through three successive freeze–thaw cycles in the Hoke cylinder. Then D_2 (6.5 atm, 65 mmol) was drawn into the evacuated cylinder over a period of 0.5 min at approximately −150 °C. Valves C and D were closed, and after thawing to room temperature, the cylinder was placed in an oven maintained at 80 °C. Gas samples were taken periodically. After 16.7 days, the cylinder was opened, and by repeated gradual leaks into a calibrated system, the final pressure was ascertained. The solution was filtered, and the benzene removed under vacuum and retained in a liquid N_2 trap.

Protonation of Metal Hydrogen To Provide an Internal ^{1}H NMR Reference To Determine the Extent of Ring Deuteration. The solid residue from the experiment above was extracted three times with 20-mL portions of 6 M HCl, and the solution was filtered and stirred for 40 h. The solution was neutralized with aqueous NaOH, and the resultant yellow precipitate was extracted three times with 40-mL portions of benzene, dried over anhydrous $MgSO_4$, and filtered. After removal of benzene under vacuum, the product was sublimed at approximately 100 °C (10^{-2} mm).

Deuteration of $(C_5H_5)_2WH_2$ by D_2 Gas and 9.6 mol % $Mn_2(CO)_{10}$ in Toluene. Toluene (60 mL, 0.565 mol), $(C_5H_5)_2WH_2$ (0.440 g, 1.39 mmol), $Mn_2(CO)_{10}$ (0.052 g, 0.133 mmol), and D_2 (136 mmol) were reacted at 80 °C for 15.7 days. The reaction was monitored by mass spectra. After opening of the bomb, the toluene was removed and collected under vacuum. The residue was metal protonated with 6 M HCl as described above.

Control Experiment of D_2 with $(C_5H_5)_2WH_2$ in Toluene. A 100-mL toluene solution of $(C_5H_5)_2WH_2$ (0.430 g, 1.36 mmol) and D_2 (135 mmol) was heated to 80 °C and reacted for 17.0 days. The toluene was removed under vacuum, and the residue was metal protonated with 6 M HCl as described above.

Control Experiment of D_2 with $Mn_2(CO)_{10}$ in Toluene. Toluene (100 mL, 0.942 mol), $Mn_2(CO)_{10}$ (0.201 g, 0.515 mmol), and D_2 (135 mmol) were reacted at 80 °C for 16.2 days. The reaction was monitored by mass spectra of gas samples and analyzed from the NMR of the toluene recovered.

Reaction of $(C_5H_5)_2Fe$ and 23.7 mol % $Mn_2(CO)_{10}$ and D_2 in Toluene. Ferrocene (0.802 g, 4.31 mmol), $Mn_2(CO)_{10}$ (0.199 g, 0.510 mmol), and D_2 (135 mmol) in 100 mL of toluene were reacted for 6.0 days at 80 °C and 5.2 days at 112 °C. After 6 days at 80 °C, the amount of H in the gas was 0.51% (uncalibrated) out of a possible maximum 14%. After 5.25 days more at 112 °C, the gas was 1.14% H (uncalibrated). There was evidence of some slight reaction in the observation of a small amount of $(C_5H_5)Mn(CO)_3$ in the infrared spectrum of the product, as previously reported by Abel and co-workers in the absence of D_2.[9] It has not been determined whether the hydrogen–deuterium exchange involved the cyclopentadienyl rings of ferrocene or involved solvent.

Reaction of $(C_5H_5)_2ZrCl_2$ and 27.4 mol % $Mn_2(CO)_{10}$ and D_2 in Toluene. A solution of $(C_5H_5)_2ZrCl_2$ (0.751 g, 2.57 mmol) and $Mn_2(CO)_{10}$ (0.137 g, 0.352 mmol) in 150 mL of toluene was reacted with D_2 for 9.7 days at 80 °C and 2.2 days at 110 °C. No H_2, HD, or HCl was detected in the gas phase. The reaction mixture was not further analyzed.

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Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $(C_5H_5)_2WH_2$, 1271-33-6; $(C_5H_5)_2Fe$, 102-54-5; D, 7782-39-0.

Supplementary Material Available: Table II (mass spectral calibration data) and Figures 4–6 (mass spectral peak heights as functions of % H and time in spectrometer) (4 pages). Ordering information is given on any current masthead page.

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(1) (a) Material taken in part from the Ph.D. dissertation of R. J. Hoxmeier, UCLA, 1972, and the M.S. dissertation of J. R. Blickensderfer, UCLA, 1971. This is part 16 of a series of papers on metalation reactions. (b) Part 15: R. J. Hoxmeier, C. B. Knobler, and H. D. Kaesz, *Inorg. Chem.*, companion article in this issue. (c) Part 14: R. J. Hoxmeier, J. R. Blickensderfer, and H. D. Kaesz, *ibid.*, companion article in this issue.

