

Synthesis and Molecular Structure of the Novel Bimetallic Complex $[\{\text{CoCl}_2\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2]$, containing a 14-Membered Ring

Saud I. Al-Resayes,[†] Peter B. Hitchcock and John F. Nixon*

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, UK

The novel 14-membered ring complex $[\{\text{CoCl}_2\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2]$ 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 $[\{\text{CoCl}_2\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2]$, **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), $[\{\text{CoCl}_2\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_n]$, **2**.

Although the coordination chemistry of phosphine oxides, $\text{R}_3\text{P}(\text{O})$, with transition metals,⁷⁻⁹ lanthanides¹⁰ and actinides¹¹ has been extensively studied, less emphasis has been placed on bis(phosphine oxides), e.g. $\text{Ph}_2\text{P}(\text{O})(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2$ or hybrid phosphine-phosphine oxide ligands such as $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2$ ($n = 1-4$).¹²

Treatment of CoCl_2 in acetone with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ gave a green solution, which on careful addition of H_2O_2 afforded the bis(diphenylphosphine oxide) complex $[\{\text{CoCl}_2\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2]$, **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 $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2$], but there are considerable similarities in bond lengths and bond angles in **1** and **2** (see Table 1). Interestingly the $\text{Co}(1)-\text{O}(1)-\text{P}(1)$ bond angles in molecules **1** and **2** of complex **1** [138.9(2) and 137.7(2)° respectively], show significant differences from the corresponding $\text{Co}(1')-\text{O}(2)-\text{P}(2)$ bond angles [145.9(2) and

[§] *Crystal data:* $\text{C}_{52}\text{H}_{48}\text{Cl}_4\text{Co}_2\text{O}_4\text{P}_4$, $M = 1120.5$, triclinic, space group $P\bar{1}$, $a = 10.558(2)$, $b = 13.907(3)$, $c = 18.347$ Å, $\alpha = 75.35(1)$, $\beta = 81.40(1)$, $\gamma = 78.68(1)^\circ$, $U = 2541.3$ Å³, $Z = 2$, $D_c = 1.45$ g cm⁻³, monochromated Mo-K α radiation, $\lambda = 0.71069$ Å, $\mu = 8.6$ 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.

[†] *Present address:* Chemistry Department, King Saud University, Riyadh, Saudi Arabia.

[‡] Satisfactory elemental analyses were obtained.

