Contribution from the Departments of Chemistry, The Ohio State University, Columbus, Ohio 43210,
and Northwestern University, Evanston, Illinois 60201

Tridentate Tertiary Phosphine–Olefin Ligands. 1. Syntheses of (3-(Diphenylphosphino)propyl)(3-butenyl)phenylphosphine, $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH{=}CH_2$ (ppol), and Some Rh(I) Complexes of ppol and the X-ray Structure of RhCl(ppol)

KWOLIANG DAVID TAU,[1a] DEVON W. MEEK,*[1a] THEOPHILUS SORRELL,[1b] and JAMES A. IBERS*[1b]

Received March 23, 1978

The synthesis of (3-(diphenylphosphino)propyl)(3-butenyl)phenylphosphine, $Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH{=}CH_2$, where Ph = phenyl and where the molecule is abbreviated ppol, is described. This molecule is designed as a tridentate ligand, with cis phosphines and an olefinic portion capable of ligating. The syntheses of several Rh(I) complexes of ppol are described, including RhCl(ppol), $[Rh(ppol)(PPh_3)][AsF_6]$, $[Rh(CO)(ppol)(PPh_3)][AsF_6]$, and $[Rh(CO)_2(ppol)][AsF_6]$. These complexes have been characterized by chemical and spectroscopic means. In addition, the crystal structure of RhCl(ppol) has been determined from counter diffraction data collected at room temperature. The material crystallizes with four molecules in space group C_{2h}^5-$P2_1/n$ of the monoclinic system in a cell of dimensions $a = 10.474$ (5) Å, $b = 16.752$ (10) Å, $c = 13.487$ (7) Å, and $\beta = 95.68$ (1)°. Full-matrix least-squares refinement of the 148 variables has led to a conventional R index of 0.047 for the 3569 observations. The coordination of the cis P atoms, the olefinic portion of ppol, and the Cl ligand about the central Rh atom is essentially square planar, with the olefinic portion nearly perpendicular to the basal plane. Considerable weakening of the olefin coordination as a result of the trans influence of the phosphine group is observed.

Introduction

Since Osborn et al.[2] first reported the rapid catalytic homogeneous hydrogenation of olefins by $RhCl(PPh_3)_3$, extensive synthetic and mechanistic studies have been performed on this and related complexes.[3] More recently, complexes of the type $[Rh(diene)L_n]^+A^-$ (L = a tertiary phosphine, arsine, or phosphite, $n = 2$ or 3; or L_n = a chelating diphosphine or diarsine; $A^- = ClO_4^-$ or PF_6^-)[4] have been used very successfully as hydrogenation catalysts, particularly for catalytic asymmetric syntheses.[5] The effectiveness of the latter complexes may result either from dissociation of the diene in solution or from oxidative addition of H_2 to rhodium, hydride transfer to the diene, and reductive elimination of the alkane. Either of these possible routes would give a vacant coordination site around the metal that could subsequently lead to activation of hydrogen and reduction of unsaturated substrates.

Unsaturated tertiary phosphines can react with transition metals in a variety of ways. For example, *o*-styryldiphenylphosphine has been shown to undergo (1) intramolecular hydride addition to form stable σ-alkyl complexes,[6,7] (2) protonation and reduction of the vinyl group to an ethyl group,[8] and (3) coupling of two vinyl groups to give a tetradentate olefin–diphosphine ligand.[9] In order to obtain more stereochemical and stoichiometric control over such reactions, we have designed and synthesized mixed ligands L which incorporate the advantages of the basicity and stability of a chelating cis diphosphine and at the same time contain an olefin group capable of ligation.[10] Complexes of the type RhClL and $PtClL^+$, where L is a properly designed mixed phosphine–olefin ligand, would be expected as a result of the imposition of cis phosphine geometry to have the olefin trans to a phosphorus atom in a planar arrangement about the metal. No complexes with this geometry have been reported previously. An advantage of the Pt(II) and Rh(I) planar systems is that detailed structural and bonding information can be obtained from M–P and P–P coupling constants through the use of ^{31}P NMR methods.

This paper reports the synthesis of one such mixed phosphine–olefin ligand, namely, $Ph_2PCH_2CH_2CH_2P(Ph)$-$CH_2CH_2CH{=}CH_2$ (ppol), and the synthesis of several Rh(I)–ppol complexes and their characterization, including an X-ray structure determination of RhCl(ppol).

Experimental Section

Reagents and Chemicals. 4-Chloro-1-butene was purchased from Chemical Samples Co. and was used as obtained. The preparation of 1-(diphenylphosphino)-3-(phenylphosphino)propane will be published later. Benzene, diethyl ether, and hexane were dried over freshly pressed sodium wire or distilled from sodium. Dichloromethane was dried over Linde 4 Å molecular sieves. Rhodium trichloride trihydrate ($RhCl_3 \cdot 3H_2O$) was purchased from Engelhard Industries, Newark, N.J. All other chemicals were reagent grade quality and were used without further preparation.

Instrumentation and Physical Measurements. Infrared spectra were measured on a Perkin-Elmer Model 337 grating spectrometer from 400 to 4000 cm^{-1} as Nujol mulls between polished potassium bromide plates or as pressed potassium bromide pellets. A polystyrene film was used for calibration.

Proton magnetic resonance spectra were collected on a Varian A60-A, Varian HA-100, or Bruker HX-90 spectrometer, generally with Me_4Si as an internal reference. Fourier-mode, proton-noise-decoupled phosphorus-31 NMR spectra were collected on a Bruker HX-90 spectrometer operating at 36.43 MHz with a Bruker B-NC12 data system. The samples were run in 10-mm tubes with deuterated solvents (10–20% of the sample volume) providing an internal deuterium lock and an insert tube of phosphoric acid (85%) providing an external reference. Positive chemical shifts are measured downfield from H_3PO_4.

Elemental analyses were performed by M-H-W Laboratories, Phoenix, Ariz.

General Experimental Procedures. Standard techniques for the manipulation of air-sensitive compounds[11] (e.g., manipulation of Schlenk-type vessels and transfer of air-sensitive solutions with stainless steel needles) were used for all of the chemical experiments. High-purity nitrogen was used to provide an inert atmosphere. Solvents were deaerated by purging them with nitrogen or by the freeze–thaw method.

