

Preliminary communication

PHOSPHORUS-31 NMR SPECTRUM AND MOLECULAR STRUCTURE OF A DIRHODIUM COMPLEX THAT CONTAINS A RHODIUM—RHODIUM BOND, BRIDGING DIPHENYLPHOSPHIDO LIGANDS, AND A TETRAHEDRAL RHODIUM

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Summary

The syntheses, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, and a structure of "mixed" 1,5-cyclooctadienebis(tertiary phosphine)dirhodium complexes are described. These unusual complexes possess a rhodium—rhodium bond, bridging diphenylphosphido groups, and two different stereochemistries around the rhodium atoms. One rhodium is tetrahedral and surrounded by four phosphorus atoms and the other rhodium (bonded to COD) is nearly planar.

In contrast to the stepwise replacement of 1,5-cyclooctadiene (COD) from $[(\text{COD})\text{Rh}(\mu\text{-PPh}_2)]_2$ by chelating diphosphine ligands [1], reactions with monodentate phosphines (viz. PPh_3 , PMePh_2 , and PEt_3) give products of a very different nature, as indicated by $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Since all three monodentate phosphine ligands function similarly, the details of only the triphenylphosphine case are presented below for illustration.

Addition of 2.0 equivalents of PPh_3 (a 1/1 Rh/ PPh_3 ratio) to a THF solution of $[(\text{COD})\text{Rh}(\mu\text{-PPh}_2)]_2$ at room temperature caused the color of the solution to change from green to brown. In addition, the ^{31}P NMR peaks of $[(\text{COD})\text{Rh}(\mu\text{-PPh}_2)]_2$ disappear, being replaced by resonances attributed to $[(\text{COD})\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{PPh}_3)_2]$. Further addition of PPh_3 leads only to the appearance of an additional ^{31}P resonance due to free PPh_3 ; surprisingly, the second COD molecule is not displaced by monodentate phosphines under these or more forcing conditions, e.g., refluxing the THF solution for 1 h. In solu-

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tions containing a 2.0/1 ratio of PPh_3 and $[(\text{COD})\text{Rh}(\mu\text{-PPh}_2)]_2$, the ^{31}P spectra show a doublet of doublets at 216 ppm and a doublet at 51 ppm. The magnitudes of the spin-spin splitting are unique to each resonance multiplet and no phosphorus-phosphorus coupling is observed. The large downfield chemical shift of the organophosphido resonance is evidence that these phosphorus atoms are bridging across a metal-metal (i.e., Rh-Rh) bond. The lack of phosphino-phosphido coupling precludes a planar geometry about that rhodium atom since a *trans*-P-P coupling is expected to be in the range 250–400 Hz [2,3]. Also, one of the Rh-P coupling constants is significantly larger than usually observed in planar rhodium(I) complexes, which implies a greater amount of "s" orbital character in the Rh-P bond of the resulting PPh_3 complex. The infrared and proton NMR spectra show that one COD molecule remains bonded to rhodium. Thus, we postulated [1] on the basis of the total spectroscopic evidence in solution that the PR_3 ligands formed di-rhodium-bis(diphenylphosphido)-bridged complexes that contain a Rh-Rh bond and a pseudo-tetrahedral rhodium bonded to the monodentate phosphines [4].

The observed chemical behavior and unusual NMR, and particularly the prospects for a tetrahedral rhodium in a "mixed" olefin-phosphine dinuclear complex of the type $[(\text{R}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})]$ prompted an X-ray structure determination of the PEt_3 derivative.

Suitable crystals of $[(\text{Et}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})]$ were obtained from a THF/acetone mixture and the X-ray data were collected on a Syntex P1 four-circle diffractometer at $T = -78^\circ\text{C}$: Space group $P2_1/c$; a 18.618(1), b

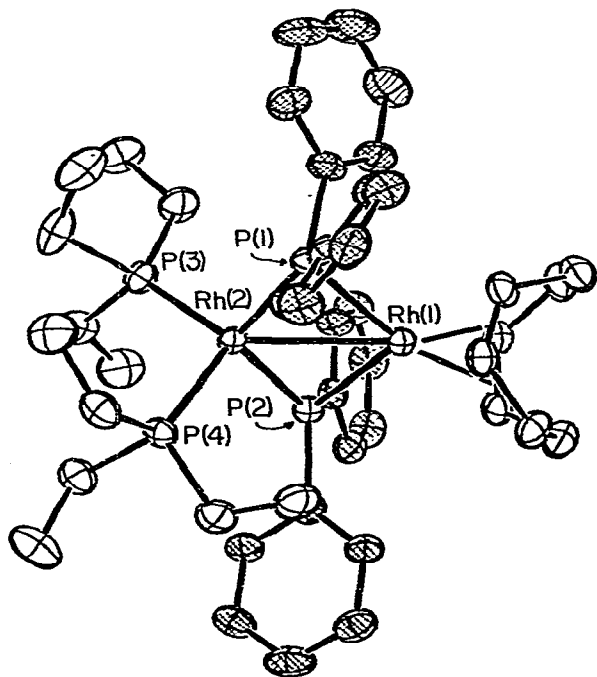


Fig. 1. The ORTEP representation of the molecular structure of $(\text{Et}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$, excluding the hydrogen atoms. The phenyl groups on the bridging diphenylphosphido groups are shaded for clarity.

