Table I. Principal Components, Isotropic Values, and Anisotropies of the ^{13}C Shielding Tensors for (η-C_6H_6)Cr$(CO)_2$(CS) and (η-C_6H_6)Cr$(CO)_3$[a,b]

species		σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	δ_i	η
(η-C_6H_6)Cr$(CO)_2$(CS)	CS[c]	533	517	−5	530	350	0.05
	CS[d]	532	500	0	521	347	0.09
	ring[d]	161	145	4	149	103	0.16
(η-C_6H_6)Cr$(CO)_3$	CO[c]	382	382	−68	450	239	0
	CO[d]	382	382	−63	445	234	0
	ring[e]	152	138	7	138	99	0.15
CS_2[f]		333	333	−92	425	121	0
OCS[g]		275	275	−90	365	153	0
NCS^-[h]		240	240	−81	321	133	0

[a] Values of principal elements are in ppm, relative to external TMS. [b] Uncertainties are ±10 and ±15 ppm for the data obtained from static and CP-MAS spectra, respectively. [c] Obtained from static spectra. [d] Obtained from CP-MAS spectra. [e] From ref 23. [f] From ref 15. [g] From ref 16. [h] From ref 17.

it is in $Cr(CO)_6$[13] may account for this difference, since the additional π-back-bonding may either slightly reduce the excitation energy (ΔE) or increase the population on the CO π^* orbitals,[14] resulting in the downfield shift of $\sigma_\perp{}^p$.

The three components of the ^{13}C shift tensor of the thiocarbonyl group in (η-C_6H_6)Cr$(CO)_2$(^{13}CS) are nondegenerate, but the powder pattern is still very close to axial symmetry ($\eta = 0.05$). The shift anisotropy is much larger than that for carbonyls. The ^{13}C chemical shift tensor of the free CS molecule is not known, but the elements of the chemical shift tensors for several linear molecules containing C═S double bonds have been reported (Table I).[15–17] The $\sigma_\parallel$ values for these compounds are about −90 ppm, while the σ_{33} value for the CS ligand in (η-C_6H_6)Cr$(CO)_2$(CS) is 0 ppm. This large difference may indicate a breakdown in the pseudolinear approximation (vide infra) for metal-bound CS, possibly because of interactions between the CS ligand and the neighboring CO groups.

Since the ^{13}C signal for (η-C_6H_6)Cr$(CO)_2$(CS) has a very small asymmetry parameter, its shift tensor can be considered (in order to make a comparison with the CO analogue) as having axial symmetry with σ_{11} equal to $\sigma_\perp$. The chief difference in the chemical shift tensors of the CS and CO groups is that the $\sigma_\perp$ component for thiocarbonyl is much more deshielded. The magnitudes of the perpendicular components (533 ppm) and anisotropy (530 ppm) observed for the CS group in (η-C_6H_6)Cr$(CO)_2$(CS) are the largest values yet reported for a ^{13}C nucleus. The large $\sigma_\perp$ component can be explained by the paramagnetic term, eq 2, where the difference in excitation energies between the CS and CO ligands is the dominant term. The ΔE term can be associated with the 5s → 2p transition of CO. Molecular orbital calculations[18,19] have shown that, in the CS molecule, the carbon "lone-pair" 7s orbital is higher in energy than the corresponding 5s orbital in CO, due to the lower stability of sulfur atomic functions. On the other hand, the interaction between the carbon and sulfur p orbitals is also reduced, with the result that the π^* (3p) orbitals are lower in energy compared to the corresponding π^* (2p) orbitals in CO. Therefore, the 7s → 3p excitation transition energy in CS is smaller than the 5s → 2p transition energy in CO. Molecular orbital calculations for (η-C_6H_6)Cr$(CO)_2$(CS) have established that this is also true when the CS and CO ligands coordinate to a metal, and this result has been used to interpret ^{13}C chemical shift data in solution.[20] It has also been suggested[2] that when CO is complexed to a metal, the metal d orbitals stabilize the excited state formed from the 5s → 2p transition and lower the excitation energy, which results in an increase in the paramagnetic contribution. This effect will increase with increasing d-orbital energy. It is known that, for CS, in addition to the expected $\sigma + \pi$ synergistic interaction, there is an interaction between the filled π-bonding orbitals of CS and the filled metal d orbitals.[19,21] This interaction increases the energy of the antibonding combination, which is mainly metal d in character.[21] Overall, these properties lead to a smaller ΔE term for CS than for CO, thus accounting for the large $\sigma_\perp$ value. Although ΔE is the predominant term in eq 2, there are other factors to be considered.[22] The much better π-acceptor ability of the CS group increases the electron density perpendicular to the CS-bond axis, and this may also contribute to $\sigma_\perp{}^p$.

