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Structural Determinations of Chlorobis(triisopropylphosphine)rhodium Compounds in the +2 and +3 Oxidation States

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The compounds $[(i\text{-Pr})_3P]_2RhCl_2$ (**1**), $[(i\text{-Pr})_3P]_2RhH_2Cl$ (**2**), and $[(i\text{-Pr})_3P]_2RhHCl_2$ (**3**) have been crystallographically characterized. Compound **1**: monoclinic, space group $P2_1/c$, $a = 8.127$ (1) Å, $b = 8.953$ (2) Å, $c = 16.189$ (3) Å, $\beta = 92.52$ (1)°, $R = 0.020$, $R_w = 0.020$. Compound **2**: triclinic, space group $P\bar{1}$, $a = 11.807$ (2) Å, $b = 14.681$ (3) Å, $c = 14.743$ (3) Å, $\alpha = 111.66$ (1)°, $\beta = 92.18$ (1)°, $\gamma = 93.29$ (1)°, $R = 0.026$, $R_w = 0.027$. Compound **3**: monoclinic, space group $P2_1/c$, $a = 8.092$ (1) Å, $b = 8.961$ (1) Å, $c = 16.270$ (3) Å, $\beta = 92.56$ (1)°, $R = 0.020$, $R_w = 0.026$. All data were obtained at 173 K. Compounds **1**, **3**, and the previously-reported dinitrogen compound $[(i\text{-Pr})_3P]_2Rh(N_2)Cl$ (**4**) are isostructural and allow a unique comparison of Rh–P and Rh–Cl bond distances among Rh(I), Rh(II), and Rh(III) oxidation states. From this isostructural series (compounds **1**, **3**, and **4**) the Rh(I)–P distance is 2.348 (1) Å, the Rh(II)–P distance is 2.366 (1) Å, and the Rh(III)–P distance is 2.367 (1) Å; the Rh(II)–Cl distance is 2.298 (1) Å, and the Rh(III)–Cl distance is 2.324 (1) Å. The dihydrido chloro compound **2** resembles the earlier-reported compound $[(t\text{-Bu})_3P]_2RhH_2Cl$ in that it has an acute H–Rh–H angle (65 (2), 66 (2)°).

Introduction

Monomeric, paramagnetic phosphine-containing Rh(II) compounds have been known for many years, sometimes isolated from the reactions between hydrated Rh(III) chloride and phosphine ligands[1-4] and sometimes observed as impurities in the reactions between chlororhodium(I)–olefin compounds and phosphines[5,6] or prepared by oxidation of Rh(I) compounds.[7] Recent reports[8] indicate this class of compounds has diverse and fascinating coordination, electron-transfer, and organometallic chemistry, and Rh(II) compounds may prove to be as useful and important in catalytic reactions[9] as the more commonly encountered Rh(I) and Rh(III) compounds. As structural data for this class of compound are scarce,[2,6,8,10] in this article we report crystal structure determinations of the Rh(II) compound $[(i\text{-Pr})_3P]_2RhCl_2$ (**1**) together with the related dihydridochloro compound $[(i\text{-Pr})_3P]_2RhH_2Cl$ (**2**) and the hydridodichloro compound $[(i\text{-Pr})_3P]_2RhHCl_2$ (**3**). Given the previously-reported structure of the dinitrogen compound $[(i\text{-Pr})_3P]_2Rh(N_2)Cl$ (**4**)[5,11] we now have available structures of very closely-related chloro-*trans*-bis(trialkylphosphino)rhodium compounds in the +1, +2, and +3 oxidation states, all with the same phosphine ligand.

Results and Discussion

The Rh(II) compound $[(i\text{-Pr})_3P]_2RhCl_2$ (**1**) was previously proposed[5] as the paramagnetic impurity in the compound $[(i\text{-Pr})_3P]_2Rh(N_2)Cl$ (compound **4**) and as an intermediate in the preparation of $[(i\text{-Pr})_3P]_{2,3}RhH$,[12] but never reported in pure form. We first encountered compound **1** as a reaction byproduct, the true nature of which was revealed by a preliminary X-ray structure determination. Subsequently we prepared compound **1** by deliberate chlorination of the Rh(I)–dinitrogen compound **4** (see Scheme I) and verified its structure. We also prepared samples of the related known Rh(III) compounds $[(i\text{-Pr})_3P]_2RhH_2Cl$ (**2**)[13] and $[(i\text{-Pr})_3P]_2RhHCl_2$ (**3**)[14] (see Scheme I) and determined their structures for purposes of comparison with the Rh(II) compound **1**. Crystal structure information for compounds **1**–**3** is summarized in Table I, and coordinates for the Rh, Cl, P, C, and hydrido hydrogen atoms are listed in Tables II–IV for compounds **1**–**3** respectively.