Synthesis of the Ligand (3-(Diphenylphosphino)propyl)(3-butenyl)phenylphosphine (ppol). To a benzene solution (100 mL) containing 1-(diphenylphosphino)-3-(phenylphosphino)propane, $Ph_2PCH_2CH_2CH_2P(Ph)H$[10] (13.2 g, 0.039 mol), was slowly added 30 mL of a 1.6 M hexane solution of *n*-butyllithium (0.048 mol). A red color developed immediately and the solution was stirred at room temperature for 2.5 h and then at 55–65 °C (oil bath temperature) for 1 h; a pale yellow solid formed during the reaction. After the mixture was cooled to room temperature, 4-chloro-1-butene (7 mL in 20 mL of benzene) was added dropwise. The resulting mixture was stirred at room temperature for 1 h and then refluxed at 80–90 °C (oil bath temperature) for 2.5 h. Another 5 mL of 4-chloro-1-butene was added and refluxing was continued for 2.5 h. The reaction mixture was cooled to room temperature and stirred overnight. The resultant pale yellow solution was then treated sequentially with absolute ethanol (20 mL) and distilled water (50 mL) to destroy any excess *n*-butyllithium or phosphide. The two layers were separated, the water layer was washed with benzene (50 mL), and the combined organic portions were dried over anhydrous sodium sulfate. The solvent

0020-1669/78/1317-3454$01.00/0

was removed at 0.20–0.33 Torr and 72–75 °C (oil bath temperature) to give a transparent orange-yellow oil: yield 14.1 g (92%); mass spectrum showing the parent ion M^+ at *m/e* 390; IR (neat) C═C stretching frequency at 1640 cm^{-1}; ^1H NMR ($CDCl_3$) τ 2.45–3.35 (m, phenyl), 4.1–4.6 (m, –CH═), 4.9–5.35 (m, $═CH_2$), 7.65–9.40 (m, methylene); ^{31}P NMR ($C_6H_6 + C_6D_6$) –18.2 (δ_{PPh_2}), –27.1 ppm (δ_{PPh}).

Syntheses of the Rh(I)–ppol Complexes. (1) RhCl(ppol). To a solution of $[RhCl(COD)]_2$ (0.7532 g) (COD = 1,5-cyclooctadiene) in absolute ethanol (40 mL) was added a solution of ppol (9 mL; 0.3585 M in benzene); the resultant solution was refluxed for 2 h. After it had cooled to room temperature, the solution was filtered; orange crystals started to precipitate when the wall of the flask was scratched with a spatula. These crystals were collected on the frit of a Schlenk filter and then washed with hexane (35 mL) and dried in vacuo; yield 0.9696 g. Anal. Calcd for $C_{25}H_{28}ClP_2Rh$: C, 56.78; H, 5.35; Cl, 6.70. Found: C, 56.68; H, 5.47; Cl, 6.93.

(2) $[Rh(ppol)(PPh_3)][AsF_6]$. To a suspension of $RhCl(COD)(PPh_3)$ (0.3538 g) in absolute ethanol (35 mL) was added $NaAsF_6$ (0.1469 g) and 2.2 mL of the ppol solution (0.3585 M in benzene); this mixture was refluxed for 2 h. The resultant yellow solid was collected on the frit of a Schlenk filter and then extracted with dichloromethane. The dichloromethane solution was evaporated to ca. 10 mL and then treated sequentially with absolute ethanol (5 mL) and diethyl ether (35 mL). The orange-yellow microcrystals that separated were collected and washed with diethyl ether (30 mL) and dried in vacuo; yield 0.3584 g. Anal. Calcd for $C_{43}H_{43}AsF_6P_3Rh$: C, 54.67; H, 4.60; P, 9.84. Found: C, 54.44; H, 4.73; P, 10.06.

(3) $[Rh(CO)(ppol)(PPh_3)][AsF_6]$. A solution of $[Rh(ppol)(PPh_3)][AsF_6]$ (0.364 g) in dichloromethane (20 mL) was treated with CO gas bubbles for 0.5 h. The original red solution changed to greenish yellow within 5 min after exposure to CO. After adding diethyl ether (20 mL) to precipitate the product, we set the resulting mixture in a freezer overnight. The resultant yellow crystalline solid was collected, washed with diethyl ether, and dried in vacuo. Anal. Calcd for $C_{44}H_{43}AsF_6OP_3Rh$: C, 54.33; H, 4.47; F, 11.72; P, 9.55. Found: C, 54.11; H, 4.67; F, 11.55; P, 9.29.

(4) $[Rh(CO)_2(ppol)][AsF_6]$. A suspension of RhCl(ppol) (0.4291 g) in absolute ethanol (25 mL) was treated with CO gas for 15 min to yield a greenish yellow solution. This solution was treated with $NaAsF_6$ (0.2191 g), and a light yellow solid precipitated. The resultant mixture turned to an orange solution on being refluxed for 20 min under a CO atmosphere. The CO gas bubbles were maintained for 0.5 h while the solution was cooled to room temperature. A light greenish yellow precipitate formed when this solution was treated with 30 mL of diethyl ether. The solid was collected, washed with distilled water (35 mL) and diethyl ether (40 mL) under CO gas, and then dried with a stream containing a mixture of CO and N_2 gases. Anal. Calcd for $C_{26}H_{28}AsF_6O_2P_2Rh$: C, 43.92; H, 3.83; F, 15.44. Found: C, 43.75; H, 4.01; F, 15.23.

Crystallographic Study of RhCl(ppol). Preliminary Weissenberg and precession photographs of a suitable crystal of the orange RhCl(ppol) complex showed monoclinic symmetry and systematic absences (0*k*0, *k* odd; *h*0*l*, *h* + *l* odd) consistent with space group C_{2h}^5-$P2_1/n$ (an alternative setting of $P2_1/c$). On the basis of the diffractometer setting angles of 11 manually centered reflections (20 < 2θ (Mo $K\alpha_1$) < 30°) the cell constants of Table I were obtained. Data were collected at room temperature on a Picker FACS-I diffractometer using methods general in this laboratory.[12] Important details of data collection are presented in Table I.