The chemical shift tensor of the aromatic carbons in the thiocarbonyl complex was measured from the spinning sideband intensities (Table I). The shift anisotropy of the ring carbons in the related tricarbonyl complex has been reported,[23] and the effect of coordinating benzene to the metal, such as changing the directions of the principal components, has been discussed. The three components for both complexes are almost identical, within experimental error, indicating that substitution of CS for CO has little effect on the ring carbon chemical shift anisotropy.

Acknowledgment. This research was supported by grants to I.S.B. and D.F.R.G. from the NSERC (Canada) and FCAR (Quebec).

Registry No. (η-C_6H_6)Cr$(CO)_2$(^{13}CO), 137916-08-6; (η-C_6H_6)Cr$(CO)_2$(^{13}CS), 79483-61-7.

---

(13) English, A. M.; Plowman, K. R.; Butler, I. S. *Inorg. Chem.* **1982**, *21*, 338.
(14) Brown, D. A.; Rawlinson, R. M. *J. Chem. Soc. A* **1969**, 1530.
(15) Pines, A.; Rhim, W.-K.; Waugh, J. S. *J. Chem. Phys.* **1971**, *54*, 5438.
(16) Beeler, A. J.; Orendt, A. M.; Grant, D. M.; Cutts, P. W.; Michl, J.; Zilm, K. W.; Downing, J. W.; Facelli, J. C.; Schindler, M. S.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1984**, *106*, 7672.
(17) Dickons, R. M.; McKinnon, M. S.; Britten, J. F.; Wasylishen, R. E. *Can. J. Chem.* **1987**, *65*, 941.
(18) Richards, W. G. *Trans. Faraday Soc.* **1967**, *63*, 275.
(19) Lichtenberger, D. L.; Fenske, R. F. *Inorg. Chem.* **1976**, *15*, 2015.
(20) Czech, P. T.; Ye, X.-Q.; Fenske, R. F. *Organometallics* **1990**, *9*, 2016.
(21) Hubbard, J. L.; Lichtenberger, D. L. *Inorg. Chem.* **1980**, *19*, 3866.
(22) Brown, D. A.; Chester, J. P.; Fitzpatrick, N. J.; King, I. J. *Inorg. Chem.* **1977**, *16*, 2497.
(23) Maricq, M. M.; Waugh, J. S.; Fletcher, J. L.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 6902.

Contribution No. 5922 from Central Research and Development,
E. I. du Pont de Nemours and Company,
Wilmington, Delaware, 19880-0228

$[(t\text{-Bu})_3P]_2$Rh(CO)Cl: A Simple Rhodium(I) Complex Which Is Not Square-Planar?

Richard L. Harlow,* Stephen A. Westcott, David L. Thorn, and R. Thomas Baker

Received July 3, 1991

Introduction

When Schumann, Heisler, and Pickardt[1] (hereafter SHP) originally determined the structure of the title compound, they noted that the coordination geometry was unusual. In particular, the four coordinating atoms adopted a flattened-tetrahedral

---

(1) Schumann, H.; Heisler, M.; Pickardt, J. *Chem. Ber.* **1977**, *110*, 1020–1026.

Table I. Crystal Structure Information for the Two $[(t\text{-Bu})_3P]_2Rh(CO)Cl$ Crystalline Forms

	unsolvated compd	toluene solvate
formula	$C_{25}H_{54}ClOP_2Rh$	$C_{32}H_{62}ClOP_2Rh$
fw	571.02	663.16
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)
a, Å	8.426 (3)	12.861 (5)
b, Å	22.839 (7)	16.379 (6)
c, Å	14.742 (3)	16.467 (6)
β, deg	91.54 (2)	
V, Å^3	2835.9	3468.8
Z	4	4
ρ_{obsd}, g cm^{-3}	1.346	1.276
μ, cm^{-1}	8.18	6.77
transm factors	0.77–0.82	0.73–0.74
R^a	0.031	0.042
$R_w{}^a$	0.030	0.041

$^a R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w(F_o) = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$.

conformation instead of the square-planar geometry expected for a four-coordinate Rh(I) complex. The trans P–Rh–P and Cl–Rh–C angles, for example, were reported to be 162.3 (5) and 148.7 (3)°, respectively. From a crystallographic viewpoint, there were two other worrisome features besides the deviant coordination geometry: (1) the Rh–C–O angle was bent, 164.7 (8)°, with a very short C–O bond length of 0.987 (11) Å; (2) the β angle of the monoclinic cell differed from 90° by only 1 standard deviation, 90.04 (4)°.