Scheme I

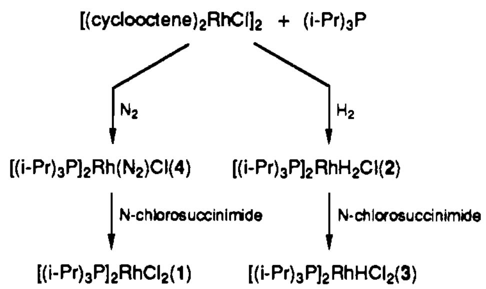

Table I. Crystal Structure Information

	$[(i\text{-Pr})_3P]_2$-$RhCl_2$ (**1**)	$[(i\text{-Pr})_3P]_2$-RhH_2Cl (**2**)	$[(i\text{-Pr})_3P_2]$-$RhHCl_2$ (**3**)
formula	$C_{18}H_{42}Cl_2P_2Rh$	$C_{18}H_{44}ClP_2Rh$	$C_{18}H_{43}Cl_2P_2Rh$
fw	494.30	460.86	495.31
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a, Å	8.127 (1)	11.807 (2)	8.092 (1)
b, Å	8.953 (2)	14.681 (3)	8.961 (1)
c, Å	16.189 (3)	14.743 (3)	16.270 (3)
α, deg		111.66 (1)	
β, deg	92.52 (1)	92.18 (1)	92.56 (1)
γ, deg		93.29 (1)	
V, Å^3	1176.8	2366.3	1178.6
T, K	173	173	173
Z	2	4	2
D_x, g cm^{-3}	1.385	1.291	1.403
μ, cm^{-1}	10.69	9.54	10.81
R^b	0.020^a	0.026	0.020
$R_w{}^b$	0.020	0.027	0.026

[a] Two quadrants of data were collected twice and averaged with a merge R of 0.016. [b] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$.

The structure of compound **1** is shown in Figure 1; important interatomic distances and angles are included in Table V.

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Table II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $[(i\text{-Pr})_3P]_2RhCl_2$

atom	x	y	z	B_{equ}, Å^2
Rh(1)	0.5000	0.5000	0.5000	1.494 (4)
Cl(1)	0.52419 (8)	0.30822 (5)	0.59411 (3)	3.91 (1)
P(1)	0.37302 (5)	0.33476 (4)	0.40263 (2)	1.54 (1)
C(11)	0.2663 (2)	0.1757 (2)	0.4500 (1)	2.3 (1)
C(12)	0.1339 (3)	0.2259 (3)	0.5071 (2)	4.1 (1)
C(13)	0.2029 (3)	0.0521 (3)	0.3927 (1)	3.7 (1)
C(21)	0.2335 (2)	0.4290 (2)	0.3260 (1)	2.4 (1)
C(22)	0.1655 (3)	0.3345 (3)	0.2545 (1)	3.9 (1)
C(23)	0.0948 (3)	0.5116 (4)	0.3671 (2)	4.8 (1)
C(31)	0.5296 (2)	0.2449 (2)	0.3401 (1)	2.1 (1)
C(32)	0.6284 (3)	0.3608 (3)	0.2952 (1)	3.4 (1)
C(33)	0.6436 (3)	0.1441 (3)	0.3917 (2)	3.9 (1)

Table III. Fractional Coordinates and Isotropic or Equivalent Isotropic Thermal Parameters[a] for $[(i\text{-Pr})_3P]_2RhH_2Cl$

atom	x	y	z	$B_{iso/equ}$, Å^2
Rh(1)	0.0428 (1)	0.2740 (1)	0.2734 (1)	1.570 (5)
Rh(2)	0.4794 (1)	0.2299 (1)	0.7775 (1)	1.582 (5)
Cl(1)	0.1919 (5)	0.3174 (5)	0.1859 (5)	2.83 (2)
Cl(2)	0.3347 (5)	0.1730 (5)	0.6438 (5)	3.13 (2)
P(1)	0.1535 (5)	0.1686 (4)	0.3141 (4)	1.88 (2)
P(2)	−0.0769 (5)	0.3752 (4)	0.2357 (4)	1.56 (1)
P(3)	0.3646 (5)	0.1878 (4)	0.8809 (4)	1.72 (2)
P(4)	0.6001 (5)	0.2823 (4)	0.6841 (4)	1.73 (2)
C(11)	0.0917 (2)	0.1029 (2)	0.3890 (2)	2.7 (1)
C(12)	−0.0166 (3)	0.0392 (3)	0.3406 (3)	4.0 (1)
C(13)	0.0687 (3)	0.1743 (3)	0.4918 (2)	3.3 (1)
C(14)	0.1961 (2)	0.0720 (2)	0.2011 (2)	2.8 (1)
C(15)	0.2526 (4)	−0.0117 (3)	0.2186 (3)	4.5 (1)
C(16)	0.0999 (3)	0.0342 (2)	0.1217 (2)	3.6 (1)
C(17)	0.2890 (2)	0.2278 (2)	0.3872 (2)	2.8 (1)
C(18)	0.3915 (3)	0.2281 (3)	0.3279 (3)	4.1 (1)
C(19)	0.2708 (3)	0.3339 (2)	0.4516 (2)	3.4 (1)
C(21)	−0.2228 (2)	0.3769 (2)	0.2781 (2)	2.1 (1)
C(22)	−0.2871 (2)	0.2764 (2)	0.2350 (3)	3.4 (1)
C(23)	−0.2242 (3)	0.4157 (2)	0.3891 (2)	2.8 (1)
C(24)	−0.1080 (2)	0.3457 (2)	0.1019 (2)	2.2 (1)
C(25)	−0.0306 (3)	0.4032 (2)	0.0579 (2)	3.0 (1)
C(26)	−0.1023 (3)	0.2353 (2)	0.0438 (2)	3.3 (1)
C(27)	−0.0169 (2)	0.5049 (2)	0.2840 (2)	1.9 (1)
C(28)	0.0413 (2)	0.5348 (2)	0.3862 (2)	2.4 (1)
C(29)	−0.1006 (3)	0.5794 (2)	0.2793 (2)	2.9 (1)
C(31)	0.4264 (2)	0.2008 (2)	1.0032 (2)	2.2 (1)
C(32)	0.4641 (3)	0.3069 (2)	1.0668 (2)	2.8 (1)
C(33)	0.5247 (3)	0.1359 (2)	0.9962 (2)	3.3 (1)
C(34)	0.2401 (2)	0.2639 (2)	0.9145 (2)	2.3 (1)
C(35)	0.1354 (2)	0.2217 (3)	0.8438 (2)	3.3 (1)
C(36)	0.2735 (3)	0.3683 (2)	0.9207 (2)	2.9 (1)
C(37)	0.3013 (2)	0.0595 (2)	0.8251 (2)	2.4 (1)
C(38)	0.2397 (3)	0.0222 (3)	0.8955 (3)	3.5 (1)
C(39)	0.3867 (3)	−0.0120 (2)	0.7687 (2)	3.2 (1)
C(41)	0.7415 (2)	0.3395 (2)	0.7413 (2)	2.2 (1)
C(42)	0.7312 (3)	0.4282 (2)	0.8362 (2)	3.3 (1)
C(43)	0.8151 (3)	0.2663 (3)	0.7618 (2)	3.5 (1)
C(44)	0.5351 (2)	0.3749 (2)	0.6440 (2)	2.6 (1)
C(45)	0.4551 (3)	0.4353 (3)	0.7161 (3)	3.8 (1)
C(46)	0.6167 (3)	0.4439 (3)	0.6155 (3)	4.4 (1)
C(47)	0.6235 (2)	0.1820 (2)	0.5656 (2)	2.8 (1)
C(48)	0.7172 (4)	0.2044 (3)	0.5062 (3)	5.0 (1)
C(49)	0.6370 (3)	0.0847 (2)	0.5773 (2)	4.0 (1)
H(1)	−0.0511 (26)	0.2148 (22)	0.2773 (23)	4.3 (7)
H(2)	−0.0100 (28)	0.3066 (24)	0.3715 (25)	5.2 (8)
H(3)	0.5785 (35)	0.2079 (30)	0.8178 (31)	7.9 (11)
H(4)	0.5311 (29)	0.3130 (25)	0.8666 (26)	5.4 (8)

