$$2Tl_2C_2B_9H_{11} + 4GaCl_3 \rightarrow Tl[Ga(C_2B_9H_{11})_2] + 3TlGaCl_4$$

This equation is analogous to that proposed for the synthesis of the aluminum sandwich from the reaction of an alkylaluminum chloride with $Tl_2[7,8\text{-}C_2B_9H_{11}]$ which produced thallium salts of alkylchloroaluminates. Attempts to synthesize compound **2** by using alkylgallium reagents were unsuccessful. Work continues on the group 13 metallacarboranes including indium and thallium and will be reported elsewhere.

Acknowledgment. The support of this work by the National Science Foundation (Grant CHE-88-06179) is gratefully acknowledged.

Supplementary Material Available: Tables of positional and thermal parameters and interatomic distances and angles (7 pages). Ordering information is given on any current masthead page.

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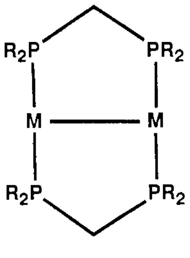
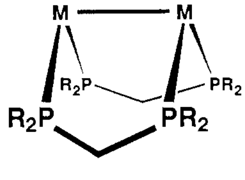
A Ligand-Imposed Cradle Geometry for a Dicobalt Tetracarbonyl Tetratertiary Phosphine Complex

Most transition-metal dimers bridged by two bis(phosphino)-methane-type linkages adopt a geometry in which the two $R_2PCH_2PR_2$ ligands are oriented trans to one another and are commonly referred to as A-frames.[1,2] A few bimetallic complexes have the two $R_2PCH_2PR_2$ ligands in a cisoidal bridging arrangement,[3] which have been referred to as W-frame[4] or cradle[5] geometries. The A-frame geometry has been compared to a flat metal catalyst surface, while the cradle geometry correlates to the more reactive edge or kink of a metal.[6] Unfortunately, aside from working with metal atoms that have tetrahedral coordination geometries which require a cisoidal orientation of two bis(phosphino)methane ligands, methods for the rational preparation of this unusual ligand arrangement are lacking.



trans,trans-$M_2(R_2PCH_2PR_2)_2$
"A-Frame"



cis,cis-$M_2(R_2CH_2PR_2)_2$
"Cradle"

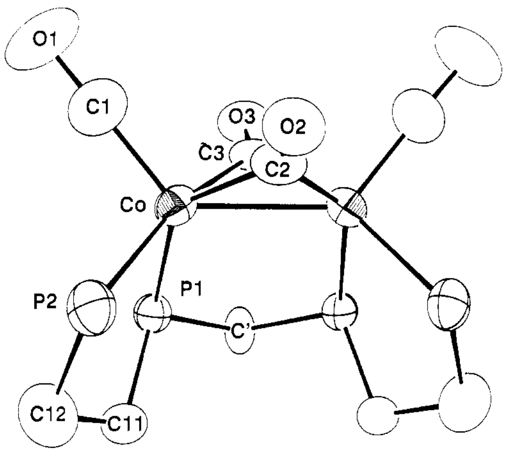


Figure 1. ORTEP plot of *meso*-$Co_2(\mu\text{-}CO)_2(CO)_2$(eLTTP) (**1**), with the phenyl and terminal ethyl groups removed for clarity. The molecule lies on a crystallographic mirror plane that passes through the bridging carbonyl ligands and the central methylene bridge of eLTTP. Ellipsoids are shown at the 33% probability level. Important bond distances (Å) and angles (deg): Co–Co′ = 2.513 (4), Co–P1 = 2.212 (4), Co–P2 = 2.236 (4), Co–C1 = 1.73 (2), Co–C2 = 1.93 (2), Co–C3 = 1.92 (2); P1–Co–P2 = 85.2 (2), P1–Co–Cl = 118.0 (6), P1–Co–C2 = 138.7 (5), P1–Co–C3 = 87.1 (5), P2–Co–C1 = 97.6 (6), P2–Co–C2 = 94.7 (6), P2–Co–C3 = 167.5 (5), C1–Co–C2 = 102.9 (8), C1–Co–C3 = 94.7 (7), C2–Co–C3 = 84.8 (7), P1–C′–P1′ = 111.5 (8).

