Crystallographic Disorder in the Orthorhombic Form of $RhCl(CO)(PPh_3)_2$: Relevance to the Reported Structure of the Paramagnetic Impurity in Wilkinson's Catalyst

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Samples of Wilkinson's catalyst, $RhCl(PPh_3)_3$, prepared from $RhCl_3{\cdot}xH_2O$ are inevitably contaminated by a paramagnetic impurity, the exact nature of which has eluded researchers for years.[1] Recently, Ogle, Masterman, and Hubbard (OMH) communicated the isolation of a small quantity of a yellow, air-stable paramagnetic material formulated as $RhCl_2(PPh_3)_2{\cdot}2CH_2Cl_2$ (**1**).[2,3] The compound was reported as an impurity in samples of (cod)RhCl(PPh_3) synthesized from $[Rh(cod)Cl]_2$ and PPh_3 in chloroform or dichloromethane. The molecular structure revealed that the rhodium atom resides on an inversion center in the orthorhombic space group *Pcab* with a square-planar arrangement of trans phosphine and chloride ligands. Characterization of the sample included far-IR, ^1H NMR, and EPR spectroscopies and mass spectrometry. Unfortunately, detailed studies were hampered by the authors' inability to reproduce the result either by the original serendipitous route beginning with $[Rh_2(cod)_2Cl_2]$ or by other more rational methods.[2] Herein we report our deliberate synthesis and full characterization of the orthorhombic solvated form of $RhCl(CO)(PPh_3)_2$, viz., $RhCl(CO)(PPh_3)_2{\cdot}2CH_2Cl_2$ (**2**); these results, when taken together with spectroscopic data, suggest that the orthorhombic crystal structures reported for "$RhCl_2(PPh_3)_2$" and $RhCl(CO)(PPh_3)_2$ are in fact the same. During the course of our work, Chaloner et al. independently reported the orthorhombic form of $RhCl(CO)(PPh_3)_2{\cdot}2CH_2Cl_2$ as a byproduct isolated from a purification of *trans*-$[Rh_2(PPh_3)_2(CO)_2\{\mu\text{-}SCH_2)_4S\}]$.[4,5]

Experimental Section

Synthesis of $RhCl(CO)(PPh_3)_2$ (2). A quantity of $[Rh(cod)Cl]_2$ (0.100 g, 0.2 mmol) was dissolved in 5 mL of THF under a CO atmosphere and treated with 4 equiv of PPh_3 (0.213 g, 0.8 mmol). The reaction was stirred for 10 min, after which time the resulting yellow precipitate was collected by suction filtration in air. Additional solid was obtained from the filtrate by addition of diethyl ether. The combined solids were recrystallized from a minimal volume of hot THF and Et_2O; yield 0.242 g (86%). IR (Nujol mull/CsI, cm^{-1}): $\nu_{CO} = 1965$ s; other bands, 1480 m, 1440 m, 1100 m, 1025 m, 1000 w, 745 m, 725 w, 705 m, 695 m, 575 m, 555 w, 525 m, 510 m, 454 w, 437 w, 420 w, 400 vw, 310 w. ^1H NMR (C_6D_6): δ 7.02 (mult, 3 H), 7.93 (mult, 2 H). FAB mass spectrum in nitrobenzyl alcohol: *m/z* 627 ($Rh(PPh_3)_2^+$), 655 ($Rh(PPh_3)_2(CO)^+$), 662 ($Rh(PPh_3)_2Cl^+$), 692 ($Rh(PPh_3)_2(CO)(Cl)^+$).