Although four-coordinate rhodium(I) complexes with "flattened"-tetrahedral geometry are known for compounds with at least three bulky phosphines,[2] the SHP structure stood out as the only example of such a conformation among complexes with only two bulky phosphines. In addition, the magnitude of the distortion was equivalent to the most distorted complexes among the trisphosphines. Since the time of the SHP publication, a number of structures containing a $P_2Rh(CO)Cl$ moiety have been reported: P = triphenylphosphine,[3] tris(*p*-fluorophenyl)phosphine,[4] and diphenylmethylphosphine;[5] P_2 = ((μ-bis(diphenylphosphino)methyl)phenylarsine),[6] (μ-bis(diphenylphosphino)methane),[7] (*N*,*N'*-bis(2-(diphenylphosphino)phenyl)propane-1,3-diamine),[8] and (bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene).[9] These seven structures all have relatively uniform, square-planar coordination geometries with the following ranges: Rh–P, 2.310–2.341 Å; Rh–Cl, 2.363–2.395 Å; Rh–C, 1.785–1.820 Å; P–Rh–P, 173.6–179.5°; Cl–Rh–C, 168.3–178.7°. A more detailed comparison of the SHP structure now shows that not only are the angles about the Rh atoms unusual but the Rh–P (2.433 (1) and 2.435 (1) Å), Rh–Cl (2.412 (1) Å) and Rh–C (1.838 (9) Å) distances are all longer than expected. Although the unusual geometry could be arbitrarily ascribed to steric factors, a reinvestigation of the structure using low-temperature, X-ray diffraction data was thought to be in order. During the crystal selection process, it was noted that two crystalline forms were present; data were collected on both forms, one of which was determined to be a toluene solvate. This provided us an additional opportunity to compare the structure of this complex in different packing environments.

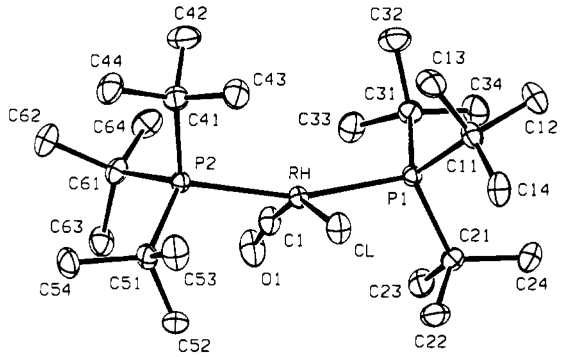

Figure 1. ORTEP drawing (50% Ellipsoids) of $[(t\text{-Bu})_3P]_2Rh(CO)Cl$.

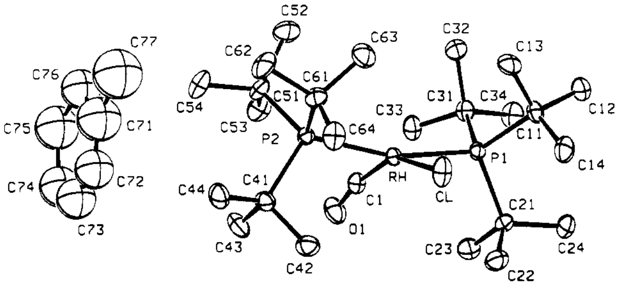

Figure 2. ORTEP drawing (50% Ellipsoids) of $[(t\text{-Bu})_3P]_2Rh(CO)Cl\cdot C_6H_5CH_3$.

Experimental Section

Synthesis. $[(t\text{-Bu})_3P]_2Rh(CO)Cl$. A solution of 380 mg (1.9 mmol) of $P(t\text{-Bu})_3$ in 20 mL of toluene was added dropwise to a solution of 175 mg (0.45 mmol) of $[Rh(CO)_2Cl]_2$ in 20 mL of toluene. The solution turned orange to red-orange. After being stirred for 1 h, the solution was concentrated in vacuo to 5 mL and cooled at −30 °C for 24 h. The resulting orange and red crystals were filtered off, washed with 5 mL of cold (−30 °C) pentane, and dried in vacuo, yielding 269 mg. A second crop of 89 mg obtained similarly brought the total yield to 358 mg (70% based on the unsolvated complex).