Our synthesis of the powerful binucleating linear tetrakis(phosphine) ligand $(Et_2PCH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PEt_2)$, eLTTP, which exists as racemic and meso diastereomers, has produced a structurally characterized open-mode Rh(I) bimetallic complex with the racemic ligand.[7] Molecular models of *meso*-eLTTP suggest that for bimetallic complexes with M–M bonds this ligand must adopt a cradle-like arrangement of the four phosphine ligands around the metal centers. Herein, we report the synthesis and structural characterization of the Co(0) dimer *meso*-$Co_2(\mu\text{-}CO)_2(CO)_2$(eLTTP), which has the predicted cradle geometry.

The reaction of $Co_2(\mu\text{-}CO)_2(CO)_2(\text{norbornadiene})_2$[8] with eLTTP in cyclohexane produces a dark orange-brown mixture of the racemic and meso diastereomeric dimer complexes that analyzes as $Co_2(CO)_4$(eLTTP).[9] Slow evaporation of a THF solution crystallizes a diamagnetic orange material that has terminal and bridging ν_{CO} bands at 1925 and 1720 cm^{-1}. These bands are similar to those seen in the dppe-substituted dimer $Co_2(\mu\text{-}CO)_2(CO)_2(\text{dppe})_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$).[10] The ^{31}P NMR spectrum also suggests a symmetrical Co–Co-bonded eLTTP-substituted species with cobalt quadrupole-broadened resonances at 64.5 and 84.4 ppm.

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(1) Cf.: (a) Olmstead, M. M.; Hope, H.; Brenner, L. S.; Balch A. L. *J. Am. Chem. Soc.* **1977**, *99*, 5502. (b) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 6129. (c) Cowie, M.; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 3628. (d) Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Inorg. chem.* **1979**, *18*, 2808. (e) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3637.

(2) For the most recent review article on A-frame complexes see: Kubiak, C. P. *Polyhedron*, submitted for publication.

(3) (a) DeLaet, D. L.; del Rosario, R.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1987**, *109*, 754. (b) Berry, D. H.; Eisenberg, R. *Organometallics* **1987**, *6*, 1796. (c) Cotton, F. A.; Dunbar, K. R.; Verbruggen, M. G. *J. Am. Chem. Soc.* **1987**, *109*, 5498. (d) Wu, J.; Fanwick, P. E.; Kubiak, C. P. *J. Am. Chem. Soc.* **1988**, *110*, 1319.

(4) Karsch, H. H.; Milewski-Mahrla, B.; Besenhard, J. O.; Hofman, P.; Stauffert, P.; Albright, T. A. *Inorg. Chem.* **1986**, *25*, 3811.

(5) DeLaet, D. L.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1986**, *5*, 1807.

(6) Osborn, J. A.; Stanley, G. G.; Bird, P. H. *J. Am. Chem. Soc.* **1988**, *110*, 2117.

(7) Laneman, S. A.; Fronczek, F. R.; Stanley, G. G. *J. Am. Chem. Soc.* **1988**, *110*, 5585.

(8) Winkhaus, G.; Wilkinson, G. *J. Chem. Soc.* **1961**, 602.