X-ray Crystallographic Procedures. Single crystals of $RhCl(CO)(PPh_3)_2{\cdot}2CH_2Cl_2$ (**2**) were obtained by slow diffusion of petroleum ether into a dichloromethane solution of **2**. A thin rodlike crystal of approximate dimensions $0.15 \times 0.15 \times 0.70$ mm^3 was selected and mounted on the tip of a glass fiber with epoxy cement. Geometric and intensity data were collected on a Rigaku AFC6S diffractometer with Mo Kα ($\lambda_{\bar{\alpha}} = 0.710\,69$ Å) radiation and were corrected for Lorentz and polarization effects. The general procedures used for data collection have been fully described elsewhere.[6] Unit cell parameters were refined by a least-squares fit of 23 reflections in the range $26 < 2\theta < 33°$. The *mmm* Laue symmetry of the lattice was confirmed by intensity measurements of symmetry-related reflections. Intensity data were collected at 23 ± 2 °C in the range $4 < 2\theta < 50°$ by the ω-2θ scan technique. A total of 3880 data were collected of which 1853 with $F_o^2 > 3\sigma(F_o)^2$ were used in the development and refinement of the structure. Periodic monitoring of three representative reflections at regular intervals throughout data collection showed no change in diffraction intensity. Azimuthal scans of three reflections were used as a basis for an empirical absorption correction.

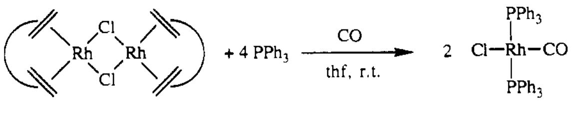
Structure Solution and Refinement. All computations were performed with VAX computers on a cluster network within the Department of Chemistry at Michigan State University by using the Texsan software package of the Molecular Structure Corp. The Rh atom was located by the direct methods program MITHRIL[7] and was found to reside on a crystallographic inversion center. The position of all other non-hydrogen atoms except for the atoms of the disordered CO and Cl groups were located by application of the phase extension program DIRDIF.[8] After several successful least-squares cycles, the position of the Cl atom ($\sim$12 e/Å^3) was clearly evident from the difference Fourier map. In addition, two peaks of much lower electron density ($\sim$2.0 and 0.5 e/Å^3) were present in the map, one on each side of the Cl atom directly along the Rh–Cl vector. At this stage, further refinement of the structure was completed by using two different models. Pertinent crystallographic parameters for both models are summarized in Table I.

(i) Refinement of 2 as $RhCl(CO)(PPh_3)_2{\cdot}2CH_2Cl_2$ (2a). After successful refinement of the Cl atom, the two regions of electron density to either side of Cl were assigned to carbon and oxygen atoms. The Cl and CO groups were then refined at 50% occupancy. Thermal parameters for all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions as fixed contributors to the structure factor calculation and were not refined. Final least-squares fit of 232 parameters resulted in residuals of $R = 0.030$ and $R_w = 0.025$ and a quality-of-fit of 1.53. The highest peak in the final difference Fourier map was 0.42 eV/Å^3.

(ii) Refinement of 2 as $RhCl_2(PPh_3)_2{\cdot}2CH_2Cl_2$ (2b). In the dichloride model, the peaks of low electron density appearing as "ghosts" around a much higher peak in the map were left unassigned, and the highest peak was assigned to a fully occupied Cl atom. As before, hydrogen atoms were placed at calculated positions and were treated as fixed contributors to the structure factor calculation. All non-hydrogen atoms were refined anisotropically. Least-squares refinement of 214 variables led to residuals R and R_w of 0.038 and 0.033, respectively. The standard deviation of an observation of unit weight was 2.00. The highest peak in the final Fourier difference map was 0.63 e/Å^3 and is associated with Cl(1).

Results

Synthesis. $RhCl(CO)(PPh_3)_2$ (**2**) was prepared conveniently and in high yield by simple displacement of the coordinated diene from $[Rh(cod)Cl]_2$ by PPh_3 in the presence of CO in THF (eq 1). The resulting product is fairly insoluble in THF and was harvested directly from the reaction solution as a yellow crystalline solid. Additional product was retrieved from the filtrate by the careful addition of diethyl ether. This method is similar to the



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† Camille and Henry Dreyfus Teacher-Scholar 1991-95. Fellow of the Alfred P. Sloan Foundation 1992-94.

