

Unexpected oxidation of a diphosphine by bis(1,3-diphenylpropane-1,3-dionato)cobalt(II), [Co(dbm)₂]

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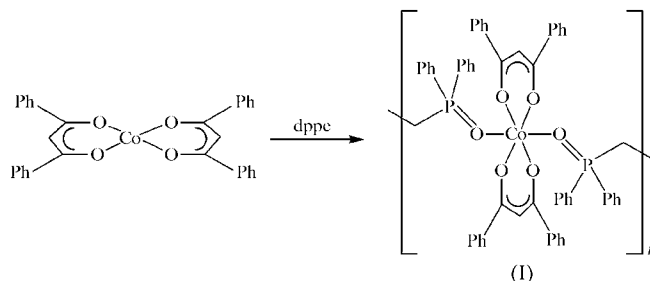
The reaction of bis(1,3-diphenylpropane-1,3-dionato)cobalt(II), [Co(dbm)₂], with bis(diphenylphosphino)ethane (dppe) affords the coordination polymer *catena*-poly[[bis(1,3-diphenylpropane-1,3-dionato- κ^2O,O')cobalt(II)]- μ -ethylenebis(diphenylphosphine oxide)- $\kappa^2O:O'$], *trans*-[Co(C₁₅H₁₁O₂)₂(C₂₆H₂₄O₂P₂)_n], as a result of oxidation of the diphosphine. The Co atom is octahedral, with a CoO₆ coordination sphere, and the chelating dbm ligands adopt a *trans* configuration. The Co atom also lies on a centre of inversion, with a further symmetry centre bisecting the bridging ethylenebis(diphenylphosphine oxide) ligand.

Comment

Adducts of Co(acac^R)₂ (acac is acetyl acetate; R = Me, CF₃, C₆H₅, 'Bu) have been studied for a number of applications, notably as volatile precursors in the preparation of cobalt oxide thin films (Pasko *et al.*, 2004; Barreca *et al.*, 2001), molecular magnets when organic radicals are used as ligands (Ishii *et al.*, 2006; Koreneva *et al.*, 2003), and polymerization and addition reaction catalysts (Sciannamea *et al.*, 2006; Wang *et al.*, 2002). However, of particular relevance to this paper has been their use as oxidation catalysts converting alkanes and alkenes into alcohols (or ketones) and epoxides, respectively (Isayama, 1990; Chavez *et al.*, 1999). We report here the first example of oxidation of a diphosphine by a Co(acac^R)₂ complex.

The addition of bis(diphenylphosphino)ethane (dppe) to a solution of [Co(dbm)₂] (Hdbm is dibenzoylmethane) in tetrahydrofuran and subsequent crystallization yields not the expected monomer, [Co(dbm)₂(dppe)], but rather a coordination polymer, *trans*-[Co(dbm)₂(μ -dppe-O₂)_n], (I), in which the diphosphine has been oxidized. This coordination polymer represents, to the best of our knowledge, the first example of oxidation of a diphosphine by a cobalt β -diketonate complex.

The oxidation of the phosphine is confirmed by IR spectroscopy, which shows a P=O stretch at 1211 cm⁻¹, indicative of a coordinated P=O group, while a C—O stretch at 1596 cm⁻¹ suggests a bidentate coordination mode for the dbm ligand



(Nakamoto, 1986). Although the exact mechanism of oxidation remains unclear, we suggest that the phosphine coordinates in a monodentate fashion *cis* to an oxygen molecule and the metal then mediates oxidation. A similar mechanism has been suggested for the oxidation of aldehydes to carboxylic acids by metal β -diketonate complexes (Nishida *et al.*, 1992).