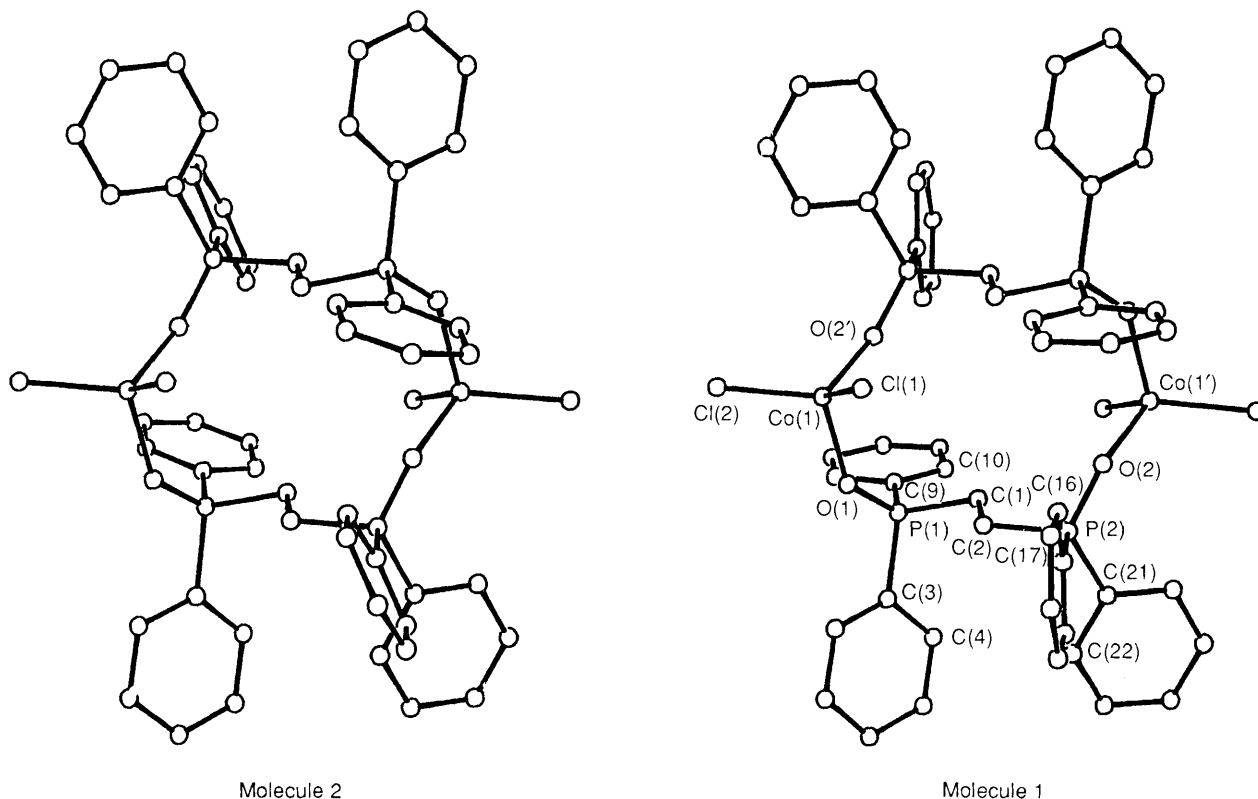


Fig. 1 Structures of the two molecules in the unit cell of the cyclic complex $[\{CoCl_2Ph_2P(O)CH_2CH_2P(O)Ph_2\}_2]$, **1**

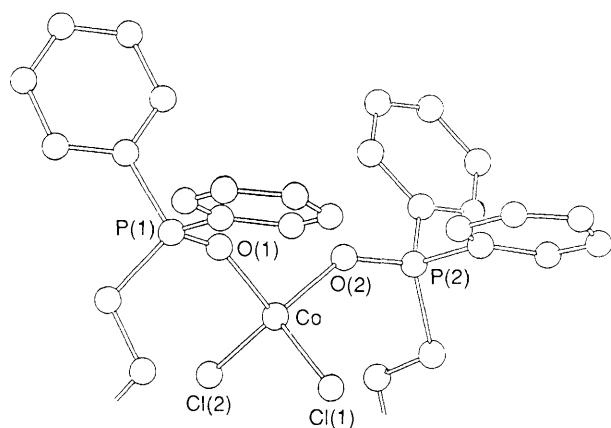


Fig. 2 Molecular structure of the *catena*-complex $[\{CoCl_2Ph_2P(O)CH_2CH_2P(O)Ph_2\}_n]$, **2** (modified from ref. 5)

Table 1 Comparison of crystallographic data for **1**^a and **2**

	14-Membered ring complex 1 ^b	<i>Catena</i> -complex 2 ^b
<i>a</i> /Å	10.558(2)	14.814(4)
<i>b</i> /Å	13.907(3)	12.195(2)
<i>c</i> /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)	108.6(2), 111.6(2)
	114.2(1), 101.9(1)	

^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 noted⁵ 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 attributed⁵ to the orientation of the phenyl rings relative to the CoCl₂ 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.

We thank the Saudi Arabian government for financial support (for S. I. Al-R).

Received, 10th September 1990; Com. 0/04121A

References

- F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley and Sons, New York, 5th edn.
- J. E. Huheey, *Inorganic Chemistry*, Harper International, 1983, 3rd edn., ch. 14.
- I. Haiduc and D. B. Sowerby, *The Chemistry of Inorganic Homo and Heterocycles*, Academic Press, London, vols. 1 and 2.
- J. D. Woollins, *Non Metal Rings, Cages and Clusters*, Wiley and Sons, 1988.
- G. R. Clark and G. J. Palenik, *Cryst. Struct. Commun.*, 1977, **8**, 261.
- S. S. Sandhu and R. S. Sandhu, *Chem. Ind.*, 1970, 626.
- N. M. Karayannis, C. M. Mikulski and L. L. Pytlewski *Inorg. Chim. Acta, Rev.*, 1971, **5**, 69.
- R. J. Butcher, B. R. Penfold and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1979, 668.
- J. F. Dewitt, M. R. Gaira and B. J. Gellatly, *Acta Crystallogr., Sect. B*, 1978, **34**, 762.
- D. C. Bradley, J. S. Ghotra, F. A. Hart, M. B. Hurthouse and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1977, 1166.
- J. G. H. du Preez, B. J. Gellatly and M. L. Gibson, *J. Chem. Soc., Dalton Trans.*, 1977, 1062.
- S. J. Higgins, R. Taylor and B. L. Shaw, *J. Organomet. Chem.*, 1987, **325**, 285 and references cited therein.