[a] All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydride atoms were refined with isotropic parameters.

Table IV. Fractional Coordinates and Isotropic or Equivalent Isotropic Thermal Parameters[a] for $[(i\text{-Pr})_3P]_2RhHCl_2$

atom	x	y	z	$B_{iso/equ}$, Å^2
Rh(1)	0.5000	0.5000	0.5000	1.394 (4)
Cl(1)	0.53242 (8)	0.30549 (4)	0.59380 (3)	3.77 (1)
P(1)	0.37293 (4)	0.33422 (4)	0.40320 (2)	1.37 (1)
C(11)	0.2695 (2)	0.1741 (2)	0.4513 (1)	1.96 (3)
C(12)	0.1387 (3)	0.2217 (2)	0.5105 (1)	3.56 (5)
C(13)	0.2021 (3)	0.0521 (2)	0.3936 (1)	3.29 (5)
C(21)	0.2298 (2)	0.4276 (2)	0.3275 (1)	2.16 (3)
C(22)	0.1640 (3)	0.3337 (2)	0.2551 (1)	3.61 (5)
C(23)	0.0878 (3)	0.5058 (3)	0.3696 (2)	4.1 (1)
C(31)	0.5294 (2)	0.2464 (2)	0.3393 (1)	1.85 (3)
C(32)	0.6263 (2)	0.3638 (2)	0.2936 (1)	3.01 (4)
C(33)	0.6457 (3)	0.1447 (2)	0.3889 (1)	3.43 (5)
H(1)[b]	0.673 (7)	0.465 (5)	0.469 (3)	5.1 (12)

[a] All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydride atom was refined with an isotropic parameter. [b] Refined with an occupancy of 0.5.

Table V. Comparison of the (a) Bond Lengths (Å) and (b) Angles (deg) of $[(i\text{-Pr})_3P]_2RhCl_2$ and $[(i\text{-Pr})_3P]_2RhHCl_2$