The structure was solved in a facile manner, using procedures and computer programs detailed before.[13] The positions of the rhodium and one of the phosphorus atoms were located on an origin-removed, sharpened Patterson function. All remaining nonhydrogen atoms were found in a subsequent difference Fourier map. Ultimately, the positions of all the hydrogen atoms were determined from a difference map. The positions of hydrogen atoms, except those of the olefinic part of the ligand, were idealized (C–H = 0.95 Å and $B_H = B_C + 1.0$ Å^2), and their contributions to F_c were fixed in subsequent calculations. The three hydrogen atoms on the olefinic carbon atoms were refined isotropically. The phenyl rings were refined as rigid groups. Full-matrix least-squares refinement, minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, of the 148 variables converged to values of R and R_w of 0.047 and 0.056, respectively, for the 3569 observations. The error in an observation of unit weight is 1.50 electrons. The maximum electron density on the final difference Fourier map, of 1.1 e/Å^3, occurs in the vicinity of the carbon atoms of the phenyl rings. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices shows no unexpected trends.

Table I. Crystal Data and Data Collection Procedures for RhCl(ppol)

formula	$C_{25}H_{28}ClP_2Rh$
fw	528.81 amu
space group	C_{2h}^5-$P2_1/n$
a	10.474 (5) Å
b	16.752 (10) Å
c	13.487 (7) Å
β	95.68 (1)°
V	2354.8 Å^3
Z	4
ρ_c	1.491 g/cm^3
ρ_o	1.46 (1) g/cm^3
temp	21 °C
cryst shape	rectangular prism with major bounding faces {010}, {101}, and and {$10\bar{1}$}; approximate dimensions 0.16 × 0.16 × 0.51 mm
cryst vol	0.0118 mm^3
radiation	Mo Kα (λ(Mo $K\alpha_1$) 0.70930 Å) monochromatized from mosaic graphite
linear abs coeff	9.71 cm^{-1}
transmission factors	0.845–0.876
detector aperture	3.9 mm wide × 4.5 mm high, 32 cm from cryst
takeoff angle	2.7°
scan speed	2.0° in 2θ/min
2θ limits	3.5–53.0°
bkgd counts	10 s at each end of scan with rescan option
scan range	0.8° below $K\alpha_1$ to 0.8° above $K\alpha_2$
data collected	5281
p	0.04
unique data for $F_o^2 > 3\sigma(F_o^2)$	3569

The final atomic parameters and their errors for all nongroup atoms are given in Table II. Parameters for the group atoms are found in Table III. The idealized positions of the hydrogen atoms are given in Table IV.[13] Table V lists the observed and calculated structure amplitudes (×10) for those reflections used in the refinement.[13]

Results and Discussion

The potentially tridentate ligand $Ph_2P(CH_2)_3P(Ph)(CH_2)_2CH═CH_2$ reacts readily with $[RhCl(COD)]_2$ in refluxing ethanol to give orange crystals whose infrared spectra show a bonded C═C stretching frequency at 1510 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of the product shows two doublets of doublets at 53.7 and 5.3 ppm downfield from H_3PO_4 (Table VI). The phosphorus resonance at δ 53.7 is assigned to the P nucleus from the >PPh group on the basis that the >PPh group is part of a 5.5-membered chelate ring[14] which usually displays a large downfield chemical shift from the resonance position of the free ligand.[15] The proton NMR spectrum (in C_6D_6) shows the following resonances: τ 1.8–3.2 (m, phenyl), 5.0–5.2 (m, –CH═), 6.5–6.6, 6.7–6.8 (two m, $═CH_2$), 7.7–9.7 (m, methylene). The elemental analysis of the product is consistent with the formula RhCl(ppol) and the spectral data suggest to us that ppol functions as a tridentate ligand. The X-ray analysis (see below) has confirmed this interpretation.

For $[Rh(ppol)(PPh_3)][AsF_6]$ the C═C stretching frequency could not be identified definitively, probably because of overlap with the numerous phenyl absorptions in the 1500–1600-cm^{-1} region where a bonded C═C group would absorb. The ^1H NMR spectrum of the complex in CD_2Cl_2 has resonances at τ 2.2–4.0 (m, phenyl), 4.7–5.1 (b, –CH═), 5.9–6.3 and 6.5–6.9 (two broad peaks, $═CH_2$), and 7.1–9.1, and this indicates that the olefin group remains bonded to the rhodium atom. The $^{31}P\{^1H\}$ NMR spectrum also is consistent with a square-planar, four-coordinate $[Rh(ppol)PPh_3]^+$ cation, as the observed

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $RhCl(Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH{=}CH_2)$

ATOM	X[A]	Y	Z	B11[B] OR B,A²	B22	B33	B12	B13	B23
RH	0.111141(36)	0.229437(26)	0.055283(28)	65.13(40)	35.59(19)	38.28(24)	-6.95(22)	15.03(22)	-2.56(18)
CL	0.02937(15)	0.30164(10)	-0.09007(10)	130.9(18)	52.02(74)	49.29(85)	-1.86(94)	8.52(97)	9.50(64)
P(1)	0.20153(12)	0.162692(90)	0.182880(94)	59.3(12)	40.71(63)	39.53(75)	-2.95(70)	9.72(74)	-5.53(56)
P(2)	-0.06046(13)	0.260019(89)	0.14128(10)	66.8(13)	38.73(63)	44.27(77)	-2.24(71)	13.40(80)	-1.97(57)
C(1)	0.24588(54)	0.17318(41)	-0.03908(45)	83.5(58)	48.6(30)	51.9(37)	-7.2(34)	20.1(38)	-10.4(28)
C(2)	0.30876(55)	0.23532(43)	0.01186(45)	85.1(60)	48.0(30)	57.2(36)	-10.6(36)	32.3(38)	-1.6(30)
C(3)	0.40582(52)	0.22395(38)	0.09940(47)	71.0(54)	51.1(31)	78.3(44)	-16.0(34)	25.8(40)	-19.3(31)
C(4)	0.37364(46)	0.15638(39)	0.16583(40)	61.6(50)	57.4(32)	57.2(36)	0.3(32)	9.5(34)	-15.3(28)
C(5)	0.19145(49)	0.20422(36)	0.30722(36)	79.2(53)	52.2(29)	38.2(29)	-7.1(31)	4.4(31)	-9.3(23)
C(6)	0.05331(53)	0.21030(37)	0.33355(37)	97.1(59)	52.9(31)	38.3(30)	-5.2(33)	11.0(33)	-7.9(24)
C(7)	-0.02732(52)	0.27428(37)	0.27623(39)	85.1(54)	55.9(31)	45.0(31)	6.5(34)	18.5(33)	-10.4(26)
H(1)C(1)	0.2691(41)	0.1154(30)	-0.0168(32)	4.1(10)					
H(2)C(1)	0.2023(56)	0.1838(38)	-0.0992(45)	4.5(17)					
H(1)C(2)	0.2987(55)	0.2833(35)	-0.0217(43)	3.1(16)					