The crystal structure of (I) is shown in Fig. 1 and relevant bond lengths are detailed in Table 1. The Co^{II} environment is approximately octahedral, with the chelating dbm ligands adopting a *trans* configuration and the remaining coordination sites occupied by the O atoms of bridging dppe-O₂ ligands. The Co^{II} metal atom also lies on a centre of inversion, with a further symmetry centre bisecting the bridging dppe-O₂ ligand. The Co—O bond distances of the dbm ligand are 2.0296 (15) and 2.0232 (15) Å and these are similar to the values observed in [Co(dbm)₂{3-(2-amino-4-methoxypyrimidin-6-yl)pyridine}] and [Co(dbm)₂{1-(2-amino-4-methylpyrimidin-6-yl)-2-(3-methoxypyridin-5-yl)ethyne}] (Aakeröy *et al.*, 2005). In contrast, the Co—O bond distances for the dppe-O₂ ligand are considerably longer [2.1497 (17) Å],

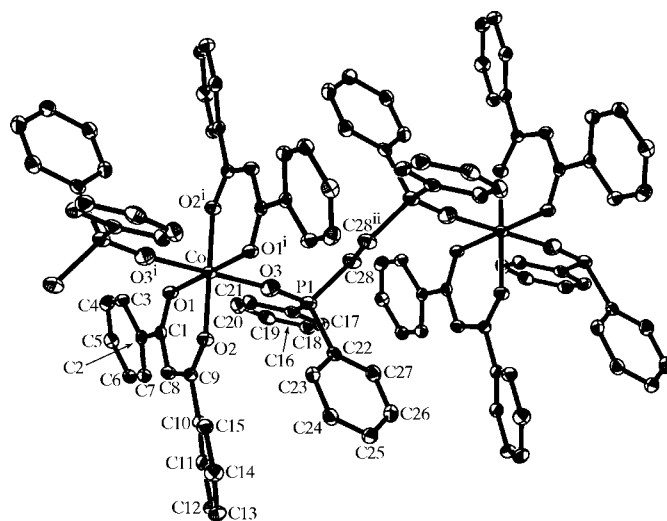


Figure 1
The molecular structure of (I), showing the atom-labelling scheme of the independent part of the structure and the coordination polyhedron. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) 1 - x, 1 - y, 1 - z; (ii) 2 - x, 1 - y, 1 - z.]

reflecting the neutral charge of the ligand. The β -diketonate ligand is essentially planar [maximum deviation = 0.012 (1) Å for atom C8], indicative of complete delocalization of the negative charge over the dbm framework, with the C2–C7 and C10–C15 phenyl rings being rotated by 22.5 (1) and 25.2 (1)°, respectively, out of this plane. The geometry around the P atom is tetrahedral, with bond angles ranging from 102.94 (11) to 112.89 (12)°, while the dppe-O₂ ligand is linearly coordinated to the cobalt metal centre [P1–O3–Co1 = 173.85 (11)°].

A further point of interest is the packing within the crystal structure of (I). There are four intermolecular C–H... π bonds, of which there are two distinct types, one occurring within a single polymer chain (intrachain) and one occurring between adjacent chains (interchain). These interactions are shown in Fig. 2. The intrachain interaction is between atoms H18 and H26 from the two phenyl rings of the PPh₂ group to the phenyl rings of the dbm ligands [C18–H18...Cg3(*x* + 1, *y*, *z*) = 3.503 (3) Å and C26–H26...Cg4(*x* + 1, *y*, *z*) = 3.520 (3) Å; Cg3 and Cg4 are the centroids of rings C2–C7 and C10–C15, respectively]. In total, there are four such intrachain interactions (two sets) between neighbouring Co^{II} metal centres. The interchain interaction is between atoms H13 and H14 of the dbm phenyl ring and two phenyl rings on adjacent P atoms of a single bridging ligand in which the dbm phenyl ring is wedged [C13–H13...Cg5(–1 + *x*, 1 + *y*, *z*) = 3.528 (2) Å and C14–H14...Cg6(1 – *x*, 2 – *y*, 1 – *z*) = 3.669 (3) Å; Cg5 and Cg6 are the centroids of the rings C16–C21 and C22–C27, respectively]. As before, there are four such interchain interactions (two sets) between neighbouring Co^{II} metal centres.

