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A binuclear rhodium(I) complex with two tetraphosphine ligands at 100 K

Clinton Hunt Jr,[a] Brent D. Nelson,[b] Elisa G. Harmon,[c] Frank R. Fronczek,[a]* Steven F. Watkins,[a] Damon R. Billodeaux[a] and George G. Stanley[a]

[a]Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA, [b]Department of Chemistry, Mesa State College, Grand Junction, CO 81502, USA, and [c]Department of Chemistry, University of Oklahoma, Norman, OK 73019, USA
Correspondence e-mail: fronz@chxray1.chem.lsu.edu

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Bis(μ-3,11-diethyl-6,8-diphenyl-3,6,8,11-tetraphosphatridecane-κ^4P^3,P^6:P^8,P^{11})dirhodium(I) bis(tetrafluoroborate), $[Rh_2(C_{25}H_{40}P_4)_2](BF_4)_2$, is a bimetallic complex containing two binucleating tetra-tertiary phosphine ligands. The distance between the metal centers is 5.4555 (11) Å, with no metal–metal bond. The Rh—P bond distances range from 2.2483 (14) to 2.3295 (14) Å. The geometry about the Rh^I atoms is tetrahedrally distorted square planar and the dihedral angle between the two coordination planes is 66.28 (5)°.

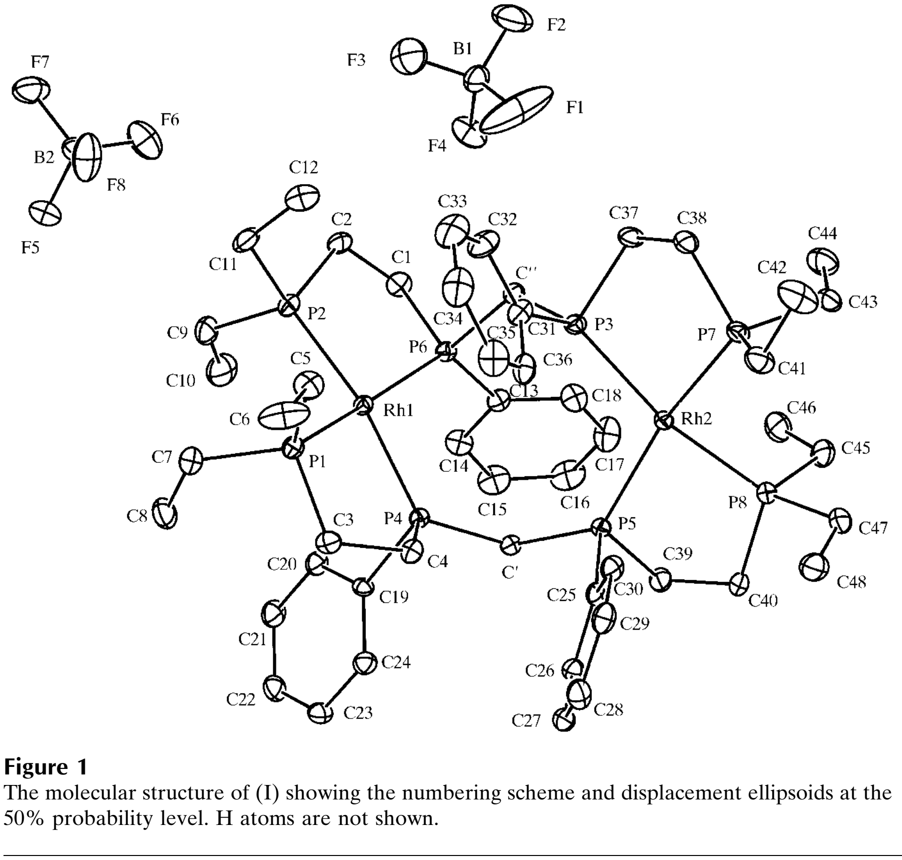
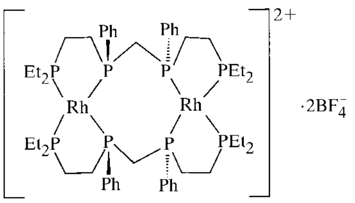


Figure 1
The molecular structure of (I) showing the numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are not shown.