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

Table III. Derived Parameters for the Rigid-Group Atoms of $RhCl(Ph_2PCH_2CH_2CH_2P(Ph)CH_2CH_2CH{=}CH_2)$

ATOM	X	Y	Z	B,A²	ATOM	X	Y	Z	B,A²
C(11)	0.15692(34)	0.05828(17)	0.19897(27)	3.50(10)	C(24)	-0.28664(42)	0.49290(23)	0.06763(35)	6.65(17)
C(12)	0.05668(32)	0.02623(20)	0.13547(24)	4.12(11)	C(25)	-0.35300(27)	0.42363(29)	0.08832(36)	7.22(18)
C(13)	0.02395(32)	-0.05408(22)	0.14338(27)	4.91(13)	C(26)	-0.28612(36)	0.35269(23)	0.10972(32)	5.74(14)
C(14)	0.09145(39)	-0.10233(17)	0.21479(30)	5.03(13)	C(31)	-0.17971(31)	0.18072(19)	0.12332(26)	3.58(10)
C(15)	0.19169(38)	-0.07028(22)	0.27829(27)	5.96(15)	C(32)	-0.23419(36)	0.14251(23)	0.20082(19)	4.47(12)
C(16)	0.22442(31)	0.01003(24)	0.27038(26)	5.24(13)	C(33)	-0.31753(38)	0.07834(23)	0.18039(25)	5.33(13)
C(21)	-0.15287(36)	0.35103(20)	0.11042(29)	3.94(10)	C(34)	-0.34639(36)	0.05237(21)	0.08246(30)	5.45(14)
C(22)	-0.08651(27)	0.42030(26)	0.08973(31)	5.46(14)	C(35)	-0.29191(38)	0.09059(23)	0.00496(21)	5.24(13)
C(23)	-0.15339(42)	0.49123(21)	0.06833(33)	6.43(16)	C(36)	-0.20857(35)	0.15476(22)	0.02539(22)	4.27(11)

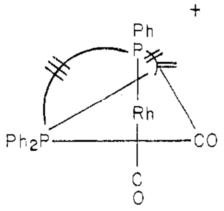
RIGID GROUP PARAMETERS

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
RING1	0.12418(23)	-0.02203(16)	0.20688(18)	-1.7247(28)	-2.3924(25)	-3.0034(30)
RING2	-0.21975(27)	0.42196(18)	0.08903(19)	2.0693(25)	-2.9430(27)	2.9806(26)
RING3	-0.26305(23)	0.11655(15)	0.10289(19)	-0.6972(26)	2.7543(20)	1.6056(26)

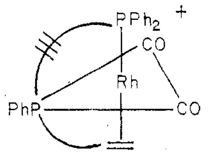
[A] X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

spectrum is the ABM portion of an ABMX pattern (Figure 1). Specific assignment of the A and B nuclei (i.e., to $-PPh_2$ and PPh_3) was solved by comparing the present data with the results obtained by Blum.[16] She found that all of a large number of rhodium(I) complexes of $PhP(CH_2CH_2CH_2PPh_2)_2$ have P–P coupling constants $^2J_{PPh_2-PPh}$ in the range 47–58 Hz. For the $[Rh(ppol)(PPh_3)][AsF_6]$ complex it is reasonable to assume that the $^2J_{PPh_2-PPh}$ value occurs in the same range; the ^{31}P NMR parameters for this complex are assigned on this basis and they are given in Table VI.

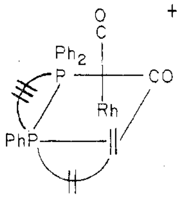
A suspension of RhCl(ppol) in ethanol reacts with carbon monoxide very rapidly to give a clear, greenish yellow solution; a carbonyl-containing compound can be precipitated by adding diethyl ether while maintaining a carbon monoxide atmosphere. However, when N_2 is bubbled through the greenish yellow solution, the CO is lost and RhCl(ppol) is recovered. The $^{31}P\{^1H\}$ NMR spectrum of the greenish yellow solution is consistent with a five-coordinate dicarbonyl complex. In fact, if the solution is treated with $NaAsF_6$, the dicarbonyl complex $[Rh(CO)_2(ppol)][AsF_6]$ is obtained. Two strong CO infrared bands occur at 2105 and 2060 cm⁻¹; these bands are similar to those observed (2100 and 2068 cm⁻¹ in CH_2Cl_2) in $[Rh(CO)_2(bdpps)][BF_4]$ (bdpps = *o*-$Ph_2PC_6H_4CH{=}CHC_6H_4PPh_2$-*o*)[17], which is presumed to have a trigonal-bipyramidal structure with the two CO groups in equatorial positions. However, note that $[Rh(CO)_2(bdpps)][BF_4]$ is colorless, whereas $[Rh(CO)_2(ppol)][AsF_6]$ is yellow. As with $[Rh(ppol)(PPh_3)][AsF_6]$, no C=C stretching frequency (Nujol mull) was observed for $[Rh(CO)_2(ppol)][AsF_6]$, which suggests that the $-CH{=}CH_2$ moiety remains bonded. The $^{31}P\{^1H\}$ NMR spectrum of $[Rh(CO)_2(ppol)][AsF_6]$ (in CD_3NO_2) shows two nonequivalent phosphorus signals (Table VI). As reasoned above, the resonance at 37.3 ppm is assigned to the phosphorus nucleus of the >PPh group. The spectral data are consistent with one of the following three structures for $[Rh(CO)_2(ppol)]^+$:



1



2



3

The complex $[Rh(CO)(ppol)(PPh_3)[AsF_6]$ is prepared by bubbling carbon monoxide through a dichloromethane solution of $[Rh(ppol)(PPh_3)][AsF_6]$. The lower carbonyl stretching frequency (1985 cm⁻¹ in Nujol) compared with those in $[Rh(CO)_2(ppol)][AsF_6]$ can be attributed to the more basic rhodium atom. The $^{31}P\{^1H\}$ NMR spectrum of $[Rh(CO)(ppol)(PPh_3)][AsF_6]$, which resembles that of $[Rh(ppol)(PPh_3)][AsF_6]$, is the ABM portion of an ABMX pattern.

