Synthesis and Molecular Structure of the Novel Bimetallic Complex [{$CoCl_2Ph_2P(O)CH_2CH_2P(O)Ph_2$}$_2$], containing a 14-Membered Ring

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The novel 14-membered ring complex [{$CoCl_2Ph_2P(O)CH_2CH_2P(O)Ph_2$}$_2$] is the cyclic analogue of the previously described infinite chain *catena*-complex.

Inorganic ring and chain compounds have been widely studied but examples of both cyclic and oligomeric chain isomers are mainly encountered in main group chemistry.[1–4] We now describe the synthesis and structural characterisation of the novel bimetallic complex [{$CoCl_2Ph_2P(O)CH_2CH_2P(O)Ph_2$}$_2$], **1**, containing a 14-membered ring, which is the cyclic analogue of the previously reported[5,6] polymeric chain compound *catena*-dichloro-μ-[1,2-bis(diphenylphosphinoyl)ethane]-cobalt(II), [{$CoCl_2Ph_2P(O)CH_2CH_2P(O)Ph_2$}$_n$], **2**.

Although the coordination chemistry of phosphine oxides, $R_3P(O)$, with transition metals,[7–9] lanthanides[10] and actinides[11] has been extensively studied, less emphasis has been placed on bis(phosphine oxides), *e.g.* $Ph_2P(O)(CH_2)_2P(O)Ph_2$ or hybrid phosphine–phosphine oxide ligands such as $Ph_2P(CH_2)_nP(O)Ph_2$ (n = 1–4).[12]

Treatment of $CoCl_2$ in acetone with $Ph_2PCH_2CH_2PPh_2$ gave a green solution, which on careful addition of H_2O_2 afforded the bis(diphenylphosphine oxide) complex [{$CoCl_2Ph_2P(O)CH_2CH_2P(O)Ph_2$}$_2$], **1**, as bright blue crystals (80% yield).‡ The molecular structure of **1** established by a single crystal X-ray study§ is shown in Fig. 1. The unit cell contains two molecules of the complex each containing the novel 14-membered ring system. The cobalt atoms are in a roughly tetrahedral environment ligated to two oxygens and two chlorine atoms. The cyclic structure of **1** is completely different from that previously reported for the *catena*-isomer **2** shown in Fig. 2 [which was synthesised directly from $CoCl_2$ and $Ph_2P(O)CH_2CH_2P(O)Ph_2$], but there are considerable similarities in bond lengths and bond angles in **1** and **2** (see Table 1). Interestingly the Co(1)–O(1)–P(1) bond angles in molecules 1 and 2 of complex **1** [138.9(2) and 137.7(2)° respectively], show significant differences from the corresponding Co(1′)–O(2)–P(2) bond angles [145.9(2) and

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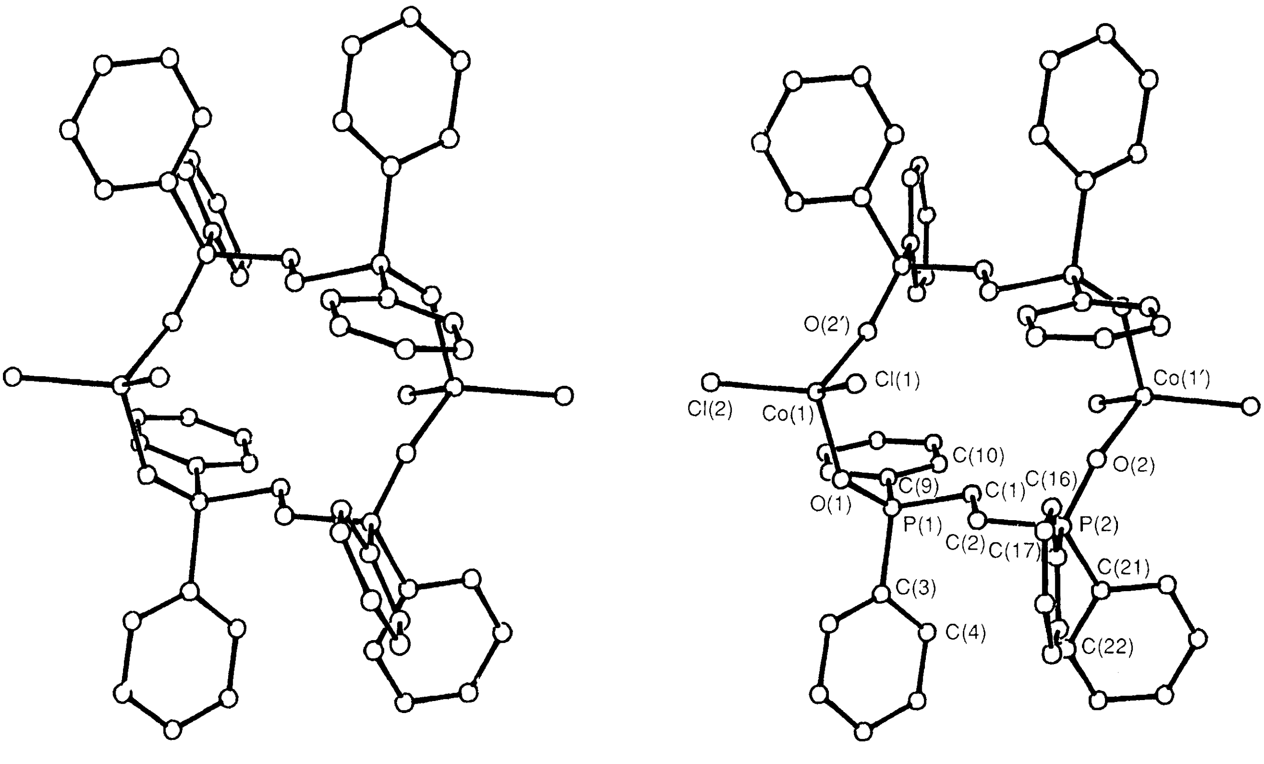
‡ Satisfactory elemental analyses were obtained.