(9) All manipulations were carried out under inert-atmosphere conditions with appropriately dried and degassed solvents. A 0.232-g (0.5-mmol) sample of eLTTP[7] in 20 mL of cyclohexane is added to a suspension of 0.207 g (0.5 mmol) of $Co_2(\mu\text{-}CO)_2(CO)_2(\text{norbornadiene})$[8] in 30 mL of cyclohexane and the mixture refluxed for 15 h. During this time the solution changes from an orange slurry to a dark purplish brown solution with a fair amount of dark precipitate. The dark brown precipitate, which is a mixture of *rac*- and *meso*-$Co_2(CO)_4$(eLTTP) diastereomers, is collected and washed with cyclohexane to give an overall yield of ca. 60–70% (ca. 30–35% yield of the meso diastereomer). The solid is very soluble in THF, benzene, and CH_2Cl_2; slightly soluble in acetone, diethyl ether, toluene, acetonitrile, and MeOH; and insoluble in hexane and H_2O. Orange crystals that initially form from the slow evaporation of a THF solution are *meso*-$Co_2(\mu\text{-}CO)_2(CO)_2$(eLTTP). IR (KBr, ν_{CO}): 1925 (s) and 1720 (m) cm^{-1}. ^{31}P NMR (toluene-d_8, ppm, H_3PO_4 reference): 64.46 and 84.35 (P–P couplings are obscured by quadrupolar relaxation from the cobalt atoms). Satisfactory analytical data (C, H) were obtained on recrystallized samples of **1** (Oneida Research Services, Whitesboro, NY).

(10) Behrens, V. H.; Aquila, W. *Z. Anorg. Allg. Chem.* **1967**, *356*, 8.

0020-1669/89/1328-1206$01.50/0

Single-crystal X-ray analysis[11] of the orange crystals that initially form from the slow evaporation of a THF solution confirms the presence of *meso*-eLTTP in a cradle geometry that is bridging and chelating a Co–Co dimer. An ORTEP plot of *meso*-$Co_2(\mu\text{-}CO)_2(CO)_2$(eLTTP) (**1**) is shown in Figure 1, with important bond distances and angles. The molecule lies on a crystallographic mirror plane that passes through the bridging carbonyl ligands and the central methylene group of the eLTTP ligand. The Co–Co bond length of 2.513 (4) Å is typical for a Co–Co single bond.[12] The local coordination geometry about the cobalt atoms (ignoring the Co–Co bond) is a distorted trigonal bipyramid with the equatorial plane defined by P1, C1 and C2. This can be contrasted with the structure of the starting material $Co_2(\mu\text{-}CO)_2(CO)_2$(norbornadiene), which has a square-pyramidal coordination geometry.[12a] The *meso*-eLTTP ligand symmetrically bridges and chelates both cobalt centers with the two five-membered chelate rings eclipsed and oriented syn to one another. Due to the crystallographic mirror plane, all four phosphorus atoms lie in the same plane. The distorted trigonal-bipyramidal coordination environment about the cobalt centers results from the predicted coordination requirements of the eLTTP ligand.

The cradle-like geometry imposed by *meso*-eLTTP about the two cobalt centers is clearly seen in Figure 1. The fusing of a bis(phosphino)methane bridging unit with two syn-oriented five-membered chelate rings creates a binucleating framework that is unique among polydentate ligand systems. Several differences between **1** and traditional cradle $M_2(R_2PCH_2PR_2)_2$ complexes exist, the most obvious being the presence of only a single P–CH_2–P bridge. Another difference is that cisoidal P–M–P angles in cradle complexes range between 98 and 138°, with most values clustered around 109°. In **1**, however, the five-membered chelate rings rigorously enforce the considerable smaller angle of 85°. Perhaps the most important advantage for our complex is the *ligand-enforced* cradle geometry in *meso*-LTTP. Cradle complexes based on $R_2PCH_2PR_2$ ligands can often readily reconvert to A-frame orientations,[3b,3d] while a *meso*-M_2(eLTTP) dimer, on the other hand, *cannot* rearrange this way.

The ability of eLTTP to enforce this new bimetallic cradle coordination geometry in Co–Co-bonded dimers opens a new synthetic route to cradle complexes of other metals. By enforcing this cradle geometry on the dimer, we anticipate the ability to access and extend the unique reactivities observed in other cradle dimer systems.[3a,b,d,5] We are exploring the reactivity of this new eLTTP-based bimetallic complex and will report these studies in the near future.