11.923(1), c 19.199(2) Å, β 92.04(1)°, λ (Mo- $K\alpha$, graphite crystal monochromator) 0.71069 Å, ρ calc = 1.43 for $Z = 4$; 9595 independent reflections were measured (of which 5861 have $I \geq 3\sigma$ above background) and used in the structure solution and refinement to date. Absorption corrections have not been made, but we expect no substantial changes in the results reported here. The structure was solved by heavy-atom Patterson methods and refined by conventional Fourier and least-squares techniques to a current $R(F)$ factor of 7.3% [5]. Thermal parameters for all non-hydrogen atoms were refined anisotropically. The molecular structure of $[(Et_3P)_2Rh(\mu-PPh_2)_2Rh(COD)]$ is shown in Fig. 1. A schematic representation (with selected bond distances) of the coordination spheres about the rhodium atoms is shown in Fig. 2. The bond angles around the Rh_2P_2 core are given in Table 1. The crystal structure consists of discrete neutral rhodium complexes which each contain two bridging diphenylphosphido groups, two triethylphosphine ligands and a bidentate 1,5-cyclooctadiene ligand. The M_2P_2 core configuration is almost planar; the angle between the planes formed by atoms Rh(1), P(1), Rh(2), and atoms Rh(2), P(2), Rh(1) is 169.3(1)°.

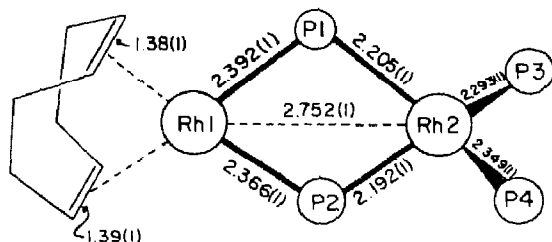


Fig. 2. A schematic drawing of the coordination spheres around the rhodium atoms with the important bond distances.

TABLE 1

SELECTED ANGLES WITHIN THE Rh_2P_2 CORE OF $[(Et_3P)_2Rh(\mu-PPh_2)_2Rh(COD)]$

Angle	Degrees ^a
P(2)—Rh(1)—P(1)	99.60(4)
P(2)—Rh(2)—P(1)	111.48(4)
P(3)—Rh(2)—P(1)	106.92(4)
P(4)—Rh(2)—P(1)	116.78(4)
P(3)—Rh(2)—P(2)	111.27(4)
P(4)—Rh(2)—P(2)	101.91(4)
P(4)—Rh(2)—P(3)	108.46(4)
Rh(2)—P(2)—Rh(1)	73.42(4)
Rh(2)—P(2)—Rh(1)	74.16(4)
C(1)—Rh(1)—P(2)	86.3(1)
C(3)—Rh(1)—P(2)	96.3(1)
C(4)—Rh(1)—P(1)	95.8(1)
C(5)—Rh(1)—P(1)	87.1(1)

^a Standard deviations in the least significant digits are given in parentheses here and throughout this paper.

If one excludes the stereochemical effect of the M—M bond, the geometry of Rh(2) is remarkable in being tetrahedral, with an average P—Rh(2)—P angle of 109.5°. This compares with the average L—I—L angle of 109.2° in $[Ir(\mu-PPh_2)(CO)(PPh_3)]_2$ [6,7]. The geometry of the center is also unusual be-

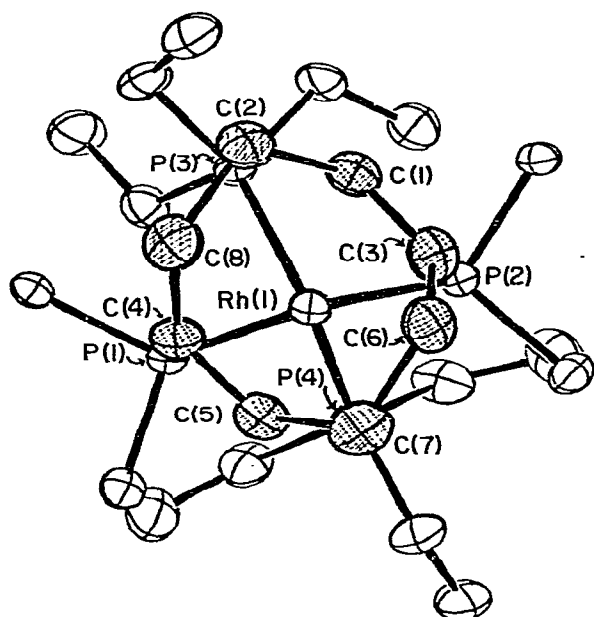


Fig. 3. An ORTEP representation of $(\text{Et}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$ viewed directly down the Rh—Rh bond axis; the carbon atoms of the COD ligand are shaded for clarity.

cause of the orientation of the cyclooctadiene ligand, which is shown in Fig. 3; the perspective is directly down the Rh—Rh bond axis, looking through the cyclooctadiene ring. The coordinated double bonds of the COD ligand do not lie in the same plane as the metal and the diphenylphosphido ligands, nor do they lie in a plane perpendicular to the P—M—P plane. Thus, the coordination geometry of Rh(1), while neither tetrahedral nor planar, is much closer to planar [8].