[1] Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1712.

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[3] The CH_2Cl_2 lattice solvent occupies a general position with a multiplicity twice that of the metal complex; therefore, although the authors (incorrectly) referred to their crystal form as $RhCl_2(PPh_3)_2{\cdot}CH_2Cl_2$, we write it as $RhCl_2(PPh_3)_2{\cdot}2CH_2Cl_2$ (**1**).

[4] Chaloner, P. A.; Claver, C.; Hitchcock, P. B.; Masdeu, A. M.; Ruiz, A. *Acta Crystallogr.* **1991**, *C47*, 1307.

[5] These authors also overlooked the fact that there were two CH_2Cl_2 molecules for each molecule of $RhCl(CO)(PPh_3)_2$; thus, the molecular formula of their crystal should be $RhCl(CO)(PPh_3)_2{\cdot}2CH_2Cl_2$ and not $RhCl(CO)(PPh_3)_2{\cdot}CH_2Cl_2$.

[6] (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G. *J. Organomet. Chem.* **1973**, *50*, 227.

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Table I. Summary of Crystallographic Data for $RhCl(CO)(PPh_3)_2{\cdot}2CH_2Cl_2$ (**2**) and $RhCl_2(PPh_3)_2{\cdot}2CH_2Cl_2$ (**1**)[a]

Data Collection Parameters

	2	**1**[a]
formula	$RhCl_5P_2OC_{39}H_{34}$	$RhCl_6P_2C_{38}H_{32}$
fw	860.82	868.27
space group	*Pbca*	*Pcab*
a, Å	20.527 (4)	8.0565 (16)
b, Å	8.054 (4)	20.546 (6)
c, Å	23.343 (4)	23.348 (7)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
V, Å^3	3859 (3)	3865 (2)
Z	4	4
temp, °C	23	21
radiation (monochromated in incident beam)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 69 Å)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å)

Refinement Statistics

	2 modeled as **2a**	**2** modeled as **2b**	**1**[a]
μ(Mo Kα), cm^{-1}	8.96	9.62	8.18
d_{calc}, g/cm^3	1.482	1.494	1.346
R[b]	0.030	0.038	0.063
R_w[c]	0.025	0.033	0.056
quality-of-fit[d]	1.53	2.00	

[a] Taken from ref 2 except for the formula and formula weight, which have been modified to include the correct number of CH_2Cl_2 molecules. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w|F_o| - |F_c|]^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [d] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

one reported by Crabtree for the synthesis of *trans*-$IrCl(CO)(PR_3)_2$ complexes.[9] Previous syntheses of **2** have involved the reduction of $RhCl_3$ in the presence of a CO source.[10] This need not be gaseous CO; in fact, it is well-known that CO can be extracted from organic sources such as aldehydes to give $RhCl(CO)(PPh_3)_2$. The dinuclear Rh(I) complex $[Rh(CO)_2Cl]_2$ also reacts with PPh_3 to form **2** in high yield.[11]

Crystallography. Crystallographic data are summarized in Table I. Refinement of the molecular unit in **2** was carried out on two different models, $RhCl(CO)(PPh_3)_2$ (**2a**) and $RhCl_2(PPh_3)_2$ (**2b**) in the space group *Pbca*. In both cases, the Rh atom resides on an inversion center and the molecule is square planar. Atomic positional parameters and equivalent isotropic thermal parameters for both models are listed in Tables II and III. Important bond distances and angles for **2a** and **2b**, together with those previously reported for $RhCl_2(PPh_3)_2$ (**1**), are tabulated in Table IV. As can be seen from these values, the cell parameters are nearly identical for the CH_2Cl_2 solvate structures of $RhCl(CO)(PPh_3)_2$ and "$RhCl_2(PPh_3)_2$". The only difference is the setting of the space group (*Pbca* versus *Pcab*), which is arbitrary. ORTEP representations of **2** modeled as $RhCl(CO)(PPh_3)_2$ (**2a**) and as $RhCl_2(PPh_3)_2$ (**2b**) are shown in Figures 1 and 2, respectively.