Comment

The most frequently used homogeneous catalytic process for producing aldehydes is hydroformylation. Current production exceeds twelve billion pounds annually. The capability for two or more metal centers to work together in heterogeneous reactions is common and has been well documented (George, 1995; Somorjai, 1992; Walther, 1989). However, the ability for two or more metal centers to cooperate in homogeneous catalytic processes is less well documented or understood (Adams *et al.*, 1994; Tsubouchi & Bruce, 1994; Zhang *et al.*, 1988; Collman *et al.*, 1983; Don & Richman, 1992; Hidai *et al.*, 1986; Suss-Fink & Herrmann, 1985). A focus of our research involves the use of a novel catalyst which contains two rhodium centers with a binucleating tetra-tertiary phosphine ligand (Broussard *et al.*, 1993). One objective of this project is to improve the characterization of our novel hydroformylation catalyst, $[Rh_2(nbd)_2(\text{racemic et,ph-P4})](BF_4)_2$ [nbd = norbornadiene; et,ph-P4 = $(Et_2PCH_2CH_2)(Ph)$;$PCH_2P(Ph)(CH_2CH_2PEt_2)$], by using $^{31}P\{^1H\}$ NMR to monitor possible side reactions which might occur during catalytic cycles. The reported complex was the first resulting from attempted synthesis of possible by-products. The ligand (et,ph-P4) exists as *meso* and racemic diastereomers, leading to a number of possible isomers for complexes. We report here the structure of the $[Rh_2(R,R\text{-et,ph-P4 and }S,S\text{-et,ph-P4})](BF_4)_2$ isomer complexed with rhodium, bis(μ-3,11-diethyl-6,8-diphenyl-3,6,8,11-tetraphosphatridecane-κ^4-P^3,P^6:P^8,P^{11})dirhodium(I) bis(tetrafluoroborate), (I).



(I)

As shown in Fig. 1, we have successfully synthesized an analog of our novel hydroformylation catalyst containing two et,ph-P4 ligands rather than only one. This new compound, (I), contains two Rh atoms and two binucleating tetra-tertiary phosphine ligands, *R,R*-et,ph-P4 and *S,S*-et,ph-P4, with two BF_4^- anions. The intramolecular distance between the two

Rh^{I} centers is 5.4555 (11) Å, precluding any direct metal–metal bonding.

The geometry about the Rh atoms is tetrahedrally distorted square planar. A least-squares plane was calculated for each RhP$_4$ group and these results showed that each Rh atom is essentially in the plane, with deviations of 0.0014 (6) for Rh1 and −0.0069 (6) Å for Rh2. The four P atoms attached to Rh1 are out of the plane, with deviations of 0.2702 (7) Å for P1, 0.2686 (7) Å for P6, −0.2626 (7) Å for P2 and −0.2694 (7) Å for P4. Similar results were obtained for the P atoms attached to Rh2, with deviations of 0.2801 (7) Å for P5, 0.3104 (8) Å for P7, −0.2749 (7) Å for P3 and −0.3169 (8) Å for P8. The distortion about each Rh center is presumably due to the five-membered chelate rings. The two coordination planes form a dihedral angle of 66.28 (5)°.

We have also obtained preliminary results for a poor crystal of [Rh$_2$(*meso*-et,ph-P4)$_2$](PF$_6$)$_2$. It is orthorhombic, space group *Fdd*2, with *a* = 29.316 (6), *b* = 29.937 (6) and *c* = 28.099 (6) Å and *Z* = 16 at 100 K. The distance between the Rh^{I} atoms is somewhat shorter at 4.771 (2) Å. Efforts to produce better crystals are underway.

Spectroscopic data (^{31}P{^{1}H} NMR) of the reported compound do not correspond with those of unidentified by-products observed in the catalytic cycle. The crystal structure reported here, along with elemental analysis, has allowed us to identify compound (I) unambiguously and to rule it out as a possible by-product of the catalytic cycle.