Structure Determinations. Crystals suitable for the X-ray diffraction studies were recrystallized from a toluene solution. Data for both structures were collected on a Syntex P3 diffractometer with the crystals cooled to −100 °C (graphite monochromator, Mo Kα radiation, λ = 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. The β angle of the unsolvated crystal clearly indicates that the cell is indeed monoclinic. A summary of the crystal data is given in Table I.

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; neither crystal 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 and empirical corrections for absorption were made in both cases.

The refinement and analysis of the two structures were carried out using a package of local programs.[10] The atomic scattering factors were taken from the tabulations of Cromer and Waber; anomalous dispersion corrections were by Cromer.[11] 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 structure of the title compound was refined from the coordinates provided by SHP. All of the non-hydrogen atoms were refined with anisotropic thermal parameters; all hydrogens were refined with isotropic thermal parameters. The hydrogen atoms bound to C(64) were found to be 2-fold disordered and refined accordingly. The atomic coordinates are given in Table II. The structure of the toluene solvate was solved by direct methods (MULTAN).[12] All of the non-hydrogen atoms were

---

(2) Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, *16*, 655–660. Thorn, D. L.; Harlow, R. L. *Inorg. Chem.* **1990**, *29*, 2017–2019 and references therein.

(3) Ceriotti, A.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1983**, *247*, 345–350. Rheingold, A. L.; Geib, S. J. *Acta Crystallogr., Sect. C* **1987**, *43*, 734–786.

(4) Monge, A.; Gutierrez-Puebla, E.; Heras, J. V.; Pinilla, E. *Acta Crystallogr., Sect. C* **1983**, *39*, 446–448.

(5) Dahan, F.; Choukroun, R. *Acta Crystallogr., Sect. C* **1985**, *41*, 704–706.

(6) Balch, A. L.; Ghedini, M.; Oram, D. E.; Reedy, P. E., Jr. *Inorg. Chem.* **1987**, *26*, 1223–1229.

(7) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *18*, 2700.

(8) Cooper, M. K.; Duckworth, P. A.; Hambley, T. W.; Organ, G. J.; Henrick, K.; McPartlin, M.; Parekh, A. *J. Chem. Soc., Dalton Trans.* **1989**, 1067–1073.

(9) Bachechi, F.; Zambonelli, L.; Venanzi, L. M. *Helv. Chim. Acta* **1977**, *60*, 2815–2823.

(10) Calabrese, J. C. Central Research and Development, E. I. du Pont de Nemours and Co., Wilmington, DE, 1991.

(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1

(12) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368–376.

Table II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $[(t\text{-Bu})_3P]_2Rh(CO)Cl$

atom	*x*	*y*	*z*	B_{equ}, Å^2
Rh(1)	0.08569 (2)	0.14574 (1)	0.29219 (1)	1.268 (4)
Cl(1)	0.33801 (8)	0.18641 (3)	0.25552 (5)	2.18 (1)
P(1)	0.00299 (7)	0.23050 (3)	0.37795 (4)	1.28 (1)
P(2)	0.15921 (7)	0.04659 (3)	0.25070 (4)	1.24 (1)
O(1)	−0.2408 (2)	0.1251 (1)	0.2293 (1)	2.8 (1)
C(1)	−0.1168 (3)	0.1302 (1)	0.2630 (2)	2.0 (1)
C(11)	0.1771 (3)	0.2667 (1)	0.4448 (2)	1.8 (1)
C(12)	0.1302 (4)	0.3063 (1)	0.5244 (2)	2.7 (1)
C(13)	0.2856 (4)	0.2175 (2)	0.4830 (2)	2.5 (1)
C(14)	0.2808 (4)	0.3045 (1)	0.3839 (2)	2.4 (1)
C(21)	−0.0899 (3)	0.2886 (1)	0.2999 (2)	1.7 (1)
C(22)	0.0123 (4)	0.2912 (1)	0.2153 (2)	2.5 (1)
C(23)	−0.2571 (4)	0.2709 (1)	0.2667 (2)	2.3 (1)
C(24)	−0.1034 (4)	0.3505 (1)	0.3402 (2)	2.4 (1)
C(31)	−0.1507 (3)	0.2101 (1)	0.4667 (2)	1.8 (1)
C(32)	−0.0684 (4)	0.1756 (1)	0.5446 (2)	2.7 (1)
C(33)	−0.2783 (4)	0.1679 (1)	0.4288 (2)	2.4 (1)
C(34)	−0.2387 (4)	0.2629 (1)	0.5064 (2)	2.4 (1)
C(41)	0.3024 (3)	0.0173 (1)	0.3431 (2)	1.9 (1)
C(42)	0.2123 (4)	0.0054 (2)	0.4294 (2)	2.8 (1)
C(43)	0.4258 (4)	0.0643 (1)	0.3687 (2)	2.5 (1)
C(44)	0.3940 (4)	−0.0385 (1)	0.3181 (2)	2.6 (1)
C(51)	0.2597 (3)	0.0419 (1)	0.1354 (2)	1.8 (1)
C(52)	0.1681 (4)	0.0848 (1)	0.0726 (2)	2.5 (1)
C(53)	0.4314 (4)	0.0630 (2)	0.1422 (2)	2.7 (1)
C(54)	0.2634 (4)	−0.0190 (1)	0.0905 (2)	2.4 (1)
C(61)	−0.0171 (3)	−0.0074 (1)	0.2459 (2)	1.7 (1)
C(62)	0.0290 (4)	−0.0728 (1)	0.2484 (2)	2.5 (1)
C(63)	−0.1173 (4)	0.0020 (1)	0.1583 (2)	2.3 (1)
C(64)	−0.1269 (4)	0.0028 (2)	0.3269 (2)	2.4 (1)