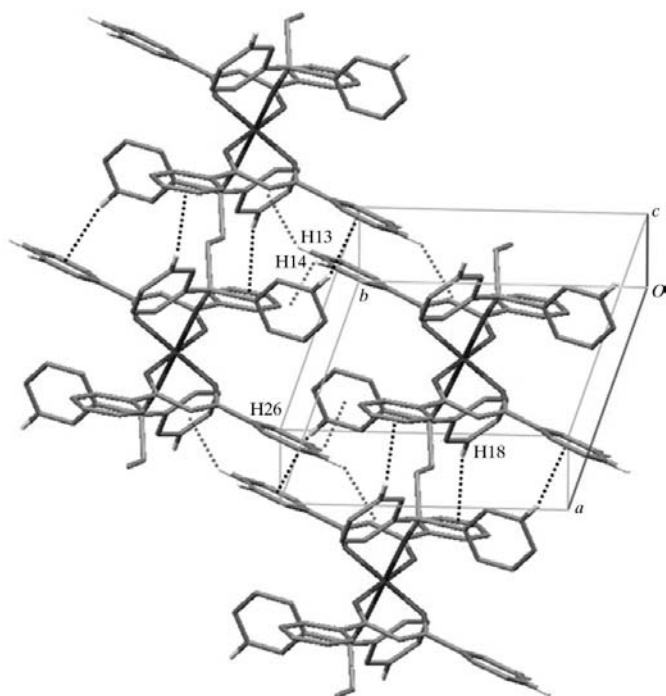


Figure 2
The molecular packing in (I), showing the intrachain (black) and interchain (grey) intermolecular C–H... π interactions. Only selected H atoms and intermolecular interactions are labelled or shown, for clarity.

Experimental

[Co(dbm)₂(H₂O)₂] was prepared according to the literature method of Cotton & Fackler (1960). [Co(dbm)₂(H₂O)₂] (164 mg, 0.30 mmol) was dissolved in tetrahydrofuran (30 ml) with gentle heating to give an orange solution. Bis(diphenylphosphino)ethane (118 mg, 0.30 mmol) was dissolved in dichloromethane (10 ml) and then added to the [Co(dbm)₂(H₂O)₂] solution and the mixture was stirred for 2 h. The solution was then filtered through Celite and layered with *n*-hexane (50 ml) to give yellow crystals of the title complex (yield 179 mg, 64%). Analysis calculated for C₅₆H₄₆CoO₆P₂: C 71.9, H 5.0%; found: C 71.7, H 5.0%. IR (KBr, cm^{–1}): 1596 [νCO (dbm)], 1211 (νP=O).

Crystal data

[Co(C ₁₅ H ₁₁ O ₂) ₂ (C ₂₆ H ₂₄ O ₂ P ₂)]	γ = 71.349 (7)°
<i>M_r</i> = 935.80	<i>V</i> = 1119.9 (3) Å ³
Triclinic, <i>P</i> $\bar{1}$	<i>Z</i> = 1
<i>a</i> = 9.2994 (13) Å	Mo <i>K</i> α radiation
<i>b</i> = 10.9817 (16) Å	μ = 0.51 mm ^{–1}
<i>c</i> = 11.6053 (17) Å	<i>T</i> = 150 (2) K
α = 85.816 (7)°	0.28 × 0.05 × 0.03 mm
β = 88.349 (6)°	

Data collection

Bruker SMART CCD area-detector diffractometer	25062 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2005)	6735 independent reflections
<i>T</i> _{min} = 0.871, <i>T</i> _{max} = 0.985	4402 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.072

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.052	297 parameters
<i>wR</i> (<i>F</i> ²) = 0.128	H-atom parameters constrained
<i>S</i> = 1.02	$\Delta\rho_{\max}$ = 0.78 e Å ^{–3}
6735 reflections	$\Delta\rho_{\min}$ = –1.03 e Å ^{–3}

Table 1

Selected bond lengths (Å).

Co1–O2	2.0234 (14)	P1–C28	1.814 (2)
Co1–O1	2.0299 (15)	O1–C1	1.269 (2)
Co1–O3	2.1495 (17)	O2–C9	1.267 (3)
P1–O3	1.4569 (18)	C1–C8	1.409 (3)
P1–C16	1.800 (2)	C8–C9	1.402 (3)
P1–C22	1.810 (2)		

H atoms were positioned geometrically and refined isotropically using a riding model, with C–H = 0.95–0.98 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: XSCANS (Bruker, 2005); cell refinement: XSCANS; data reduction: SHELXTL (Bruker, 2005); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3025). Services for accessing these data are described at the back of the journal.

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