Table VI. ^{31}P NMR Data[a] for the ppol[b] Ligand and the RhCl(ppol) Complexes

compd	solvent	δ_{P_1}, ppm	δ_{P_2}, ppm	δ_{P_3},[c] ppm	$^1J_{Rh-P_1}$, Hz	$^1J_{Rh-P_2}$, Hz	$^1J_{Rh-P_3}$, Hz	$^2J_{P_1-P_2}$, Hz	$^2J_{P_1-P_3}$, Hz	$^2J_{P_2-P_3}$, Hz	Δ_{P_1},[d] ppm	Δ_{P_2},[e] ppm	Δ_{P_3},[f] ppm
ppol	$C_6H_6 + C_6D_6$	−27.1	−18.2					~0					
RhCl(ppol)	$C_6H_6 + C_6D_6$	53.7	5.3		156	153		53			80.8	23.5	
[Rh(ppol)(PPh$_3$)][AsF$_6$]	$CH_2Cl_2 + CD_2Cl_2$	29.1	7.3	34.3	122.5	146	120	49	302	33.8	56.2	25.5	40.1
[Rh(CO)$_2$(ppol)][AsF$_6$]	$CH_3NO_2 + CD_3NO_2$	37.3	−1.7		88	115		47			64.4	16.5	

[a] Accuracy and reproducibility on the NMR data give a standard deviation on the chemical shifts and coupling constants of ±0.05 ppm and ±0.5 Hz, respectively. Positive chemical shifts are downfield from the standard. [b] ppol = $Ph_2P^2CH_2CH_2CH_2P^1(Ph)CH_2CH_2CH{=}CH_2$; the numbers superscripted to the P atoms are labels to distinguish the different P nuclei. [c] P_3 is the phosphorus nucleus PPh_3. [d] $\Delta_{P_1} = \delta_{\text{coord } P_1} - \delta_{\text{free } P_1}$. [e] $\Delta_{P_2} = \delta_{\text{coord } P_2} - \delta_{\text{free } P_2}$. [f] $\Delta_{P_3} = \delta_{\text{coord PPh}_3} - \delta_{\text{free PPh}_3}$.

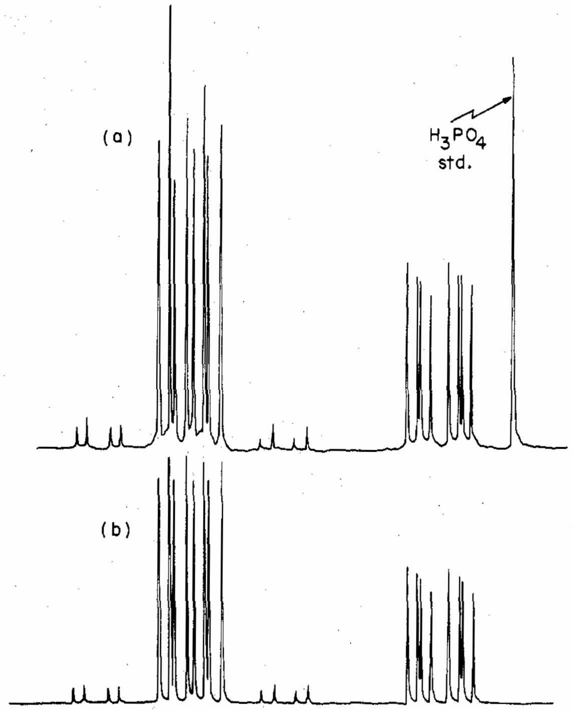
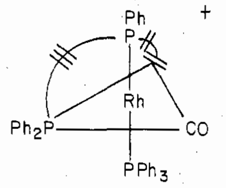


Figure 1. (a) Fourier-transform, proton-decoupled phosphorus-31 NMR spectrum of [Rh(ppol)(PPh$_3$)][AsF$_6$] in CH_2Cl_2 solution. (b) Computer simulation of the ^{31}P NMR spectrum of [Rh(ppol)(PPh$_3$)][AsF$_6$], using the refined parameters for the complex given in Table VI.

Here, however, the value of $^2J_{AB}/\Delta\delta_{AB}$ is sufficiently large that the two outer lines for each of the four AB spectra are too weak to be observed. Only two definitive NMR parameters can be obtained from this spectrum, i.e., $\delta_{PPh_2} = 7.3$ ppm and $^1J_{Rh-PPh_2} = 113$ Hz. The possible structures for this complex are **4** and **5**.



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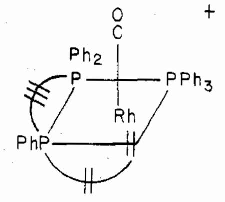

5

In order to provide support for these structural assignments and to establish the tridentate, chelating nature of the ppol ligand, the crystal structure of RhCl(ppol) has been determined. A perspective view of the molecular structure, along with the numbering scheme used, is shown in Figure 2. The inner coordination sphere, with some relevant distances and angles, is shown in Figure 3. Additional distances and angles are presented in Table VII. A stereoview of the unit cell, showing the discrete, well-separated molecules, is given in Figure 4.

The coordination about the Rh atom consists of cis phosphorus atoms, the chloro ligand, and the olefin portion of the ppol ligand in essentially a square-planar geometry. Pertinent least-squares planes are presented in Table VIII. Note that the Rh, Cl, P(1), P(2) plane is a very good one and that this plane makes an angle of 81.2 (3)° with the Rh, C(1), C(2) plane: the olefin portion of the ppol ligand is nearly perpendicular to the basal plane about the Rh atom. In this orientation, the olefin portion exhibits a sliding along the C═C bond such that atom C(1) is 0.59 Å below and atom C(2) is 0.77 Å above the Rh, Cl, P(1), P(2) basal plane. Consistent with this sliding is the 7° difference in the P(2)–Rh–C(1) and

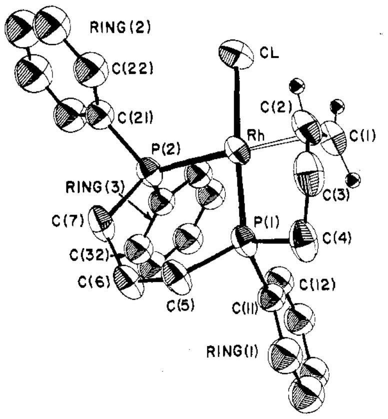

Figure 2. Overall geometry and labeling scheme of RhCl(ppol). The 50% vibrational ellipsoids are shown, except for the olefinic protons which have been made artificially small.