Table III. Fractional Coordinates and Isotropic or Equivalent Isotropic Thermal Parameters for $[(t\text{-Bu})_3P]_2Rh(CO)Cl\cdot C_6H_5CH_3$

atom	*x*	*y*	*z*	$B_{iso/equ}$, Å^2
Rh(1)	0.27958 (3)	0.37720 (2)	0.13801 (2)	1.35 (1)
Cl(1)	0.3682 (1)	0.4015 (1)	0.2628 (1)	2.61 (3)
P(1)	0.2575 (1)	0.5212 (1)	0.1085 (1)	1.39 (3)
P(2)	0.2497 (1)	0.2338 (1)	0.1671 (1)	1.41 (3)
O(1)	0.3066 (3)	0.3408 (2)	−0.0344 (2)	2.7 (1)
C(1)	0.2833 (5)	0.3549 (3)	0.0325 (3)	1.8 (1)
C(11)	0.2248 (5)	0.5827 (3)	0.2054 (3)	1.8 (1)
C(12)	0.1734 (5)	0.6654 (3)	0.1911 (4)	2.4 (1)
C(13)	0.1534 (5)	0.5317 (4)	0.2594 (3)	2.4 (1)
C(14)	0.3241 (5)	0.6004 (4)	0.2558 (4)	2.6 (1)
C(21)	0.3790 (4)	0.5663 (3)	0.0606 (3)	1.9 (1)
C(22)	0.4731 (4)	0.5290 (4)	0.1044 (4)	2.6 (1)
C(23)	0.3892 (5)	0.5393 (4)	−0.0276 (4)	2.7 (1)
C(24)	0.3886 (5)	0.6606 (3)	0.0631 (4)	2.5 (1)
C(31)	0.1428 (4)	0.5392 (3)	0.0363 (3)	1.8 (1)
C(32)	0.0406 (4)	0.5214 (4)	0.0806 (4)	2.4 (1)
C(33)	0.1428 (4)	0.4807 (3)	−0.0364 (3)	2.2 (1)
C(34)	0.1368 (4)	0.6263 (4)	0.0002 (3)	2.4 (1)
C(41)	0.3643 (4)	0.1680 (3)	0.1362 (4)	2.0 (1)
C(42)	0.4646 (4)	0.2152 (4)	0.1593 (4)	2.4 (1)
C(43)	0.3691 (5)	0.1568 (4)	0.0447 (4)	2.7 (1)
C(44)	0.3696 (5)	0.0826 (3)	0.1735 (4)	2.7 (1)
C(51)	0.1291 (4)	0.1939 (3)	0.1116 (3)	2.0 (1)
C(52)	0.0316 (4)	0.2338 (4)	0.1488 (4)	3.0 (2)
C(53)	0.1267 (5)	0.2234 (4)	0.0224 (4)	2.6 (1)
C(54)	0.1168 (5)	0.1012 (4)	0.1104 (4)	3.0 (1)
C(61)	0.2245 (5)	0.2140 (3)	0.2810 (3)	2.1 (1)
C(62)	0.1679 (5)	0.1320 (4)	0.3012 (4)	3.1 (1)
C(63)	0.1568 (5)	0.2841 (4)	0.3144 (4)	2.8 (1)
C(64)	0.3249 (5)	0.2139 (4)	0.3307 (3)	2.5 (1)
C(71)	0.2435 (11)	−0.1142 (9)	0.2406 (8)	9.4 (3)
C(72)	0.3356 (9)	−0.1260 (8)	0.2229 (7)	7.2 (2)
C(73)	0.3624 (9)	−0.1340 (7)	0.1540 (7)	7.4 (3)
C(74)	0.3054 (8)	−0.1297 (8)	0.0834 (7)	7.7 (3)
C(75)	0.1892 (10)	−0.1218 (9)	0.0865 (9)	9.2 (3)
C(76)	0.1522 (8)	−0.1104 (7)	0.1747 (7)	7.3 (3)
C(77)	0.1902 (12)	−0.1068 (10)	0.3215 (10)	11.7 (5)