atoms	P_2RhCl_2	P_2RhHCl_2
(a) Bond Lengths		
Rh(1)–Cl(1)	2.298 (1)	2.342 (1)
Rh(1)–P(1)	2.366 (1)	2.367 (1)
Rh(1)–H(1)		1.54 (6)
P(1)–C(11)	1.851 (2)	1.852 (1)
P(1)–C(21)	1.847 (2)	1.852 (2)
P(1)–C(31)	1.845 (2)	1.849 (1)
C(11)–C(12)	1.517 (3)	1.524 (2)
C(11)–C(13)	1.519 (3)	1.526 (2)
C(21)–C(22)	1.519 (3)	1.525 (2)
C(21)–C(23)	1.525 (3)	1.533 (3)
C(31)–C(32)	1.518 (3)	1.526 (2)
C(31)–C(33)	1.518 (3)	1.516 (2)
(b) Bond Angles		
Cl(1)–Rh(1)–P(1)a	90.20 (2)	90.05 (2)
Cl(1)–Rh(1)–P(1)	89.80 (2)	89.95 (2)
Cl(1)–Rh(1)–H(1)a		91 (2)
Cl(1)–Rh(1)–H(1)		89 (2)
P(1)–Rh(1)–H(1)a		88 (2)
P(1)–Rh(1)–H(1)		92 (2)
Rh(1)–P(1)–C(11)	113.80 (5)	113.37 (5)
Rh(1)–P(1)–C(21)	113.50 (6)	113.52 (5)
Rh(1)–P(1)–C(31)	110.32 (6)	110.68 (5)
C(11)–P(1)–C(21)	110.2 (1)	110.5 (1)
C(11)–P(1)–C(31)	103.8 (1)	103.9 (1)
C(21)–P(1)–C(31)	104.4 (1)	104.0 (1)
P(1)–C(11)–C(12)	112.5 (1)	113.0 (1)
P(1)–C(11)–C(13)	117.4 (1)	116.8 (1)
P(1)–C(21)–C(22)	116.7 (1)	116.8 (1)
P(1)–C(21)–C(23)	111.9 (1)	111.7 (1)
P(1)–C(31)–C(32)	110.9 (1)	111.1 (1)
P(1)–C(31)–C(33)	112.1 (1)	112.4 (1)
C(12)–C(11)–C(13)	110.9 (2)	110.5 (1)
C(22)–C(21)–C(23)	110.6 (2)	110.8 (2)
C(32)–C(31)–C(33)	110.3 (2)	110.7 (1)

Compound **1** has trans, planar geometry and sits on a crystallographic inversion center, like the recently-reported compound $(PPh_3)_2RhCl_2$,[6] but compound **1** has a much shorter Rh–Cl bond (2.298 (*1*) Å, compared with 2.428 (4) Å) and somewhat longer Rh–P bonds (2.366 (1) Å, compared with 2.323 (2) Å). We were especially concerned that a hydrido hydrogen atom might be present and the "Rh(II)" compound might actually be $[(i\text{-Pr})_3P]_2RhHCl_2$ (**3**). Our evidence for the correct formulation of compound **1** as a Rh(II) compound without hydrido hydrogen atoms includes, but is not limited to, the X-ray data. There is no discernible "hydridic" electron density above/below the coordination plane, and attempts to refine a hydrogen atom artificially placed there failed dramatically. More compelling is the fact that the hydridodichlororhodium(III) compound **3** is known[14] and has a distinctly different UV–visible spectrum and a normal diamagnetic NMR spectrum. As expected, the paramagnetic compound **1** itself has no sharp NMR signals although very broad peaks can be discerned at 8 and 35 ppm in the ^1H NMR spectrum. However, small amounts of a diamagnetic compound were evident in NMR spectra of samples of compound **1**. This diamagnetic compound was indeed confirmed by UV–visible and NMR spectra (see below) to be the hydrido dichloro compound $[(i\text{-Pr})_3P]_2RhHCl_2$ (**3**), amounting to approximately 5%.

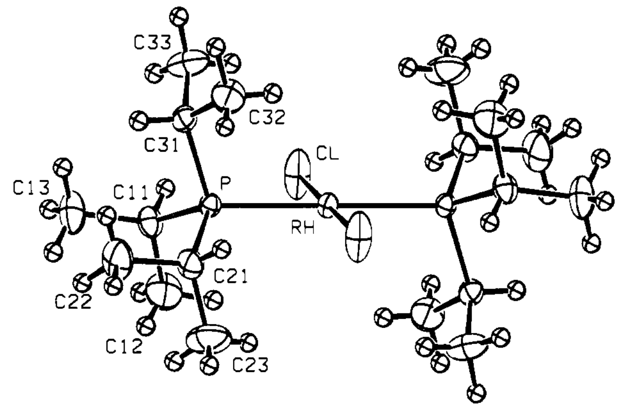

Figure 1. Molecular drawing of $[(i\text{-Pr})_3P]_2RhCl_2$ (**1**) with atom-labeling scheme. The molecule sits on a crystallographic inversion center. The radius of the hydrogen atoms has been arbitrarily assigned to correspond to an isotropic B value of 1.0 Å^2.

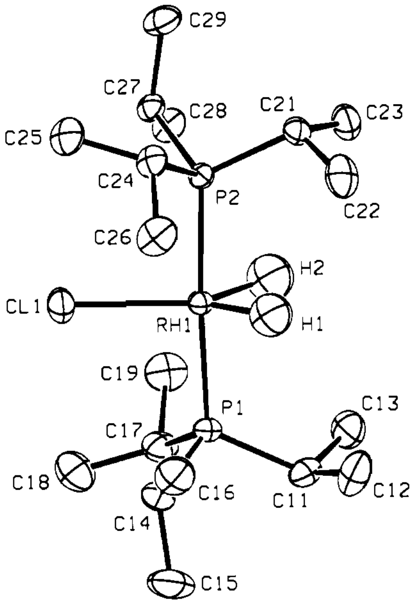

Figure 2. One of two molecules of $[(i\text{-Pr})_3P]_2Rh(H)_2Cl$ (**2**). The molecule is seen to have a *pseudo*-2-fold axis passing through the Rh and Cl atoms. The second molecule is very similar except that the orientations of two of the isopropyl groups are sufficiently different to as to destroy the pseudo-2-fold axis. Ellipsoids are scaled to include 50% probabilities.