§ *Crystal data:* $C_{52}H_{48}Cl_4Co_2O_4P_4$, M = 1120.5, triclinic, space group $P\bar{1}$, a = 10.558(2), b = 13.907(3), c = 18.347 Å, α = 75.35(1), β = 81.40(1), γ = 78.68(1)°, U = 2541.3 Å^3, Z = 2, D_c = 1.45 g cm^{-3}, monochromated Mo-Kα radiation, λ = 0.71069 Å, μ = 8.6 cm^{-1}.

The structure was solved by direct methods with 5817 reflections having $I > \sigma(I)$ measured on an Enraf-Nonius CAD4 diffractometer used in the refinement by full-matrix least-squares with anisotropic thermal parameters. The final residuals were R = 0.045, R_w = 0.054. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Molecule 2 Molecule 1

Fig. 1 Structures of the two molecules in the unit cell of the cyclic complex $[\{CoCl_2Ph_2P(O)CH_2CH_2P(O)Ph_2\}_2]$, **1**

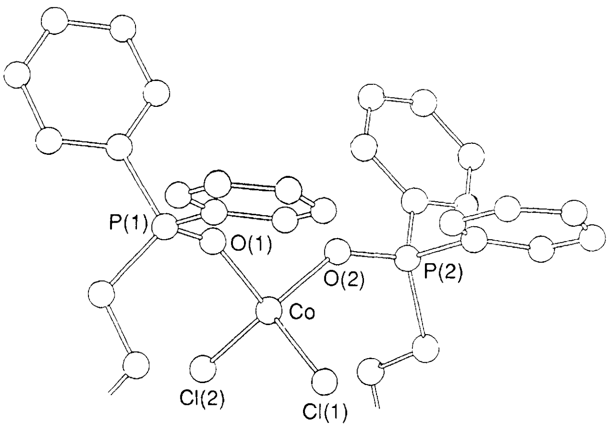


Fig. 2 Molecular structure of the *catena*-complex $[\{CoCl_2Ph_2P(O)CH_2CH_2P(O)Ph_2\}_n]$, **2** (modified from ref. 5)

Table 1 Comparison of crystallographic data for **1**[a] and **2**

	14-Membered ring complex **1**[b]	*Catena*-complex **2**[b]
a/Å	10.558(2)	14.814(4)
b/Å	13.907(3)	12.195(2)
c/Å	18.347(3)	8.834(3)
α/°	75.35(1)	115.13(1)
β/°	81.40(1)	86.57(3)
γ/°	78.68(1)	109.07(2)
Co–Cl[c]	2.244(2), 2.211(2)	2.246(3), 2.252(3)
Co–O[c]	1.975(3), 1.984(3)	1.972(6), 1.975(6)
P=O[c]	1.499(3)	1.478(6), 1.479(6)
Cl–Co–Cl[d]	115.9(6)	114.7(1)
O–Co–O[d]	101.9(1)	102.7(2)
Cl–Co–O[d]	108.4(1), 107.9(1) 114.2(1), 101.9(1)	108.6(2), 111.6(2)

[a] Bond length data for molecule 1. [b] Blue crystals, triclinic, space group $P\bar{1}$. [c] Distance in Å. [d] Angles in degrees.

148.0(2)° respectively], which exactly parallels the behaviour previously noted[5] for the Co–O–P angles in the two halves of the *catena*-complex **2** [138.7(4) and 147.8(4)° respectively]. This has been atttributed[5] to the orientation of the phenyl rings relative to the $CoCl_2$ moiety (see Figs. 1 and 2).

The *in situ* oxidation of simple mononuclear transition metal complexes containing diphosphine ligands may offer a general synthetic route to ring complexes and this is currently under study.

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