II}(\mu\text{-}dppe)_2(CO)Cl_3$ (**1**) *, and was identified by FD-mass spectrometry. Complex **1** in solution auto-oxidizes in air to give a new polynuclear cobalt carbonyl complex having mixed valence states, $[Co^I(CO)(dppe\text{-}P,P')_2]_2\{Co_2^{II}[\mu\text{-}Ph_2P(O)CH_2CH_2P(O)Ph_2]Cl_6\}$ (**2**), **.

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* In a typical run, carbon monoxide was bubbled into a THF solution of $CoCl_2 \cdot 6H_2O$ and dppe (1/1), at ambient temperature and pressure in the presence of zinc powder for 4 h. After filtration the solvent was removed in vacuum. The residue was dissolved in CH_2Cl_2 and filtered, then CH_3OH was added to the filtrate, and the volume of the solution was reduced so that precipitation of orange solid could take place. The solid product was recrystallized from CH_2Cl_2/CH_3OH to give **1** in 60% yield. IR $\nu(CO)$(KBr disc) 1900 cm^{-1}. FD-MS m/e 1047 (M^+), 1048, 1049, 1051.

** The single crystal of complex **2** was obtained by slow diffusion of methanol into a CH_2Cl_2 solution of complex **1** in air.

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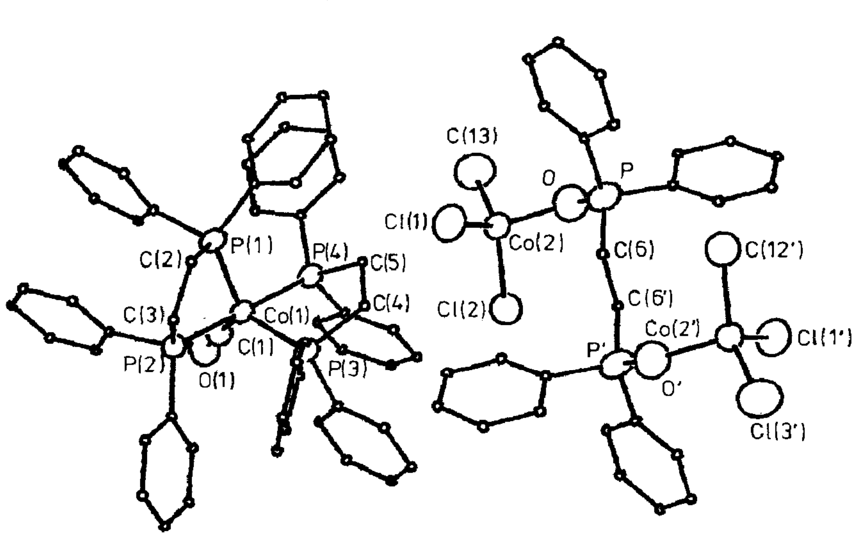
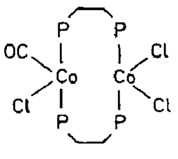
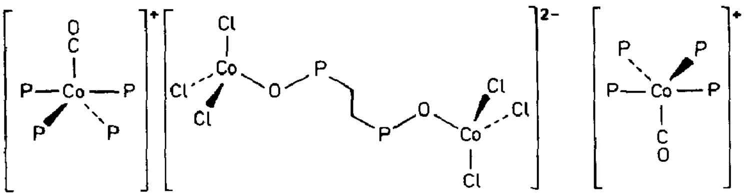


Fig. 1. The structure of 2. Co(1)–P(1) 2.245(2), Co(1)–P(2) 2.219(2), Co(1)–C(1) 1.704(7), Co(2)–O 1.947(5), Co(2)–C(11) 2.247(2) Å; P(1)–Co(1)–C(1) 126.7(2), C(1)–Co(1)–P(3) 122.7(2), Co(2)–O–P 134.4(3), C(11)–Co(2)–O 107.7(2)°.



(1)



(2)

The auto-oxidation of simple cobalt complexes with a phosphine or phosphite ligand has been investigated [3,4]. We observed this phenomenon during the crystallization of $(Ph_2Ppy)_2CoCl_2$ [5]. The detailed mechanism of the formation of complex 2 is not clear.

The molecular structure with selected bond distances and bond angles of complex 2 determined by X-ray diffraction study * is shown in Fig. 1. In the cation cobalt has a distorted trigonal bipyramidal configuration with the carbonyl lying in the equatorial plane. The Co–P(equatorial) distances (2.243 Å (av)) are longer than the Co–P(axial) distances (2.219 Å (av)). The Co–CO distance (1.704 Å) is shorter than those (1.889 Å) in similar trigonal bipyramidal Co^+ species [6]. Both five-membered rings, (Co(1)–P(1)–C(2)–C(3)–P(2) and Co(1)–P(3)–C(4)–C(5)–P(4)), posseses an envelope conformation. In the anion each cobalt is coordinated to three chlorines and one to oxygen in the dppe oxide in a distorted tetrahedral configura-

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* Crystal data. $[Co(CO)(dppe\text{-}P,P')_2]_2\{Co_2[\mu\text{-}Ph_2P(O)CH_2CH_2P(O)Ph_2]Cl_6\}\cdot 2CH_3OH$, $C_{134}H_{128}Co_4Cl_6O_6P_{10}$, $M = 2591$, triclinic, space group $P1$, a 11.76(3), b 12.860(2), c 21.428(3) Å; α 81.45(1), β 82.47(2), r 79.83(2)°; V 3136.5 $Å^3$ and $Z = 1$. $\mu(Mo\text{-}K_\alpha)$ 8.235 cm^{-1}. Intensity data in the range $4° < 2\theta < 44°$ were collected using a $\omega/2\theta$ scan technique. Absorption corrections were applied. A total 7926 unique reflections were collected of which 5679, with $I > 3\sigma(I)$, were used for all calculations.

The structure was solved by direct methods. Full-matrix least squares refinement converged to $R = 0.076$ and $R_w = 0.090$. The highest peak in a final difference map was 0.868 $eÅ^{-3}$.

A Table of the atomic coordinates and a full list of bond lengths and angles has been deposited at the Cambridge Crystallographic Data Centre.

tion. The shortest distance between non-hydrogen atoms of the cation and anion is 3.561 Å.

Two molecules of methanol are present in the unit cell and show no apparent interaction with the complex.

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