Given the tendency of the hydrido dichloro compound $[(i\text{-Pr})_3P]_2RhHCl_2$ (**3**) to occur in samples of the dichlororhodium(II) compound **1** we decided to prepare compound **3** separately and determine its structure. However, our attempt to prepare it directly from rhodium trichloride hydrate and $(i\text{-Pr})_3P$[14] again resulted in a mixture of compound **3** and the dichlororhodium(II) compound **1**, so we resorted to controlled deliberate chlorination of the dihydrido chloro compound $[(i\text{-Pr})_3P]_2RhH_2Cl$ (**2**)[13] (see Scheme I).

As we prepared samples of the dihydrido chloro compound **2** some were obtained in single-crystal form, and it was of interest to determine its structure, shown in Figure 2. Compound **2** crystallizes with two independent but similar molecules in the asymmetric unit. These molecules differ significantly only in orientations of the isopropyl groups, and only one ("molecule 1") is illustrated in Figure 2. Distances and angles within each molecule are listed in Table VI and are reminiscent of the previously reported structure of $[(t\text{-Bu})_3P]_2RhH_2Cl$,[15] especially concerning the relatively acute angle between the "hydrido" hydrogen atoms. An intriguing additional observation is that the Rh–H distances within each molecule are unequal. As always, hydrogen atoms are poorly located by X-rays and metal–hydrogen distances must be interpreted with caution. But one possible rationalization is that the pseudo-trigonal-bipyramidal Rh(III) compound **2** is almost a Jahn–Teller system and undergoes both a distortion to a "Y" geometry (acute H–Rh–H angle) and a distortion of the H–Rh distances. The hydrido dichloro compound **3** (see below) by contrast chooses a distortion to a "T" square-pyramidal geometry owing to the poorer σ-donor character of its chloro ligands.[16,17]

The reaction of the dihydrido chloro compound **2** with 1 equiv of *N*-chlorosuccinimide (Scheme I) provides the hydrido dichloro compound **3** in reasonable yield. By in situ NMR analysis there are some additional products, most likely involving chlorination of isopropyl groups, which become predominant if excess *N*-chlorosuccinimide is used, but when only a stoichiometric amount

Table VI. Selected Interatomic Distances (Å) and Angles (deg) for $[(i\text{-Pr})_3P]_2RhH_2Cl$

molecule 1		molecule 2	
(a) Interatomic Distances			
Rh(1)–Cl(1)	2.413 (1)	Rh(2)–Cl(2)	2.422 (1)
Rh(1)–P(1)	2.307 (1)	Rh(2)–P(3)	2.302 (1)
Rh(1)–P(2)	2.303 (1)	Rh(2)–P(4)	2.308 (1)
Rh(1)–H(1)	1.38 (3)	Rh(2)–H(3)	1.40 (4)
Rh(1)–H(2)	1.52 (3)	Rh(2)–H(4)	1.50 (4)
P(1)–C(11)	1.856 (3)	P(3)–C(31)	1.857 (2)
P(1)–C(14)	1.855 (3)	P(3)–C(34)	1.868 (2)
P(1)–C(17)	1.869 (3)	P(3)–C(37)	1.852 (2)
P(2)–C(21)	1.854 (2)	P(4)–C(41)	1.848 (2)
P(2)–C(24)	1.873 (2)	P(4)–C(44)	1.861 (3)
P(2)–C(27)	1.855 (2)	P(4)–C(47)	1.866 (3)
(b) Interatomic Angles			
Cl(1)–Rh(1)–P(1)	92.09 (3)	Cl(2)–Rh(2)–P(3)	92.91 (3)
Cl(1)–Rh(1)–P(2)	91.20 (2)	Cl(2)–Rh(2)–P(4)	90.67 (3)
Cl(1)–Rh(1)–H(1)	152 (1)	Cl(2)–Rh(2)–H(3)	146 (2)
Cl(1)–Rh(1)–H(2)	143 (1)	Cl(2)–Rh(2)–H(4)	148 (1)
P(1)–Rh(1)–P(2)	176.6 (1)	P(3)–Rh(2)–P(4)	175.6 (1)
P(1)–Rh(1)–H(1)	87 (1)	P(3)–Rh(2)–H(3)	93 (2)
P(1)–Rh(1)–H(2)	92 (1)	P(3)–Rh(2)–H(4)	87 (1)
P(2)–Rh(1)–H(1)	89 (1)	P(4)–Rh(2)–H(3)	85 (2)
P(2)–Rh(1)–H(2)	86 (1)	P(4)–Rh(2)–H(4)	89 (1)
H(1)–Rh(1)–H(2)	65 (2)	H(3)–Rh(2)–H(4)	66 (2)
Rh(1)–P(1)–C(11)	118.1 (1)	Rh(2)–P(3)–C(31)	118.5 (1)
Rh(1)–P(1)–C(14)	109.6 (1)	Rh(2)–P(3)–C(34)	113.1 (1)
Rh(1)–P(1)–C(17)	114.7 (1)	Rh(2)–P(3)–C(37)	112.4 (1)
Rh(1)–P(2)–C(21)	116.9 (1)	Rh(2)–P(4)–C(41)	117.2 (1)
Rh(1)–P(2)–C(24)	115.4 (1)	Rh(2)–P(4)–C(44)	111.0 (1)
Rh(1)–P(2)–C(27)	111.7 (1)	Rh(2)–P(4)–C(47)	112.2 (1)