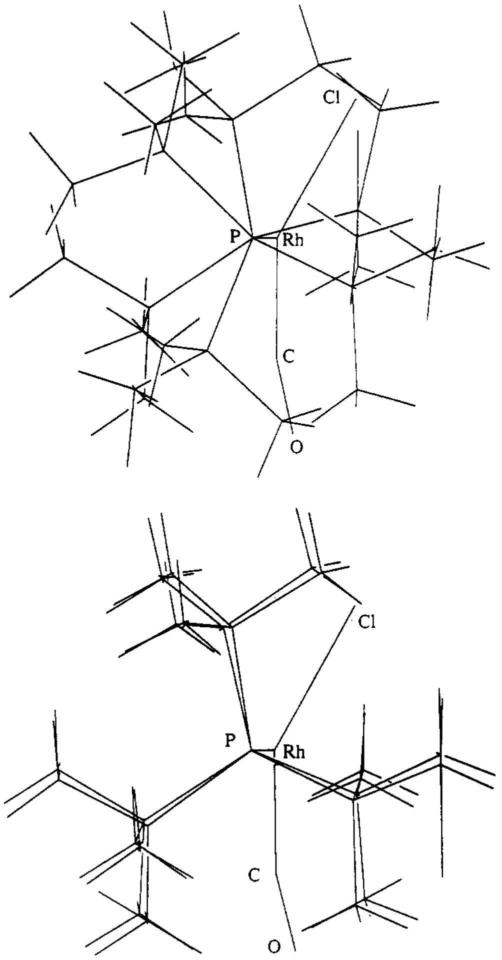

Figure 3. Projected views of the (a, top) unsolvated and (b, bottom) toluene-solvated complexes along the P(1)- -P(2) vector.

initially refined with anisotropic thermal parameters, but several of the toluene carbon atoms had unrealistic parameters. The carbons of the toluene molecule were subsequently refined with isotropic thermal parameters. Refinement of the occupation factors of these seven carbon atoms showed that they were fully occupied. The hydrogen atoms of the *tert*-butyl groups were added to the refinement, but they too tended, in some cases, toward unrealistic values. Clearly, the quality of the data had been impaired by the thermal motions of the toluene molecule. In the final cycles of the refinement, the *tert*-butyl hydrogen atoms were included in idealized positions. The hydrogen atoms of the toluene molecule were not included at all. The final atomic coordinates are given in Table III. The enantiomorphic structure converged at somewhat higher *R* values: 0.045 and 0.043 for *R* and R_w, respectively.

Results and Discussion

Bond distances and angles for the two structures, unsolvated and solvated, are listed in Tables IV and V. For easy comparison, the values of SHP are also given. Figures 1 and 2 are the corresponding ORTEP drawings for the two forms and illustrate the atom-numbering schemes. Although some of the bond distances are more in line with expected values, notably Rh–Cl and Rh–C, the most unusual aspects of the molecular geometry first noted by SHP remain. In particular the P–Rh–P, Cl–Rh–C and Rh–C–O angles are clearly far from the expected 180°. The coordination geometry about the Rh atom is distinctly that of a flattened tetrahedron. Furthermore, this unusual geometry is apparently inherent in the molecular geometry, i.e. independent of packing forces, since it is virtually the same in the two crystalline forms. In fact, the only significant difference in the geometry of the complex in the two forms is the relative orientation of the two phosphine ligands (see Figure 3). In the solvated form, the two phosphines adopt an eclipsed conformation whereas in the nonsolvated form, the phosphine containing P(2) has rotated some 40° around the Rh–P bond with further rotations occurring about the P(2)–C bonds. This indicates that, in spite of the potential steric interactions, there is some flexibility in the geometry of the molecule; i.e., it is not locked absolutely into only one conformation