Another unusual feature of the $[(\text{Et}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})]$ structure is the marked asymmetry of the diphenylphosphido bridges. The Rh(2)—P(1) and Rh(2)—P(2) distances are significantly shorter than the Rh(1)—P(1) and Rh(1)—P(2) distances, i.e., by an average of 0.18 Å. The different Rh—P bond distances are reminiscent of asymmetric CO bridges. The rhodium—rhodium distance, 2.752(2) Å, is well within the range for a bonding interaction [9–12]. Additional evidence for Rh—Rh bonding comes from the M—P—M angles around the diphenylphosphido phosphorus atoms, which average 73.8°; these angles are comparable to other M—P—M angles in the complexes that are acknowledged to possess M—M bonds [13]. The large downfield shift (approximately 290 ppm from comparable complexes of chelating diphosphine ligands) of the ^{31}P resonance of the organophosphido phosphorus nuclei gives further credence to a M—M bonding formulation. Although several reasonable formalistic ways of counting electrons in this complex can be envisaged [14], we favor the following interpretation of the bonding based on the structural result. Counting the diphenylphosphido groups as neutral three-electron donors, the nearly planar rhodium(1) is a d^8 ion (i.e., Rh(+I)), whereas the tetrahedral rhodium(2) can be viewed as a d^{10} ion (i.e., Rh(–I)); thus Rh(2) is an 18-electron case and Rh(1) has 16 electrons. The markedly different Rh—P bond

TABLE 2

THE ^{31}P $\{^1\text{H}\}$ NMR SPECTRAL PARAMETERS FOR $[(\text{R}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})]$ COMPLEXES

Compound	Phosphino resonance		Organophosphido resonance		
	δ (ppm)	$^1J(\text{Rh-P})$ (Hz)	δ (ppm)	$^1J(\text{Rh-P})$ (Hz)	$^2J(\text{P-P})$ (Hz)
$(\text{Ph}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$	51.0	190	216	94 and 166	~ 0
$(\text{MePh}_2\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$	24.1	190	219	95 and 168	~ 0
$(\text{Et}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})$	26.0	182	217	97 and 169	~ 0

distances to the two rhodium atoms differ so much that one is tempted to view the $\mu\text{-PPh}_2$ linkages as arising from a $[\text{Rh}(\text{PPh}_2)_2(\text{PEt}_3)_2]^-$ anion functioning as a chelating ligand to a $[(\text{COD})\text{Rh}]^+$ cation. Thus, Rh(1) would be electron deficient and Rh(2) electron rich. However, if the interaction between the two metals takes the form of a donor bond from Rh(2) to Rh(1) with a bond order of one, this anomaly is removed. The Rh(1)–Rh(2) distance (2.752(2) Å) compares well with other single-bond Rh–Rh distances that have been reported recently, e.g., 2.66(1) Å in $[\text{Rh}(\text{CO})\text{RhCl}_2\{(\text{PhO})_2\text{-PN}(\text{Et})\text{P}(\text{OPh})_2\}_2] \cdot \text{CHCl}_3$ [9], 2.75(ave.) Å in $\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_3(\text{PPh}_3)_2$ [10], 2.775(1) Å in $[\text{Ru}_3\text{Rh}_2(\text{CO})_{13}(\text{PEt}_3)(\mu_4\text{-PPh})]$ [11], and 2.766(1) Å in $[\text{Rh}_3(\mu\text{-PPh}_2)_3(\text{CO})_5]$ [12].

The structural features determined by X-ray crystallography for $[(\text{Et}_3\text{P})_2\text{Rh}(\mu\text{-PPh}_2)_2\text{Rh}(\text{COD})]$ are completely consistent with the structural features proposed from an analysis of the ^{31}P NMR spectra of the compound [1]; this result demonstrates the tremendous utility of ^{31}P NMR for indicating the presence of metal–metal bonds and for structural characterization of transition metal complexes that contain bridging organophosphido groups. It is particularly interesting that the unsymmetrical nature of the Rh–P bond distances in the diphenylphosphido bridge is reflected in the different magnitudes of these $^1J(\text{Rh-P})$ values (Table 2).

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- 14 Other electron-counting possibilities for this dirhodium complex would be: (1) one rhodium atom as 0 and the other as +II oxidation states, PPh₂ groups as negative, 4e⁻ donors, and a dative Rh—Rh bond; (2) both rhodium atoms as Rh⁰ with the PPh₂ groups as neutral, 3e⁻ donors and the Rh—Rh bond formation via coupling between the two d⁸ metals; and (3) both rhodium atoms could be assigned formal oxidation states of +I with the PPh₂ groups as 4e⁻ negatively charged ligands, and a dative M—M bond from Rh(2) to Rh(1).