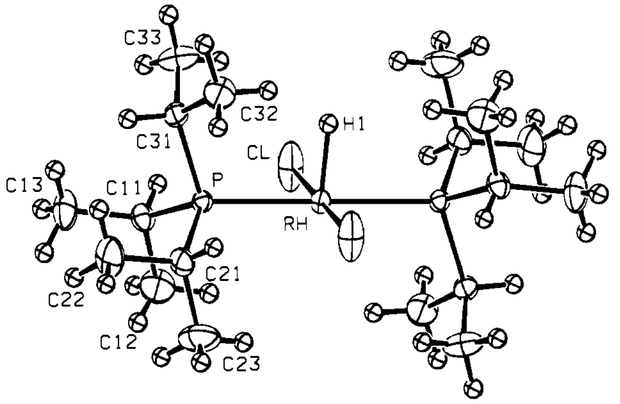

Figure 3. Molecular drawing of $[(i\text{-Pr})_3P]_2Rh(H)Cl_2$ (**3**). The drawing shows only one of two sites for the hydride atom which disorders across a center of symmetry coincident with the rhodium atom. The radius used for the hydrogen atoms has been arbitrarily assigned.

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of *N*-chlorosuccinimide is used, the hydridodichloro compound **3** can be isolated in pure crystalline form. Its structure is illustrated in Figure 3 with important distances and angles included in Table V. The hydrido hydrogen atom was located and successfully refined, even though the rhodium atom sits on a crystallographic inversion center and the hydrido hydrogen atom is necessarily disordered above and below the coordination plane. Apart from the presence of the hydrido hydrogen atom in compound **3** there is little difference between its structure and that of compound **1**, and in fact the compounds are crystallographically isostructural.

This isostructural relationship between compounds **1** and **3** requires special attention. In fact, the dichlororhodium(II) compound **1**, the hydridodichlororhodium(III) compound **3**, and the chloro(dinitrogen)rhodium(I) compound **4**[5,11] all crystallize in the same space group with very similar cell constants. Thus the presence of traces of the hydrido dichloro compound **3** in samples of the Rh(II) compound **1** should not be surprising. (Cocrystallization of diamagnetic compounds with other Rh(II) compounds is suggested in ref 4.) Likewise the presence of the Rh(II) compound **1** in crystals of the chloro dinitrogen compound **4** is not surprising[5] and increases the difficulty in assigning an end-bound or side-bound coordination of dinitrogen in compound **4**.[5,11] In all probability, compounds **1**, **3**, and **4** will mutually cocrystallize in almost any ratio; thus *recrystallization cannot reliably purify any of these compounds from small quantities of any of the others*. For this reason we sought synthetic methods that would prepare each compound free of the others. Our route, outlined in Scheme I and documented in the Experimental Section, has been reasonably successful although the dichlororhodium(II) compound **1** tends to be contaminated with a few percent of the hydrido dichloro compound **3**. In contrast, the hydrido dichloro compound **3** prepared according to Scheme I has no detectable amounts of the dichlororhodium(II) compound **1**. UV–visible absorption spectroscopy serves to analyze samples of compounds **1** and **3**, as compound **1** has a distinct peak at 583 nm (C_6H_6, $\epsilon = 160$ L/(mol cm)) whereas compound **3** has a double peak at 467 and 487 nm (C_6H_6, $\epsilon = 290$) with a shoulder at 537 nm ($\epsilon = 140$). The peak at 583 nm is responsible for the red-purple color of compound **1**; purple or blue colors seem to be characteristic of planar bis(phosphine)rhodium(II) compounds[1,4,7,8] and contrast worrisomely with the yellow color reported for $(PPh_3)_2Rh^{II}Cl_2$.[6] In fact, solvated $(PPh_3)_2Rh(CO)Cl$[18] is isostructural with "$(PPh_3)_2Rh^{II}Cl_2$", and crystals of the latter compound may well be contaminated with significant amounts of $(PPh_3)_2Rh(CO)Cl$.

The availability of low-temperature structural data for compounds **1**–**4** and other *trans*-bis(triisopropylphosphine)rhodium compounds enables us to recognize the following trends.

(1) When the rhodium atom sits on a crystallographic inversion center and the P–Rh–P angle is necessarily 180°, the Rh–P(i-Pr)$_3$ bond distances are very slightly shorter for Rh(I) ($[(i\text{-}Pr)_3P]_2Rh(N_2)Cl$, compound **4**, 2.348 (1) Å[5,11]) than for Rh(II) or Rh(III) (compounds **1** and **3**, 2.366 (1) and 2.367 (1) Å respectively).

(2) When the P–Rh–P angle deviates from 180°, all Rh–P(i-Pr)$_3$ bond distances tend to shorten but those for Rh(I) are still shorter than those for Rh(III). Compare 2.302 (1) to 2.308 (1) Å for compound **2** and 2.302 (2) to 2.321 (2) Å for another *cis*-dihydrido-*trans*-bis(triisopropylphosphine)rhodium(III) compound[19] with 2.273 (3) Å (average) for a monohydridorhodium(I) compound.[20] The Rh–P(i-Pr)$_3$ distances for the chloro(ethylene)bis(triisopropylphosphine)rhodium compound (2.361 (1), 2.363 (1) Å[5]) are anomalously long, but steric demands of the ethylene must be accommodated.