Refinement of the molecule as $RhCl(CO)(PPh_3)_2$ (**2a**), the correct formulation for the compound in the present study, necessarily involves a disorder of the trans CO and Cl groups related by an inversion center. Examples of this CO/Cl disorder have been documented for $RhCl(CO)(PPh_3)_2$ in triclinic and monoclinic crystals[12] and very recently in an independent determination of the orthorhombic CH_2Cl_2 solvate.[4] The Rh–C and C–O bond distances, 1.77 (2) and 1.14 (2) Å, are comparable to those reported for the other isomorphs of **2**.[12]

Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for **2** Modeled as $RhCl(CO)(PPh_3)_2{\cdot}2CH_2Cl_2$ (**2a**)[a]

atom	x	y	z	B
Rh(1)	0.5000	0.0000	0.0000	2.76 (2)
Cl(1)	0.5989 (3)	0.049 (1)	0.0507 (3)	4.0 (4)
P(1)	0.43699 (5)	0.1437 (1)	0.06604 (5)	2.83 (5)
O(1)	0.618 (1)	0.068 (4)	0.064 (1)	5.1 (8)
C(1)	0.4778 (2)	0.2728 (6)	0.1196 (2)	3.0 (2)
C(2)	0.4703 (2)	0.4429 (6)	0.1219 (2)	4.0 (2)
C(3)	0.5019 (3)	0.5352 (6)	0.1636 (2)	5.6 (3)
C(4)	0.5404 (3)	0.4584 (7)	0.2033 (2)	5.5 (3)
C(5)	0.5483 (2)	0.2899 (7)	0.2021 (2)	5.0 (3)
C(6)	0.5173 (2)	0.1961 (6)	0.1603 (2)	3.9 (2)
C(7)	0.3829 (2)	0.2890 (5)	0.0302 (2)	2.8 (2)
C(8)	0.3175 (2)	0.3065 (5)	0.0429 (2)	3.7 (2)
C(9)	0.2800 (2)	0.4212 (7)	0.0139 (2)	4.8 (3)
C(10)	0.3068 (2)	0.5208 (7)	−0.0271 (2)	4.9 (3)
C(11)	0.3719 (2)	0.5049 (7)	−0.0408 (2)	4.6 (2)
C(12)	0.4089 (2)	0.3880 (6)	−0.0127 (2)	3.9 (2)
C(13)	0.3855 (2)	0.0109 (6)	0.1105 (2)	2.9 (2)
C(14)	0.3565 (2)	0.0692 (5)	0.1602 (2)	3.7 (2)
C(15)	0.3188 (2)	−0.0327 (7)	0.1936 (2)	4.3 (3)
C(16)	0.3092 (2)	−0.1952 (7)	0.1783 (2)	4.5 (3)
C(17)	0.3371 (2)	−0.2561 (6)	0.1290 (2)	4.4 (3)
C(18)	0.3754 (2)	−0.1532 (6)	0.0956 (2)	3.6 (2)
C(19)	0.574 (1)	0.027 (4)	0.037 (1)	5 (1)
Cl(2)	0.85953 (9)	0.1302 (2)	0.71672 (8)	9.2 (1)
Cl(3)	0.7401 (1)	0.2499 (3)	0.66586 (6)	9.8 (1)
C(20)	0.8203 (3)	0.204 (1)	0.6562 (3)	10.0 (5)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(8\pi^2/3)[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aba^*b^*)\cos\gamma + 2U_{13}(aca^*c^*)\cos\beta + 2U_{23}(bcb^*c^*)\cos\alpha]$.