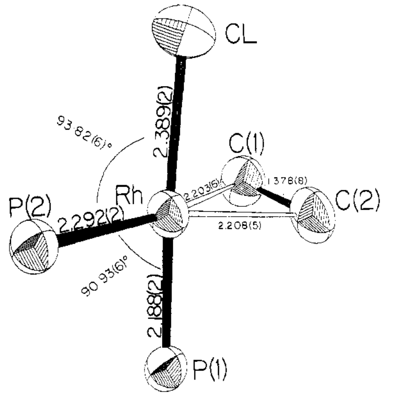

Figure 3. Inner coordination sphere of RhCl(ppol). The 50% vibrational ellipsoids are shown.

P(2)–Rh–C(2) angles. On the basis of the normalcy of bond distances and angles within the 5.5 Rh–ppol ring system (Table VII), this sliding of the olefin is apparently not a steric effect. The effect has been observed in a number of other olefin complexes.[18]

Figure 5 sketches the inner coordination spheres of $RhCl(PPh_3)_3$[19] (A), $RhCl(C_2F_4)(PPh_3)_2$[20] (B), and the present RhCl(ppol) complex (C). There are several interesting comparisons to be made. The essential equivalence of the Rh–Cl distance in these three complexes suggests that the trans influence of a P atom is nearly the same as that of a C_2F_4 group. It is known[21] that the Pt–Cl bond is sensitive to the nature of the X group in *trans*-$PtClX(PPh_3)_2$ complexes. The trans influence of the olefin group is somewhat less than that of a P atom, as judged by the Rh–P(1) distances in A and C. The mutual trans influence of phosphine groups is apparent in the lengthened Rh–P(1) and Rh–P(3) distances in A and B compared with the Rh–P(2) distances trans to Cl in A and C. Note, however, that the C_2F_4 group in B has brought about a lengthening of the cis Rh–P distances in B compared with those in A. The fact that the Rh–C distances in B are so much shorter than those in C may be ascribed in part to the greater electron-withdrawing abilities of the activated C_2F_4 ligand. Yet in Table IX we present some data on well-defined C_2H_4 complexes of Rh(I) and Pt(II). These data lead us to a number of conclusions. The trans influence of the phosphine on the olefin is apparent if one compares the Pt–C distances in $K[PtCl_3(C_2H_4)]$ with those in the present complex. Whereas the amount of electron transfer into the olefin is very small in both of these complexes, as judged by the modest increase of the C=C distance over that of 1.337 (2) Å in C_2H_4[22] and by the near-planarity of the olefin as judged by the angles α and β,[18] the Rh–C distances in the present

Table VII. Distances (Å) and Angles (deg) in RhCl(ppol)

	Distances		
Rh–C(1)	2.203 (6)	P(2)–C(31)	1.823 (4)
Rh–C(2)	2.208 (5)	C(1)–C(2)	1.378 (8)
Rh–P(1)	2.188 (2)	C(2)–C(3)	1.492 (9)
Rh–P(2)	2.291 (2)	C(3)–C(4)	1.502 (8)
Rh–Cl	2.389 (2)	C(5)–C(6)	1.527 (7)
P(1)–C(4)	1.843 (5)	C(6)–C(7)	1.527 (8)
P(1)–C(5)	1.828 (5)	H1C(1)–C(1)	1.03 (5)
P(1)–C(11)	1.829 (3)	H2C(1)–C(1)	0.91 (6)
P(2)–C(7)	1.834 (6)	H1C(2)–C(2)	0.92 (6)
P(2)–C(21)	1.832 (4)		
	Angles		
P(1)–Rh–C(1)	89.1 (2)	H2C(1)–C(1)–H1C(1)	122 (5)
P(1)–Rh–C(2)	83.5 (2)	H2C(1)–C(1)–C(2)	118 (4)
P(1)–Rh–P(2)	90.9 (1)	H1C(1)–C(1)–C(2)	118 (3)
P(1)–Rh–Cl	175.1 (1)	H1C(2)–C(2)–C(1)	113 (4)
C(1)–Rh–C(2)	36.4 (2)	H1C(2)–C(2)–C(3)	122 (4)
C(1)–Rh–P(2)	165.3 (2)	C(1)–C(2)–C(3)	123.5 (7)
C(1)–Rh–Cl	86.6 (2)	C(2)–C(3)–C(4)	113.1 (5)
C(2)–Rh–P(2)	158.0 (2)	C(3)–C(4)–P(1)	108.1 (4)
C(2)–Rh–Cl	91.7 (2)	C(4)–P(1)–Rh	106.5 (2)
P(2)–Rh–Cl	93.8 (1)	C(11)–P(1)–Rh	119.1 (1)
C(4)–P(1)–C(5)	106.4 (2)	Rh–P(1)–C(5)	117.9 (2)
C(4)–P(1)–C(11)	103.0 (2)	C(6)–C(5)–P(1)	112.4 (4)
C(5)–P(1)–C(11)	102.5 (2)	C(7)–C(6)–C(5)	114.7 (5)
C(7)–P(2)–C(21)	99.3 (2)	C(6)–C(7)–P(2)	116.9 (4)
C(7)–P(2)–C(31)	106.7 (2)	C(7)–P(2)–Rh	116.8 (2)
C(21)–P(2)–C(31)	103.7 (2)	C(21)–P(2)–Rh	119.6 (1)
		C(31)–P(2)–Rh	109.3 (1)
	Conformation Angles		
Rh–P(2)–C(7)–C(6)	−48.6 (5)	C(5)–P(1)–Rh–P(2)	−40.1 (2)
P(2)–C(7)–C(6)–C(5)	65.4 (6)	P(1)–Rh–P(2)–C(7)	33.3 (2)
C(7)–C(6)–C(5)–P(1)	−70.7 (6)	Rh–P(1)–C(4)–C(3)	23.3 (4)
C(6)–C(5)–P(1)–Rh	62.7 (5)		
	Vector-Plane Angles		
C(1)–C(2) H1C(1)–C(1)–H2C(1)	104 (5)	C(1)–C(2) H1C(2)–C(2)–C(3)	78 (4)

