Synthesis and reactivity of the ruthenium(II) dithiocarbonate complex, [Ru(k^2-S_2C=O)(dppm)$_2$] [dppm = bis(diphenylphosphino)methane]

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Supplementary Information

Cis-[$RuCl_2$(dppm)$_2$] (**1**) has served as a versatile starting point in many studies, such as in the preparation of cumulene complexes.[1] Three structural studies of this compound have been reported previously[2] and, in the course of this work, we have determined the structure of a new crystal modification (**1**·PrOH) formed upon slow diffusion of ethanol (with traces of propanol) into a dichloromethane solution of the complex (Fig. A). In common with the other structures discussed here, the structure of **1** displays a distorted octahedral geometry with *cis*-interligand angles in the range 72.10(3) - 103.39(3)°. The Ru1-Cl1 [2.4775(8) Å] and Ru1-Cl2 [2.4419(8) Å] bond lengths differ considerably despite both being *trans* to phosphorus donors. The Ru-P4 distance [2.3112(8) Å] is also extended slightly compared to Ru1-P1 [2.3032(8) Å]. The same trend is observed in the structure of the bis(methanol) solvate of **1**,[2b] however the other two determinations[2a,c] revealed structures in which the pairs of equatorial Ru-Cl and Ru-P bond lengths are the same. Otherwise, the structure of **1** is unremarkable.

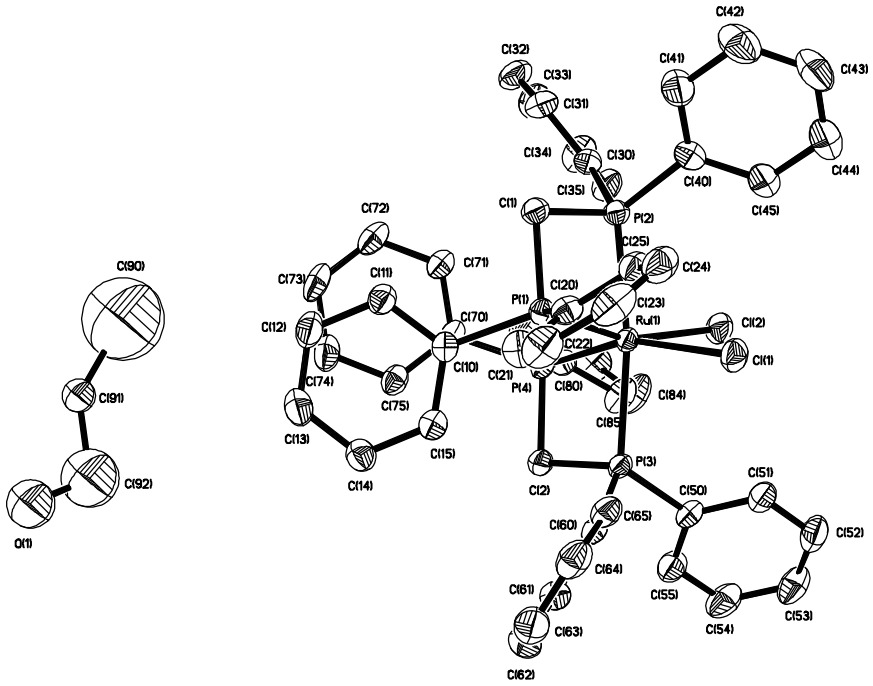

Fig. A. Structure of *cis*-[$RuCl_2(dppm)_2$]·PrOH (**1**) (only Δ-enantiomer shown).

Table A. Crystal data for compound **1**.

	1·PrOH
Chemical Formula	$C_{53}H_{52}Cl_2OP_4Ru$
Fw	1000.80
Crystal system	orthorhombic
Crystal color	yellow
Crystal size (mm)	0.24 x 0.24 x 0.20
Space group	Pbcn
a/Å	30.390(2)
b/Å	13.6805(11)
c/Å	22.4637(18)
α/°	90
β/°	90
γ/°	90
V/Å^3	9339.3(13)
Z	8
Calculated. density (g/cm^3)	1.424
T/K	150(2)
m(Mo-Kα)/mm^{-1}	0.626
F(000)	4128
Reflections collected	78463
Unique reflections (R_{int})	11307 (0.0336)
R_1 (I>2σ(I))	0.0495
wR'_2 (all data)	0.1402

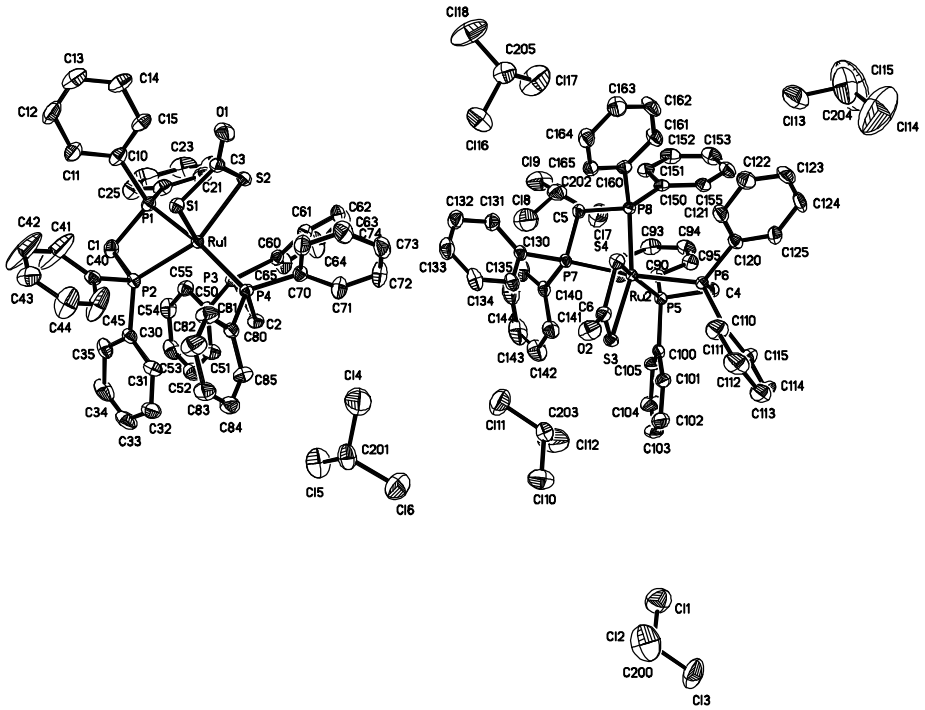

Fig. B. Structure of $[Ru(\kappa^2\text{-}S_2C{=}O)(dppm)_2]\cdot 3CHCl_3$ (**3**).

References

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