(3) For those compounds having chloride trans to chloride (**1** and **3** only) the Rh–Cl bond distance is only slightly shorter for Rh(II) than for Rh(III) (2.298 (1) and 2.324 (1) Å, respectively, Table V). This difference is slight and only marginally significant, but may reflect the different electronic structures in the following manner. *trans*-Dichlorobis(phosphine)rhodium(II) compounds are believed to have, on the average, less than two electrons in the d_{xz} orbital which is π-antibonding to chloride (see drawing **5**). This is because the ligand-field splitting between d_{xz} and d_{z^2} orbitals is small and the odd electron (and "hole") occupies a mixture of them.[7] However, in the Rh(III) compound **3** the axial hydrido ligand causes a much greater ligand-field splitting between the d_{xz} orbital and d_{z^2} orbital (see drawing **6**), forcing the d_{xz} orbital to be fully doubly occupied. This could result in slightly more π-antibonding, and longer Rh–Cl distances, in compound **3** relative to compound **1**. Oriented single-crystal ESR studies could help confirm this interpretation; for now, we note that powder and solution-phase ESR measurements on compound **1** provide parameters consistent with those reported earlier.[5,7]

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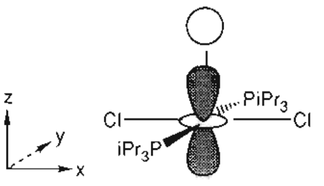

6

Summary and Conclusions

Chloro-*trans*-bis(triisopropylphosphine)rhodium compounds have now been structurally characterized with rhodium in the +1, +2, and +3 oxidation states. Compounds **1**, **3**, and **4** are isostructural; this has the advantage that very detailed structural comparisons are possible without having to consider differences in packing forces, ligand bulk, or trans influences. However, it is possible, indeed inevitable, that these isostructural compounds will mutually cocrystallize to form "compositionally disordered" crystals,[21] in which case their structures are averaged and detailed structural comparisons become problematic. We have resorted to synthetic methods that prepare these compounds reasonably cleanly and free from each other and note slight structural differences that result from the different oxidation states of the rhodium centers. In particular, Rh–P bond distances increase very slightly upon going from Rh(I) to Rh(III) oxidation states, and Rh–Cl bond distances also increase slightly upon going from Rh(II) to Rh(III).

Experimental Section

All reactions were performed in a nitrogen-filled glovebox using dried solvents. The compounds $[(i\text{-}Pr_3)P]_2Rh(N_2)Cl$ (**4**), $[(i\text{-}Pr)_3P]_2RhH_2Cl$ (**2**), and $[(cyclooctene)_2RhCl]_2$ were prepared according to literature methods.[5,13,22] Ambient-temperature NMR spectra were recorded using QE-300 instruments, and chemical shifts are given followed by coupling constants in Hz in parentheses. For reference we include the NMR parameters of compound **2**[13] (C_6D_6). ^1H NMR: −22.8, d (26) of t (14); 1.13, q; 2.13, m. $\{^1H\}^{31}P$ NMR: 63.4, d (114.5).

Bis(triisopropylphosphine)dichlororhodium(II) (1). Method a. The chloro dinitrogen compound **4** (0.32 g) and *N*-chlorosuccinimide (0.10 g) were stirred together in 5 mL of tetrahydrofuran (THF). After the mixture was stirred for several hours, the resulting red suspension was heated briefly to boiling and the solution allowed to cool slowly, depositing 0.32 g of red solids. These were washed with 20 mL of ether and recrystallized from hot benzene, providing 0.15 g of red-purple compound **1** (46%). ^1H NMR (C_6D_6): 8 (br), 35 (br).

Method b. $[(cyclooctene)_2RhCl]_2$ (0.18 g), triisopropylphosphine (0.16 g), and *N*-chlorosuccinimide (0.07 g) were stirred together in 10 mL of THF for 3 h. The mixture was filtered and cooled to −30 °C. The resulting crystalline material was recrystallized from hot THF to provide 0.045 g (18%) of compound **1** as well-formed single crystals.

Bis(triisopropylphosphine)hydridodichlororhodium(III) (3). The dihydrido chloro compound **2** (0.156 g) and *N*-chlorosuccinimide (0.056

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g) were stirred together in 5 mL of benzene for 1 h. The resulting red-brown suspension was heated and the solution allowed to cool slowly to room temperature. This formed a deposit of irregular off-white lumps and red-orange needles of compound **3**, which were manually separated to provide 0.093 g (55%) of pure compound **3**. ^1H NMR (C_6D_6): −31.2, d (33) of t (12); 1.21, q; 2.76, m. $\{^1H\}^{31}P$ NMR: 45.7, d (97).