Table III. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) and Their Estimated Standard Deviations for **2** Modeled as $RhCl_2(PPh_3)_2{\cdot}2CH_2Cl_2$ (**2b**)[a]

atom	x	y	z	B
Rh(1)	0.5000	0.0000	0.0000	2.74 (2)
Cl(1)	0.6004 (1)	0.0497 (3)	0.0519 (1)	9.7 (2)
P(1)	0.43705 (7)	0.1439 (2)	0.06609 (6)	2.77 (6)
C(1)	0.4778 (2)	0.2726 (7)	0.1195 (2)	2.9 (3)
C(2)	0.4705 (3)	0.4425 (8)	0.1219 (3)	3.9 (3)
C(3)	0.5019 (4)	0.5351 (8)	0.1633 (3)	5.5 (4)
C(4)	0.5402 (3)	0.458 (1)	0.2032 (3)	5.4 (4)
C(5)	0.5484 (3)	0.289 (1)	0.2020 (3)	4.9 (4)
C(6)	0.5173 (3)	0.1959 (7)	0.1602 (2)	3.9 (3)
C(7)	0.3830 (2)	0.2884 (7)	0.0303 (2)	2.8 (3)
C(8)	0.3174 (3)	0.3058 (7)	0.0429 (2)	3.6 (3)
C(9)	0.2798 (3)	0.4209 (9)	0.0138 (3)	4.6 (4)
C(10)	0.3063 (3)	0.5206 (9)	−0.0271 (3)	4.9 (4)
C(11)	0.3714 (3)	0.5039 (9)	−0.0406 (2)	4.7 (3)
C(12)	0.4090 (3)	0.3874 (7)	−0.0122 (2)	3.9 (3)
C(13)	0.3855 (2)	0.0109 (8)	0.1101 (2)	2.8 (2)
C(14)	0.3563 (3)	0.0692 (7)	0.1601 (2)	3.8 (3)
C(15)	0.3186 (3)	−0.0333 (8)	0.1936 (2)	4.2 (3)
C(16)	0.3090 (3)	−0.1956 (9)	0.1783 (3)	4.4 (4)
C(17)	0.3371 (3)	−0.2551 (8)	0.1289 (3)	4.4 (3)
C(18)	0.3755 (3)	−0.1530 (7)	0.0954 (2)	3.5 (3)
Cl(2)	0.8595 (1)	0.1305 (3)	0.7167 (1)	9.2 (1)
Cl(3)	0.7401 (1)	0.2497 (3)	0.66583 (8)	9.7 (1)
C(20)	0.8197 (4)	0.205 (1)	0.6559 (3)	9.9 (6)

[a] Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(8\pi^2/3)[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aba^*b^*)\cos\gamma + 2U_{13}(aca^*c^*)\cos\beta + 2U_{23}(bcb^*c^*)\cos\alpha]$.

We now turn to the centerpiece of this report, namely that a least-squares refinement of $RhCl(CO)(PPh_3)_2$ modeled as $RhCl_2(PPh_3)_2$ (**2b**) works exceedingly well. This fact is supported by the resulting metric and thermal parameters after convergence (Tables I–III). The bond distances and angles are comparable

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Table IV. Selected Bond Distances (Å) and Angles (deg) for **2** Modeled as $RhCl(CO)(PPh_3)_2$ (**2a**) and $RhCl_2(PPh_3)_2$ (**2b**) and Those Reported for $RhCl_2(PPh_3)_2$ (**1**)[a]

	$RhCl(CO)(PPh_3)_2$ (**2a**)	$RhCl_2(PPh_3)_2$ (**2b**)	$RhCl_2(PPh_3)_2$ (**1**)[a]
Rh–P	2.322 (1)	2.322 (1)	2.323 (4)
Rh–Cl	2.382 (1)	2.425 (3)	2.428 (4)
Rh–C	1.77 (1)		
C–O	1.14 (2)		
P–Rh–Cl	93.6 (1)	93.37 (6)	93.5 (1)
P–Rh–P′	180	180	180
Cl–Rh–Cl′		180	180
P–Rh–C	95 (1)		

[a] From ref 2.