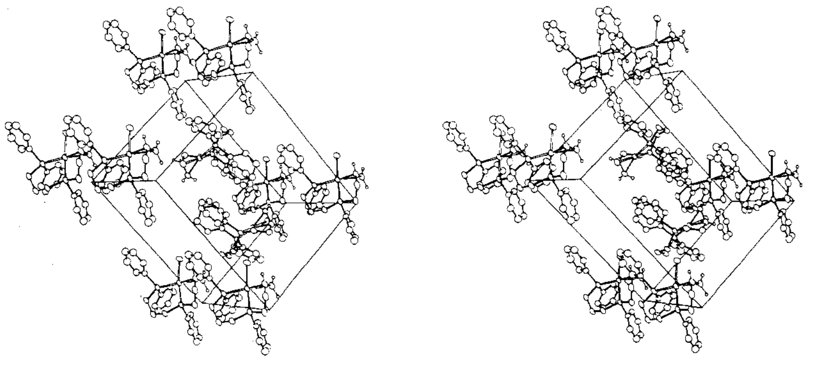

Figure 4. Stereoview of the unit cell of RhCl(ppol). The only hydrogen atoms shown are the olefinic ones. The 30% vibrational ellipsoids are shown. The view is roughly perpendicular to the 111 plane.

Table VIII

Best-Weighted Least-Squares Planes

Plane Equation: $Ax + By + Cz = D$

plane no.	A	B	C	D	atoms
1	−2.445	10.434	−9.710	1.585	Rh, C(1), C(2)
2	4.545	13.873	4.183	3.922	Rh, Cl, P(1), P(2)
3	4.530	13.940	4.082	3.927	Rh, P(1), P(2)
4	7.725	−4.803	−9.190	1.146	C(2), C(3), H(1)C(2)
5	−9.527	−1.247	6.697	−2.821	H(1)C(1), H(2)C(1), C(1)
6	7.479	−4.013	−9.781	−1.006	ring 1
7	−0.020	3.918	13.051	2.819	ring 2
8	8.040	−10.580	0.435	−3.303	ring 3

Deviations of Atoms from the Least-Squares Planes (in Å)[a]

(a) Plane (2)

Rh	−0.003 (1)	P(2)	0.001 (1)
Cl	0.019 (2)	C(1)	−0.566*
P(1)	0.016 (2)	C(2)	0.800*

(b) Plane (3)

C(1)	−0.559*	C(5)	1.041*
C(2)	0.800*	C(6)	0.607*
C(3)	1.439*	C(7)	0.900*
C(4)	0.622*		

(c) Plane (6)

C(3)	2.171*	C(6)	−2.701*
C(4)	1.551*	C(7)	−3.000*

(d) Plane (7)

C(3)	−0.653*	C(6)	2.357*
C(4)	−0.050*	C(7)	1.861*

(e) Plane (8)

C(3)	4.240*	C(6)	1.652*
C(4)	4.725*	C(7)	0.302*

Interplanar Angles (deg)

plane x	plane y	θ	plane x	plane y	θ
1	2	81.4	3	4	97.6
1	3	80.9	3	5	108.3
1	4	83.9	3	6	96.8
1	5	98.0	3	7	57.9
1	6	79.9	3	8	99.0
1	7	125.5	4	5	154.1
1	8	130.8	4	6	4.0
2	3	0.5	4	7	131.5
2	4	97.7	4	8	47.1
2	5	108.2	5	6	154.2
2	6	97.0	5	7	67.6
2	7	57.5	5	8	127.4
2	8	98.7	6	7	134.2
			6	8	51.1
			7	8	92.5

[a] Atoms with asterisked values were given zero weight in the calculation of the least-squares plane.

complex are very long indeed, and in fact are the longest of any of this type in an extensive tabulation[18] of such distances.

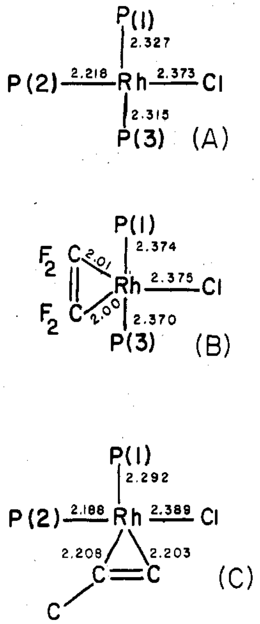

Figure 5. Comparative sketches of the inner coordination spheres of $RhCl(PPh_3)_3$ (A), $RhCl(C_2F_4)(PPh_3)_2$ (B), and RhCl(ppol) (C). Errors on the Rh–P distances in all three cases are approximately 0.002 Å. The olefins are nearly perpendicular to the Rh, Cl, P planes.

Table IX. Comparative Distances (Å) and Angles (deg) in Some C_2H_4 Complexes of Rh(I) and Pt(II)

compd	C–C	M–C	α^a	β^a	θ^a
$K[PtCl_3(C_2H_4)]^b$	1.354 (15)	2.139 (10)	34.7	72.7	87.4
$Rh(acac)(C_2H_4)(C_2F_4)^c$	1.42 (2)	2.19 (1)			87.8
$Rh(acac)(C_2H_4)_2{}^c$	1.41 (3)	2.14 (2)			87.4
$RhCl(ppol)^d$	1.378 (8)	2.206 (6)	25.9	75.9 $(78)^e$	81.2 (3)

[a] These angles have been defined previously, for example in ref 18, and measure the bending back of the olefin substituents from planarity. A planar olefin would have $\alpha = 0°$ and $\beta = 90°$. The angle θ is between the normals to the L–M–L and C–M–C planes. [b] W. C. Hamilton, K. A. Klanderman, and R. Spratley, *Acta Crystallogr., Sect. A*, **25**, S172 (1969). [c] J. A. Evans and D. R. Russell, *J. Chem. Soc. D*, 197-8 (1971) (acac = 2,4-pentanedionato). [d] This work. [e] For the CH–C end.