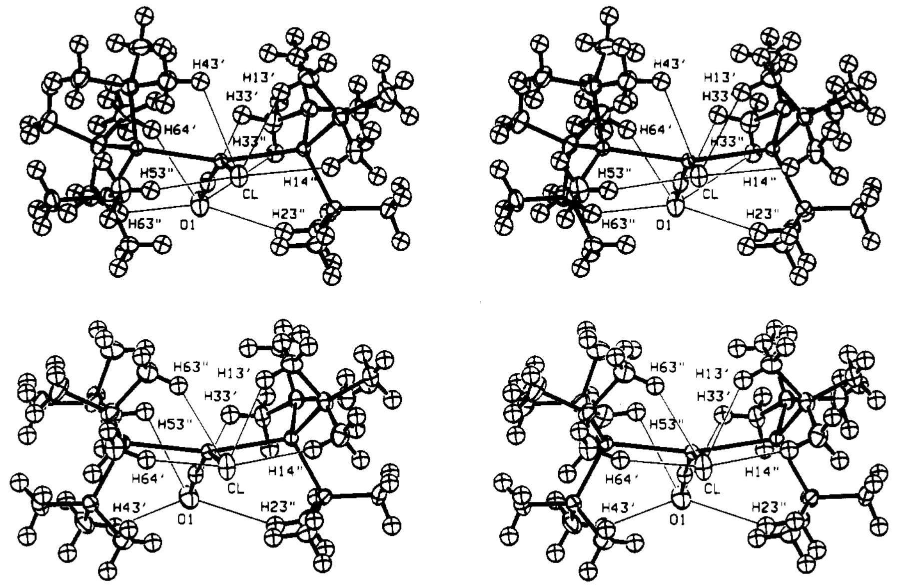

Figure 4. Stereodrawings illustrating the important H--Cl and H--O intramolecular contacts (Å) in (a, top) unsolvated and (b, bottom) toluene-solvated complexes. For the unsolvated complex: Cl--H(13)', 2.65 (1); Cl--H(14)'', 2.59 (1); Cl--H(43)', 2.86 (1); Cl--H(53)'', 2.63 (1); O--H(23)'', 2.49 (3); O--H(33)', 2.77 (3); O--H(33)'', 2.70 (3); O--H(63)'', 2.40 (3); O--H(64)', 2.48 (3). For the solvated complex with idealized hydrogen atom positions: Cl--H(13)', 2.68; Cl--H(14)'', 2.45; Cl--H(63)'', 2.62; Cl--H(64)', 2.46; O--H(23)'', 2.56; O--H(33)', 2.59; O--H(43)', 2.50; O--H(53)'', 2.69.

Table IV. Selected Interatomic Distances (Å) for the Two Forms of $[(t\text{-Bu})_3P]_2Rh(CO)Cl$ Compared with the Originally Reported Values by SHP

	SHP	unsolvated	toluene solvate
Rh(1)–Cl(1)	2.412 (2)	2.395 (1)	2.383 (2)
Rh(1)–P(1)	2.433 (1)	2.425 (1)	2.425 (1)
Rh(1)–P(2)	2.435 (1)	2.430 (1)	2.427 (2)
Rh(1)–C(1)	1.838 (9)	1.784 (3)	1.776 (5)
P(1)–C(11)	1.928 (6)	1.932 (3)	1.933 (5)
P(1)–C(21)	1.924 (5)	1.909 (3)	1.900 (5)
P(1)–C(31)	1.937 (5)	1.923 (3)	1.916 (6)
P(2)–C(41)	1.929 (5)	1.915 (3)	1.895 (5)
P(2)–C(51)	1.927 (5)	1.922 (3)	1.915 (5)
P(2)–C(61)	1.945 (5)	1.930 (3)	1.931 (5)
O(1)–C(1)	0.987 (11)	1.150 (3)	1.165 (6)

by the intramolecular interactions.[13]

Assured of the coordination geometry, a search was initiated to understand the reason for the tetrahedral distortion. The approach of a fifth ligand, for example, is known to alter the angles about the Rh atom,[14,15] but the shortest Rh--H contacts for both structures are located in the "V" of the Cl–Rh–C angle and are, therefore, clearly not responsible for the distortion. Steric interactions were then addressed. A probe of Cl--H and O--H intramolecular contacts reveals a number of short distances, which are detailed in Figure 4. Clearly, it is the positioning of the hydrogen atoms which force the Cl–Rh–C and Rh–C–O angles to bend. Linear bonds would cause the Cl and O atoms to have impossibly short X--H contacts. Also note that the shortest contacts are those which occur parallel to the P(1)--P(2) vector which accounts for the long Rh–P distances in the two structures. Even the curious disorder of the hydrogen atoms bound to C(64) in the unsolvated structure can be rationalized. In the normal staggered position [with respect to atoms attached to C(61)] there is a close contact with the O atom, while in the eclipsed sites the contacts are much longer. Thus, in every aspect, steric interactions appear responsible for the complex's unusual geometry.