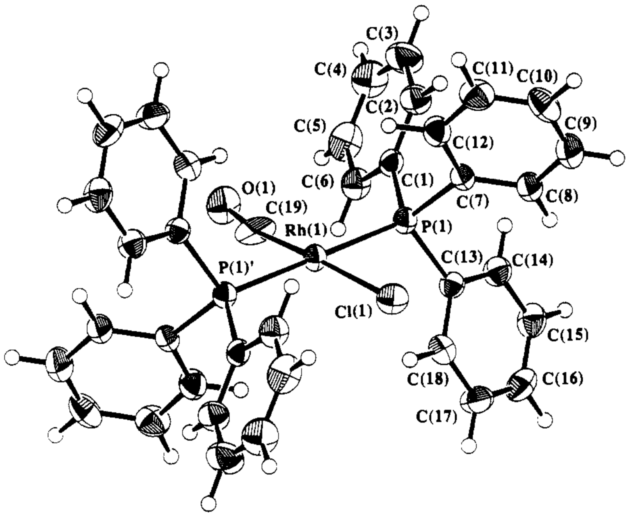

Figure 1. ORTEP representation of **2** modeled as $RhCl(CO)(PPh_3)_2$ (**2a**). Thermal ellipsoids are shown at the 40% probability level.

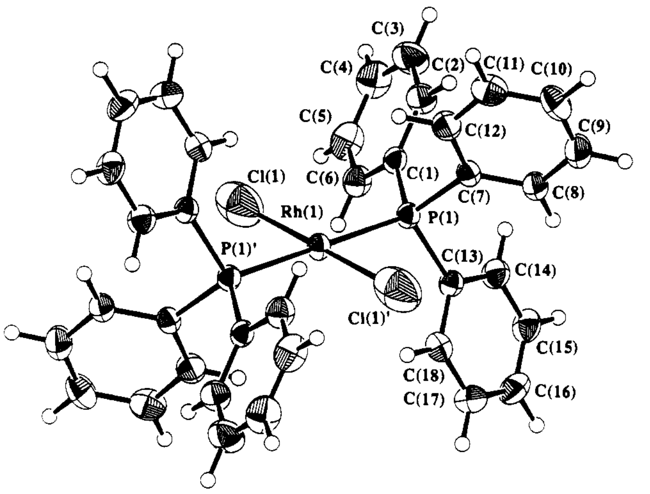

Figure 2. ORTEP drawing of **2** modeled as $RhCl_2(PPh_3)_2$ (**2b**). Thermal ellipsoids are represented at the 40% level.

to those of the correct $RhCl(CO)(PPh_3)_2$ (**2a**) model. One notable exception is the Rh–Cl bond distance, which is significantly longer in the dichloride model (2.425 (3) Å) than in the chloro-carbonyl model (2.382 (5) Å). An abnormally long Rh–Cl distance was noted in the structure report of "$RhCl_2(PPh_3)_2$" but was not explained. We propose that the unusually long Rh–Cl bond is a direct consequence of the chlorine atom compensation for the electron density of the oxygen atom of the CO ligand. The effect on the Cl atom of the unassigned electron density is dramatically illustrated by the elongated appearance of the Cl thermal ellipse (Figure 2) and the relatively high thermal parameter. After final refinement, only a small amount of residual electron density (0.63 e/Å^3) appeared in the map near the position of the chlorine atom, underscoring the ease with which a CO group can be crystallographically modeled as a Cl atom.