As we noted earlier, to date all known complexes of the type $RhCl(olefin)P_2$, where P is a phosphine, have the olefin trans to a chloro ligand (e.g., *trans*-$RhCl(C_2F_4)(PPh_3)_2$,[20] *trans*-$RhCl(C_2H_4)(PPh_3)_2$,[23] RhCl(*o*-$Ph_2PC_6H_4$-*t*-CH=$CHC_6H_4PPh_2$-*o*),[24] etc.). Since a $RhCl(olefin)(PPh_3)_2$ complex has been postulated as an active intermediate in the $RhCl(PPh_3)_3$ catalytic system,[3] the present compound is expected to show interesting chemistry. Owing to the large trans influence of the phosphorus atom, the olefin end of the ppol ligand may dissociate easily in solution to generate a vacant coordination site or it may simply be activated sufficiently to react under ambient conditions with molecular hydrogen to form an alkane and in this way generate a vacant coordination site. Studies of RhCl(ppol) as a hydrogenation catalyst are under way.

Acknowledgment. This work was kindly supported by the U.S. National Science Foundation.

Registry No. RhCl(ppol), 67674-05-9; $[Rh(ppol)(PPh_3)][AsF_6]$, 67674-07-1; $[Rh(CO)(ppol)(PPh_3)][AsF_6]$, 67689-20-7; $[Rh(CO)_2(ppol)][AsF_6]$, 67689-18-3; $[RhCl(COD)]_2$, 12092-47-6; $RhCl(COD)(PPh_3)$, 31781-57-4; ppol, 67662-77-5; $Ph_2PCH_2CH_2CH_2P(Ph)H$, 57322-05-1; 4-chloro-1-butene, 927-73-1.

Supplementary Material Available: Table IV, the idealized positions of the hydrogen atoms, and Table V, a listing of structure amplitudes (26 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506,
the Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706, and
the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

A Comparison of Room-Temperature Single-Crystal Neutron and X-ray Diffraction Studies of the Bis(triphenylphosphine)iminium Salt of the $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ Monoanion[1]

JEFFREY L. PETERSEN,*[2a] PAUL L. JOHNSON,[2b] JIM O'CONNOR,[2c] LAWRENCE F. DAHL,*[2c]
and JACK M. WILLIAMS*[2b]

Received May 3, 1978

A combined room-temperature X-ray and neutron diffraction study of the bis(triphenylphosphine)iminium salt of the $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ monoanion has been performed to investigate the effects of crystal packing on the anion and Cr–H–Cr geometry. A comparison with the earlier work on the $[Et_4N]^+$ salt has shown that the pseudo-D_{4h} geometry of the anion's nonhydrogen framework is maintained. This result indicates that the $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ anion is considerably less susceptible than the tungsten analogue to a twisting deformation from a linear, eclipsed to a bent, staggered configuration. $[(Ph_3P)_2N]^+[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ crystallizes with four molecules in a monoclinic unit cell of symmetry $C2/c$ with X-ray-determined lattice parameters of $a = 21.377$ (6) Å, $b = 16.285$ (4) Å, $c = 16.186$ (5) Å, and $\beta = 128.68$ (2)°. The $[(Ph_3P)_2N]^+$ cation lies along the twofold rotation axis which bisects the P–N–P bond angle of 154.8 (4)°; the $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ anion resides on the crystallographic center of symmetry. Only one position for the bridging hydrogen atom was resolved from the neutron diffraction data with the corresponding maximum negative nuclear density at the center of symmetry. However, the highly anisotropic character of its thermal ellipsoid strongly favors our interpretation that the observed anion structure is consistent with the slightly bent $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ anion of C_{2v}-$2mm$ geometry (previously observed for the $[Et_4N]^+$ salt) being disordered among four equivalent sites and with the off-axis placement of the bridging hydrogen atom.

Introduction

Our recent neutron diffraction analysis[3] of the tetraethylammonium salt of the $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ monoanion revealed that the Cr–H–Cr bond is slightly bent (viz. 158.9 (6)°) rather than linear as presumed from earlier single-crystal X-ray diffraction studies.[4] This raised the immediate question regarding the degree to which crystal packing forces influence the Cr–H–Cr geometry. For the tungsten analogue of the monoanion, Bau and co-workers[5] found that the cation can have an appreciable effect on the geometry of the W–H–W bond. For the tetraethylammonium salt a linear, eclipsed metal carbonyl structure exists, whereas for the bis(triphenylphosphine)iminium salt a bent, staggered carbonyl configuration is observed with the W–W separation being 0.11 Å less in the bent form. To investigate the combined influence of packing forces and the cation on the solid-state structure of the Cr–H–Cr bond, we have performed an X-ray and neutron diffraction study at room temperature of the bis(triphenylphosphine)iminium salt of the $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ monoanion. Substitution of the much larger $[(Ph_3P)_2N]^+$ cation for the $[Et_4N]^+$ one is expected to produce an appreciable change in the molecular packing.

Experimental Section

Crystal Preparation. Suitable crystals of $[(Ph_3P)_2N]^+[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ were grown from saturated and degassed ethanol solutions by slow evaporation in a N_2-filled desiccator which contained magnesium perchlorate. The bis(triphenylphosphine)iminium salt was prepared by published methods.[4,6] Samples of $[(Ph_3P)_2N]^+$ $[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ were kindly supplied by T. Hall of Dr. J. K. Ruff's research group (University of Georgia, Athens, Ga.).

Unit Cell and Space Group. The lattice parameters for $[(Ph_3P)_2N]^+[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ were determined with a Syntex $P\bar{1}$ diffractometer. A triclinic cell with measured lattice constants of $a = 13.429$ (6) Å, $b = 15.040$ (6) Å, $c = 13.445$ (5) Å, $\alpha = 107.34$ (6)°, $\beta = 105.40$ (6)°, $\gamma = 110.97$ (5)°, and $V = 2199$ Å^3 was originally used to collect the X-ray data. However, using the program TRACER II,[7] we later found that the conventional reduced cell is monoclinic. This result was verified via axial X-ray photographs and by a preliminary survey of neutron diffraction reflection intensities. The systematic absences for $\{hkl\}$ of $h + k = 2n + 1$ and for $\{h0l\}$ of $l = 2n + 1$ suggest two possible space groups, $Cc(C_s^4$, No. 9) and $C2/c$ (C_{2h}^6, No. 15). The centrosymmetric space group $C2/c$ was confirmed from the structure determined. Least-squares fits of the orientation angles 2θ, ω, χ, and ϕ for 15 automatically centered

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