Structure Determinations. Crystals of compound **1** were grown from THF solution according to method b above, crystals of compound **2** were grown from toluene at −30 °C, and crystals of compound **3** were obtained from a cooled benzene solution. Data for all of the structures were collected on a Syntex P3 diffractometer with the crystals cooled to −100 °C (graphite monochromator, Mo Kα radiation, $\lambda = 0.71069$ Å). The crystal system, space group, and approximate unit cell dimensions of each crystal were determined during a preliminary investigation. The unit cell parameters were subsequently refined from the Bragg angles of at least 48 computer-centered reflections. A summary of the crystal data is given in Table I. The presence of two independent molecules in the asymmetric unit of compound **2**, compounded by the fact that a pseudomonoclinic *A*-centered unit cell can be chosen,[23] raises the possibility that the material should be described in a higher-symmetry space group. But we have been unable to find any higher symmetry in the reflection intensities, and the final structure reveals significant differences in the orientations of the isopropyl groups such that the molecules cannot be related by symmetry.

Intensity data were collected using the ω-scan technique with background measurements at both ends of the scan (total background time was equal to the scan time). The intensities of standard reflections were monitored periodically; none of the crystals showed any signs of decomposition but both showed some variation over the data collection period and corrections were applied. Azimuthal scans also showed some variation in intensity for compound **1**, and empirical corrections for absorption were made. The azimuthal scans for compounds **2** and **3** were relatively flat, and no corrections were applied.

The refinement and analysis of the two structures were carried out using a package of local programs.[24] The atomic scattering factors were taken from the tabulations of Cromer and Waber; anomalous dispersion corrections were by Cromer.[25] In the least-squares refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weights, w, assigned as $[\sigma^2(I) + 0.0009I^2]^{-1/2}$.

The structures of compounds **1** and **2** were solved by direct methods (MULTAN);[26] the coordinates of **1** were used as a starting point for **3**. All of the non-hydrogen atoms were refined with anisotropic thermal parameters; all hydrogens were refined with isotropic thermal parameters. Table I details the results of the various refinements. The atomic coordinates are given in Tables II–IV for compounds **1**–**3**, respectively.

Acknowledgment. We thank P. Krusic for preliminary ESR measurements, and S. Hill, L. Lardear, W. Marshall, and L. J. Ayers for skilled technical assistance.

Supplementary Material Available: Tables of crystal structure information, anisotropic thermal parameters, hydrogen atom positional and thermal parameters, and complete interatomic distances and angles (20 pages); tables of structure factor amplitudes (34 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 2K6, and National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria 0001, South Africa

Aggregation of $CpRu(PPh_3)_2SR$ via Loss of PPh_3 (R = 1-C_3H_7, $CHMe_2$). Structure of [CpRuS-1-C_3H_7]$_3$, a Molecule with Short C–H···S Distances

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The complexes $CpRu(PPh_3)_2SR$, where R = 1-C_3H_7 and $CHMe_2$, lose both PPh_3 ligands in refluxing toluene to give the trimers $[CpRuSR]_3$ via intermediate dimers. The crystal structure for R = 1-C_3H_7 was determined: space group $P\bar{1}$, $a = 10.554$ (1) Å, $b = 14.033$ (2) Å, $c = 18.243$ (2) Å, $\alpha = 76.977$ (10)°, $\beta = 87.299$ (8)°, $\gamma = 89.009$ (11)°, $V = 2629.4$ (9) Å^3, and $Z = 4$. The three thiolato ligands are all on the same side of the Ru_3 triangle, each ligand bridging two ruthenium atoms. This leads to two of the 1-C_3H_7 groups occupying equatorial-like positions while the third is axial such that one proton on the α-carbon is well within the van der Waals contact distance of the sulfur atoms across the triangle. The consequences of this close approach are characterized via NMR spectroscopy and discussed as a partial model for chemisorption of thiols on metal surfaces.

Introduction

Our early attempts[2] to prepare the relatively simple complexes $CpRu(PPh_3)_2SR$ via treatment of $CpRu(PPh_3)_2Cl$ with NaSR, failed due to the generation of multiple side products which were suspected to include dimers and trimers. The desired monomers were eventually obtained by application of flash heating followed by rapid quenching of the reaction solution.[2] With the monomers in hand, their reactivity was attributed to activation via π-donation by the thiolato ligand and steric-accelerated loss of PPh_3.

The propensity of thiolato ligands to bridge metal atoms in organometallic complexes is well recognized. We have recently reported dimerization of $CpW(CO)_2(PPh_3)SR$ via loss of PPh_3 to give thiolato-bridged dimers.[3] However, aggregation of $CpRu(PPh_3)_2SR$, where R = 1-C_3H_7 or $CHMe_2$, is difficult to stop at the dimer stage and easily proceeds to the trimers $[CpRuSR]_3$, wherein all the PPh_3 ligands have been lost.[4]

Complexes of the type $[CpM(CO)]_3$, where M = Co and Rh, have been studied as models for the chemisorption of CO, a

Table I. Crystallographic Data for [CpRuS-1-C_3H_7]$_3$

chem formula: $C_{24}H_{36}Ru_3S_3$
$a = 10.554$ (1) Å
$b = 14.033$ (2) Å
$c = 18.243$ (2) Å
$\alpha = 76.977$ (10)°
$\beta = 87.299$ (8)°
$\gamma = 89.009$ (11)°
$V = 2629.4$ (9) Å^3
$z = 4$

fw = 723.95
space group: $P\bar{1}$ (No. 2)
$T = 22$ °C
$\lambda = 0.71069$ Å
$\rho_{calcd} = 1.829$ g cm^{-3}
μ(Mo Kα) = 1.897 mm^{-1}
$R^a = 0.0304$
$R_w{}^b = 0.0268$

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

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