Discussion

The aim of this paper is to compare the spectral and structural properties of the orthorhombic crystal form of $RhCl(CO)(PPh_3)_2$ to those reported by OMH for a sample formulated as $RhCl_2(PPh_3)_2$. Our crystal structure of $RhCl(CO)(PPh_3)_2{\cdot}2CH_2Cl_2$ is actually the second determination of the orthorhombic form; shortly after the paper of OMH and during the course of this investigation, another group communicated the crystal structure of the identical dichloromethane solvate, but no relevance or connection to the present topic was mentioned.[4]

There are several major reasons why we question that the bulk of the sample isolated by OMH is the Rh(II) complex $RhCl_2(PPh_3)_2$. Arguments that support our conclusion are put forth in the following sections.

i. The sample of "$RhCl_2(PPh_3)_2$" was reported as an air-stable yellow solid that exhibits both resolved, unshifted ^1H NMR and an EPR signal. These properties are in direct contrast to those reported for all other known Rh(II) complexes, including the closely related $RhCl_2\{P(o\text{-tolyl})_3\}_2$ and the recently reported $RhCl_2\{P(i\text{-Pr})_3\}_2$.[13,14] Square-planar Rh(II) complexes with bulky tertiary phosphines are blue-green or red-purple in color and exhibit NMR spectra that are indicative of paramagnetism.[13b,d,14] In the case of $RhCl_2\{P(i\text{-Pr})_3\}_2$, the ^1H resonances are broad and occur at $\delta = +8$ and 31 ppm.[14] The reported ^1H NMR spectrum of "$RhCl_2(PPh_3)_2$" with resonances at $\delta = +7.01$ and 7.95 ppm is consistent with a diamagnetic Rh(I) species and is identical to that observed for $RhCl(CO)(PPh_3)_2$ (**2**). There is no reasonable explanation as to why PPh_3 would not experience proton relaxation when attached to a paramagnetic Rh(II) center given that all other known phosphine complexes of mononuclear Rh(II) are dramatically affected. As for the EPR signal observed by OMH, it could easily be due to a very minor paramagnetic impurity in the sample. No spin counting was mentioned, so it is not necessary to conclude that the bulk of the sample was paramagnetic.

ii. The reported infrared and mass spectrometry data for **1** are not inconsistent with the formulation of **1** as $RhCl(CO)(PPh_3)_2$ (**2**). The five absorptions reported in the far-IR for **1** are at the same energies as those found for **2**.[15] The fragments reported for the FAB mass spectrum of "$RhCl_2(PPh_3)_2$" are also found in the FAB analysis of $RhCl(CO)(PPh_3)_2$, although peaks corresponding to $Rh(PPh_3)_2(CO)^+$ (m/z = 655) and $RhCl(CO)(PPh_3)_2^+$ (m/z = 692) were obviously not reported. These species, however, are present at very low relative abundances and could have easily been overlooked. It is important to note that the parent ion peak $RhCl_2(PPh_3)_2^+$ was not observed in the mass spectrum of **1**.

iii. Finally, we were unconvinced by the reported crystal structure of $RhCl_2(PPh_3)_2$ (**1**). The structure of the compound is precisely like that of a square-planar d^8 molecule. It is highly unlikely that mononuclear d^7 Rh(II) complexes would be stable in this geometry, on the basis of the demonstrated tendency for such species to disproportionate to Rh(I) and Rh(III) or to form metal–metal bonds unless ligands with large cone angles are present.[16] One would expect the crystal structure of **1**, with a phosphine that is not extremely bulky, to reflect some fundamental

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(13) (a) Bennett, M. A.; Longstaff, P. A. *J. Am. Chem. Soc.* **1969**, *91*, 6266. (b) Masters, C.; Shaw, B. L. *J. Chem. Soc. A.* **1971**, 3679. (c) Moers, F. G.; De Jong, J. A. M.; Beaumont, P. M. H. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1915. (d) Empsall, H. D.; Hyde, E. M.; Pawson, D.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1292.

(14) Harlow, R. L.; Thorn, D. L.; Baker, T.; Jones, N. L. *Inorg. Chem.* **1992**, *31*, 993.