While the bend in the Rh–C–O linkage may be steric in origin, an electronic contribution may help stabilize this geometry. Once the Rh geometry is distorted into a flattened tetrahedron, interactions between the Rh d_{xz} electrons and the π^* orbital of the carbonyl ligand may cause it to bend. The argument follows that of Summerville and Hoffmann,[16] where their orbital 57 (Appendix 1) favors bending a π-acceptor (here, the CO) in the direction actually observed. Note that their orbital 58 favors bending the CO in the direction opposite to that observed, but is unoccupied in this and other $P_2Rh(CO)Cl$ compounds.

Table V. Selected Intramolecular Angles (deg) for the Two Forms of $[(t\text{-Bu})_3P]_2Rh(CO)Cl$ Along with Those Originally Reported by SHP

	SHP	unsolvated	toluene solvate
Cl(1)–Rh(1)–P(1)	94.1 (1)	94.44 (3)	93.83 (5)
Cl(1)–Rh(1)–P(2)	93.9 (1)	94.05 (3)	93.85 (5)
Cl(1)–Rh(1)–C(1)	148.7 (3)[a]	150.7 (1)	149.9 (2)
P(1)–Rh(1)–P(2)	162.3 (5)	162.54 (2)	164.15 (4)
P(1)–Rh(1)–C(1)	90.2 (3)	89.90 (8)	90.4 (2)
P(2)–Rh(1)–C(1)	91.2 (3)	90.14 (8)	89.9 (2)
Rh(1)–P(1)–C(11)	112.8 (2)	112.52 (8)	111.5 (2)
Rh(1)–P(1)–C(21)	111.3 (2)	111.05 (8)	111.4 (2)
Rh(1)–P(1)–C(31)	111.1 (2)	111.72 (8)	111.4 (2)
Rh(1)–P(2)–C(41)	108.1 (2)[b]	107.85 (9)	112.0 (2)
Rh(1)–P(2)–C(51)	113.1 (2)	113.29 (8)	111.4 (2)
Rh(1)–P(2)–C(61)	113.8 (2)	113.77 (8)	112.4 (2)
C(11)–P(1)–C(21)	108.4 (2)[a]	107.7 (1)	108.6 (2)
C(11)–P(1)–C(31)	106.1 (2)[a]	105.8 (1)	105.4 (2)
C(21)–P(1)–C(31)	107.6 (2)[a]	107.8 (1)	108.4 (2)
C(41)–P(2)–C(51)	108.9 (2)[a]	109.0 (1)	107.9 (2)
C(41)–P(2)–C(61)	106.6 (2)[a]	105.8 (1)	107.2 (3)
C(51)–P(2)–C(61)	106.1 (2)[a]	106.8 (1)	105.7 (2)
Rh(1)–C(1)–O(1)	164.7 (8)	167.3 (3)	166.7 (5)

[a] This value was not given in the SHP paper; it was taken from the Cambridge Structural Database. The estimated standard deviation was assessed by comparison of similar angles. [b] An incorrect value was listed in Table 4 of the SHP paper; this value was also taken from the Cambridge Structural Database.

Supplementary Material Available: Tables of more detailed crystal structure information, anisotropic thermal parameters, hydrogen atom positional parameters, and complete interatomic distances and angles (12 pages); tables of structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

---

(13) The ^1H NMR spectrum at −90 °C in toluene-d_8 shows a virtual triplet for the 18 equivalent methyl groups of the trans $P(t\text{-Bu})_3$ ligands.

(14) Dunbar, K. R.; Haefner, S. C.; Swepston, P. N. *J. Chem. Soc., Chem. Commun.* **1991**, 460–462.

(15) Basson, S. S.; Leipoldt, J. G.; Venter, J. A. *Acta Crystallogr., Sect. C* **1990**, *46*, 1324–1326.

(16) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240–7254.