Experimental

All procedures, unless otherwise stated, were conducted under a nitrogen atmosphere using standard Schlenk line or glove-box techniques. [Rh(nbd)$_2$]BF$_4$ was prepared according to a modification (Broussard, 1993) of published literature procedures (Schrock & Osborn, 1971; Green *et al.*, 1971), while racemic et,ph-P4 was prepared according to published procedures (Broussard *et al.*, 1993). [Rh$_2$(et,ph-P4)$_2$](BF$_4$)$_2$ was prepared by adding [Rh(nbd)$_2$]BF$_4$ (0.157 g, 0.420 mmol) and dichloromethane (12 ml) to a 100 ml Schlenk flask. To a second 100 ml Schlenk flask were added racemic et,ph-P4 (0.199 g, 0.430 mmol) and dichloromethane (12 ml). The rhodium solution was added dropwise, *via* a cannula, to the ligand solution. After stirring overnight (17 h), the solvent was removed under vacuum and the residue brought into a glove-box. The residue was redissolved in a minimum volume of dichloromethane and washed with an equal volume of anhydrous diethyl ether, yielding a dark-red oil and an opaque yellow suspension. The yellow opaque layer was decanted into a 60 ml frit and filtered, yielding yellow solids. Crystals of (I) were obtained from the yellow solids by slow evaporation from a mixture of dichloromethane and methanol.

Crystal data

[Rh$_2$(C$_{25}$H$_{40}$P$_4$)$_2$](BF$_4$)$_2$
M_r = 1308.3
Monoclinic, *Cc*
a = 15.651 (3) Å
b = 16.048 (3) Å
c = 24.022 (5) Å
β = 108.18 (3)°
V = 5732 (2) Å^3
Z = 4
D_x = 1.516 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.7–20.8°
μ = 0.86 mm^{-1}
T = 100 K
Prism, yellow
0.48 × 0.25 × 0.23 mm

Table 1
Selected geometric parameters (Å, °).

Rh1—P6	2.2483 (14)	Rh2—P7	2.3174 (14)
Rh1—P4	2.2670 (13)	Rh2—P3	2.3295 (14)
Rh1—P1	2.3003 (15)	P3—C″	1.856 (5)
Rh1—P2	2.3039 (15)	P4—C′	1.840 (5)
Rh2—P8	2.2973 (15)	P5—C′	1.843 (5)
Rh2—P5	2.3018 (13)	P6—C″	1.840 (5)
P6—Rh1—P4	98.05 (5)	P8—Rh2—P7	91.37 (5)
P6—Rh1—P1	166.04 (5)	P5—Rh2—P7	163.27 (5)
P4—Rh1—P1	83.24 (5)	P8—Rh2—P3	163.57 (5)
P6—Rh1—P2	85.16 (6)	P5—Rh2—P3	106.31 (5)
P4—Rh1—P2	166.88 (5)	P7—Rh2—P3	83.50 (5)
P1—Rh1—P2	96.74 (6)	P6—C″—P3	125.0 (3)
P8—Rh2—P5	82.64 (5)	P4—C′—P5	124.1 (3)

Data collection

Enraf–Nonius CAD-4 diffractometer (with Oxford Cryosystems Cryostream cooler)
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.640, $T_{\max}$ = 0.821
8531 measured reflections
8531 independent reflections
7681 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 30°
$h = -20 \rightarrow 22$
$k = 0 \rightarrow 22$
$l = -33 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.095
S = 1.04
8531 reflections
631 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.05
$\Delta\rho_{\max}$ = 0.73 e Å^{-3}
$\Delta\rho_{\min}$ = −1.03 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.02 (2)

Systematic absences were consistent with *Cc* and *C*2/*c*; however, no inversion centers are present in the structure. The absolute structure was determined by refinement of the Flack parameter (Flack, 1983). The deepest hole (−1.03 e Å^{-3}) was 0.84 Å from Rh2. H atoms were placed in calculated positions with assumed C—H bond distances of 0.93 Å and with $U_{\rm iso} = 1.2U_{\rm eq}$ of the attached C atom, and thereafter treated as riding. A torsional parameter for each methyl group was refined. Refinement of the inverted structure led to a Flack parameter of 1.02 (4).

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*4 *EXPRESS* (Enraf–Nonius, 1994); data reduction: *XCAD*4 (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996; Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1112). Services for accessing these data are described at the back of the journal.

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