Acknowledgment. We thank the National Science Foundation (Grant CHE-86-13089) for supporting this research.

Supplementary Material Available: A complete ORTEP plot of **1** excluding H atoms and tables of crystal and structure refinement parameters, positional parameters, full bond distances and angles, and anisotropic thermal parameters (7 pages); a listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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[11] **1** crystallizes in the orthorhombic space group *Pnma*, with the following unit cell parameters: a = 12.086 (4) Å, b = 21.645 (3) Å, c = 14.345 (2) Å, V = 3752 (2) Å^3, Z = 4. Data were collected on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation, and an empirical absorption correction was performed. The structure was solved and refined by using the Enraf-Nonius SDP program set to give final discrepancy indices of R = 0.060 and R_w = 0.066 with a GOF = 1.11 based on 966 unique data with $F_o^2 > 2\sigma(F_o^2)$. A disordered THF solvent lying on a mirror plane was partially modeled as two overlapping, half-occupancy molecules. The data set was quite limited due to the small size of the crystal. Complete crystallographic details are included in the supplementary material.

[12] Cf.: (a) Swaminathan, S.; Lessinger, L. *Cryst. Struct. Commun.* **1978**, *7*, 621. (b) Jones, R. O.; Maslen, E. N. *Z. Kristallogr.* **1966**, *123*, 330. (c) Bird, P. H.; Fraser, A. R.; Hall, D. N. *Inorg. Chem.* **1977**, *16*, 1923.

Articles

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Magnetic Structures and Properties of α-$CrPO_4$ and α-$CrAsO_4$

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The magnetic properties of the isomorphous compounds α-$CrPO_4$ and α-$CrAsO_4$ have been investigated by magnetic susceptibility and low-temperature powder neutron diffraction methods. These materials order antiferromagnetically below 9.1 ± 1.0 and 7.7 ± 0.8 K, respectively, and the magnetic structure of α-$CrPO_4$ at 2 K reveals both ferromagnetic and antiferromagnetic Cr–O–Cr interactions, arising from different linkages of CrO_6 octahedra. The magnetic structure of α-$CrAsO_4$ at 5 K differs from that of α-$CrPO_4$ in that the ferromagnetic interactions are frustrated. This is ascribed to the Cr–O–Cr interactions in α-$CrAsO_4$ being weaker than those in α-$CrPO_4$, relative to competing antiferromagnetic interactions through the XO_4 group, as the relevant Cr–O bonds are longer in the former structure.

Introduction

Transition-metal oxo salts are of interest because of the wide range of magnetic behavior that they exhibit, enabling the magnetic exchange interactions between the cations to be investigated. As part of this effort, the superexchange interactions between spin-only cations such as Fe(III) and Cr(III) through tetrahedral oxo anions have been studied in a number of MXO_4 compounds, as previously reported.[2-5]

β-$CrPO_4$[3] and β-$CrAsO_4$[5] both contain CrO_6 octahedra in infinite, trans edge-sharing chains with XO_4 (X = P, As) tetrahedra linking the chains. Neutron powder diffraction studies have shown that at 5 K the magnetic order along the chains of

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[2] Battle, P. D.; Cheetham, A. K.; Gleitzer, C.; Harrison, W. T. A.; Long, G. J.; Longworth, G. *J. Phys. C.* **1982**, *15*, L919.

[3] Attfield, J. P.; Battle, P. D.; Cheetham, A. K. *J. Solid State Chem.* **1985**, *57*, 357.

[4] Battle, P. D.; Gibb, T. C.; Hu, G.; Munro, D. C.; Attfield, J. P. *J. Solid State Chem.* **1986**, *65*, 343.

[5] Attfield, J. P.; Cheetham, A. K.; Johnson, D. C.; Torardi, C. C. *Inorg. Chem.* **1987**, *26*, 3379.

0020-1669/89/1328-1207$01.50/0