(15) Obviously the presence of **2** could be confirmed by its carbonyl stretching vibration; unfortunately, mid-IR data were not reported by OMH for $RhCl_2(PPh_3)_2$ (**1**). However, the authors have since personally communicated the presence of a CO stetch in the IR spectrum of **1** that corresponds to $RhCl(CO)(PPh_3)_2$.

(16) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *28*, 73.

reason for its extraordinary stability; we found none in the ORTEP diagram provided for "RhCl$_2$(PPh$_3$)$_2$". We did, however, notice the elongated shapes of the Cl thermal ellipsoids and the unusually long Rh–Cl bond. Both observations point to electron density along the Rh–Cl bond vector that has not been accounted for by the model. The long Rh–Cl bond of 2.425 (3) Å is even more suspicious in light of the recent crystal structure of the related Rh(II) complex RhCl$_2${P(*i*-Pr)$_3$}$_2$ for which Rh–Cl is 2.28 Å.[14] Disorder between trans chloride and carbonyl groups effectively masks the presence of the CO ligand unless one is explicitly looking for it. Perhaps the most striking similarity, at least visually, between **1** and **2** modeled as "RhCl$_2$(PPh$_3$)$_2$" is found in an examination of the ORTEP diagrams for the two structures (see Figure 2 in the present work and Figure 1 in ref 2). Both drawings reveal that the thermal ellipsoid of the bound Cl is elongated along the Rh–Cl bond axis, implying that a chloride–carbonyl disorder may also be present in the structure of **1**.

Concluding Remarks

The striking similarities in crystal structures and spectroscopic data for RhCl$_2$(PPh$_3$)$_2$ (**1**) and RhCl(CO)(PPh$_3$)$_2$ (**2**) modeled as RhCl$_2$(PPh$_3$)$_2$ (**2b**) provide strong evidence for the reformulation of the structure of RhCl$_2$(PPh$_3$)$_2$ reported by Ogle et al. as the rhodium(I) carbonyl complex RhCl(CO)(PPh$_3$)$_2$ or as a crystal containing significant amounts of this Rh(I) species cocrystallized with RhCl$_2$(PPh$_3$)$_2$. The tendency for mononuclear Rh and Ir complexes to crystallize in forms that involve disorder of Cl and CO ligands across an inversion center is well documented.[4,12,17] In some classes of dinuclear compounds, one encounters cases in which CO and Cl are so thoroughly disordered that it is extremely difficult to distinguish between the two, even in situations where the presence of CO is known.[18] Such structures refine to excellent agreement factors without including CO in the refinement. The present study is a prime example of such a case. Comparison of the two models **2a** and **2b** clearly argues against the use of crystallography as a tool for distinguishing between RhCl(CO)(PPh$_3$)$_2$ and RhCl$_2$(PPh$_3$)$_2$, particularly in the cases where there is no logical reason to suspect the presence of CO. We note that such a situation, wherein a compositional disorder renders Cl and O atoms indistinguishable, is evidently responsible for the so-called "bond-stretch isomerism" observed in the *cis-mer*-MoOCl$_2$(PR$_3$)$_3$ systems.[19] Crystallographic disorders between Cl and CN groups have also been documented in the recent literature.[20]

Finally, we note that OMH did not report the use of CO-containing starting materials or CO(g) in the chemistry that led to the isolation of **1**. We offer one possible scenario as to how CO could have been introduced; the Rh(I) starting material used by OMH in their study, viz., [Rh(cod)Cl]$_2$, is usually prepared by a route that involves acetaldehyde as a byproduct. If the sample was not entirely free of acetaldehyde, the RhCl(PPh$_3$)$_3$ produced in the reaction of [Rh(cod)Cl]$_2$ with PPh$_3$ would readily form RhCl(CO)(PPh$_3$)$_2$.[1]

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Supplementary Material Available: Full listing of positional parameters, bond distances, bond angles, and anisotropic displacement parameters for structure **2** modeled as **2a** and **2b** (18 pages). Ordering information is given on any current masthead page.

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