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Contribution from the Department of Chemistry,
University of Colorado, Boulder, Colorado 80309

Structural Features of Chloro(dimethylphenylphosphonium (trimethylsilyl)methylide)(1,5-cyclooctadiene)palladium(II) Hexafluorophosphate

Robert M. Buchanan and Cortlandt G. Pierpont*

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Coordination complexes of ylides have been of interest as examples of compounds containing alkyl ligands which show exceptional stability due to the zwitterionic character of the ylide.[1] Itoh and co-workers have reported the preparation of palladium(II) complexes formed with the prochiral phosphonium (trimethylsilyl)methylide, $PhMe_2P{=}CH(SiMe_3)$.[2] The dimeric complex $[Pd(CH(PPhMe_2)(SiMe_3))Cl_2]_2$ was formed by treating $PdCl_2(PhCN)_2$ with $PhMe_2{=}CH(SiMe_3)$. Abstraction of chloro ligands with $AgPF_6$ in the presence of 1,5-cyclooctadiene produced the diolefin complex $[Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl]PF_6$. For establishment of the mode of coordination of the ylide ligand in this complex a molecular structure analysis was undertaken.

Experimental Section

A crystalline sample of $[Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl]PF_6$ was provided by Dr. Kenji Itoh of Toyohashi University. Preliminary photographs indicated monoclinic symmetry and an extinction pattern consistent with space group $P2_1/c$. A crystal of dimensions 0.31 × 0.27 × 0.22 mm was mounted and aligned on a Syntex $P\bar{1}$ automated diffractometer. Lattice constants of $a = 8.561$ (1) Å, $b = 22.899$ (3) Å, $c = 13.614$ (3) Å, and $\beta = 102.98$ (2)° were obtained from a least-squares refinement of the centered settings of 15 high-angle reflections. A calculated density of 1.581 g cm^{-3} agrees with an experimental value of 1.56 g cm^{-3} calculated for four formula weights per unit cell. Intensity data were collected within the angular range $3° \leq 2\theta \leq 50°$ by the θ–2θ scan technique by using Mo Kα radiation. A scan rate of 4.0°/min was used. Data were corrected for Lorentz, polarization, and absorption effects ($\mu = 10.2$ cm^{-1}). Of 4711 independent reflections measured, 3186 were found to have $F_o^2 > 3\sigma(F_o^2)$ and were included in the refinement. The structure was solved by the heavy-atom method and refined by using programs and procedures outlined previously.[3] In final cycles of refinement all nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined with isotropic thermal parameters. Final discrepancy indices of $R = 0.041$ and $R_w = 0.048$ were obtained with the standard deviation of an observation of unit weight at 1.78. Final atomic coordinates and thermal parameters for all nonhydrogen atoms and the ylide hydrogen are contained in Table I. A listing of the final observed and calculated structure factor amplitudes (×10) is available.

Results and Discussion

A view of the $Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl^+$ cation is shown in Figure 1. Selected bond distances and angles are contained in Table II. The centrosymmetric unit

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Table I. Structural Parameters for $[Pd(C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl](PF_6)$

atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	−0.05779 (5)	0.12554 (2)	0.09358 (3)	2.46 (2)	3.00 (4)	2.83 (1)	0.05 (3)	0.46 (2)	−0.34 (5)
Cl	0.1804 (2)	0.0890 (1)	0.0651 (1)	3.4 (1)	6.7 (2)	5.1 (1)	0.7 (1)	1.5 (1)	−1.7 (1)
P(1)	0.1060 (2)	0.0913 (1)	0.3237 (1)	3.9 (1)	3.3 (2)	3.1 (1)	−0.1 (2)	0.0 (1)	0.1 (1)
Si	0.1983 (2)	0.2138 (1)	0.2373 (1)	3.9 (1)	3.3 (2)	3.4 (1)	−0.5 (1)	0.7 (1)	−0.3 (1)
C(1)	0.0498 (7)	0.1517 (2)	0.2409 (4)	2.8 (2)	3.1 (2)	2.7 (2)	0.1 (2)	0.7 (2)	−0.2 (2)
RC(1)	−0.0500 (7)	0.0361 (2)	0.3036 (4)	4.1 (3)	3.1 (2)	3.1 (3)	−0.2 (2)	0.6 (2)	0.5 (2)
RC(2)	−0.0458 (8)	−0.0081 (3)	0.2359 (5)	5.3 (3)	3.6 (2)	5.0 (3)	−0.5 (2)	1.6 (2)	−0.8 (2)
RC(3)	−0.1654 (10)	−0.0513 (3)	0.2200 (6)	7.5 (6)	4.4 (4)	6.6 (4)	−0.7 (4)	1.0 (4)	−0.3 (3)
RC(4)	−0.2854 (9)	−0.0506 (3)	0.2752 (6)	5.2 (3)	5.7 (4)	5.6 (4)	−1.1 (3)	0.8 (2)	1.0 (3)
RC(5)	−0.2876 (9)	−0.0058 (4)	0.3431 (6)	5.4 (3)	6.3 (4)	5.1 (3)	0.0 (3)	1.9 (2)	1.5 (3)
RC(6)	−0.1705 (8)	0.0379 (3)	0.3583 (5)	4.5 (3)	4.8 (4)	4.6 (3)	−0.1 (2)	1.7 (2)	0.7 (2)
PC(1)	0.1279 (11)	0.1176 (3)	0.4520 (5)	9.3 (6)	6.1 (4)	2.2 (3)	−1.9 (4)	−0.7 (2)	−0.8 (2)
PC(2)	0.2901 (8)	0.0551 (3)	0.3157 (6)	3.3 (3)	4.8 (4)	4.4 (4)	0.8 (2)	0.0 (2)	1.1 (3)
SiC(1)	0.1357 (10)	0.2550 (3)	0.1160 (6)	8.5 (5)	5.7 (4)	5.3 (3)	−1.7 (4)	0.3 (3)	2.3 (3)
SiC(2)	0.1829 (12)	0.2658 (4)	0.3428 (7)	10.6 (6)	5.9 (4)	8.1 (5)	−2.8 (5)	5.0 (5)	−3.8 (3)
SiC(3)	0.4142 (8)	0.1912 (4)	0.2509 (7)	3.5 (4)	6.3 (4)	10.8 (7)	−1.0 (3)	1.5 (4)	−0.3 (3)
CODC(1)	−0.1634 (8)	0.1298 (3)	−0.0786 (4)	4.9 (3)	6.1 (3)	2.7 (2)	0.2 (3)	0.1 (1)	−0.4 (2)
CODC(2)	−0.2031 (8)	0.0782 (3)	−0.0471 (5)	4.6 (3)	5.4 (4)	4.2 (3)	−0.3 (3)	0.0 (2)	−2.0 (2)
CODC(3)	−0.3654 (9)	0.0636 (4)	−0.0273 (7)	4.4 (4)	7.1 (3)	9.5 (5)	−1.7 (4)	0.5 (3)	−3.3 (4)
CODC(4)	−0.3884 (8)	0.0777 (4)	0.0755 (7)	3.1 (3)	7.1 (4)	8.6 (5)	−2.0 (3)	1.0 (3)	−1.1 (3)
CODC(5)	−0.2932 (7)	0.1265 (3)	0.1294 (5)	2.8 (2)	5.2 (3)	5.1 (3)	0.1 (2)	1.4 (2)	−0.4 (2)
CODC(6)	−0.2698 (7)	0.1802 (3)	0.0906 (5)	3.9 (3)	4.4 (3)	4.3 (3)	1.6 (2)	0.3 (2)	−0.7 (2)
CODC(7)	−0.3452 (11)	0.2012 (3)	−0.0134 (6)	9.5 (7)	4.8 (3)	5.6 (4)	3.4 (5)	−1.5 (4)	0.1 (3)
CODC(8)	−0.2605 (11)	0.1860 (4)	−0.0932 (5)	8.9 (6)	7.7 (4)	3.7 (4)	3.2 (5)	0.0 (4)	1.7 (3)
P(2)	−0.3309 (2)	0.3734 (1)	0.0948 (1)	5.6 (2)	4.4 (2)	4.5 (2)	0.3 (1)	0.7 (1)	−0.1 (1)
F(1)	−0.4320 (9)	0.4243 (3)	0.0353 (5)	15.9 (6)	9.8 (4)	8.9 (4)	4.7 (5)	−0.5 (4)	1.9 (3)
F(2)	−0.3485 (8)	0.4034 (2)	0.1939 (4)	13.7 (5)	8.8 (4)	6.3 (3)	2.1 (4)	3.7 (3)	−0.2 (2)
F(3)	−0.2970 (9)	0.3463 (3)	−0.0051 (4)	18.2 (7)	8.4 (4)	7.9 (3)	−2.6 (5)	6.0 (4)	−2.9 (3)
F(4)	−0.1799 (9)	0.4137 (3)	0.0966 (5)	12.6 (6)	12.8 (6)	12.4 (5)	−5.1 (5)	5.2 (4)	−4.2 (4)
F(5)	−0.2390 (9)	0.3222 (3)	0.1540 (5)	16.7 (6)	10.9 (5)	9.4 (4)	8.1 (5)	3.1 (4)	2.6 (3)
F(6)	−0.4783 (10)	0.3345 (4)	0.0840 (8)	11.8 (6)	14.7 (6)	23.9 (11)	−6.8 (6)	7.0 (7)	−2.0 (7)
C(1)H	−0.037 (6)	0.169 (2)	0.263 (4)	2.6 (12)[b]					

[a] The form of the anisotropic ellipsoid is $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$ and is in units of Å². [b] Hydrogen atoms were refined with isotropic thermal parameters.

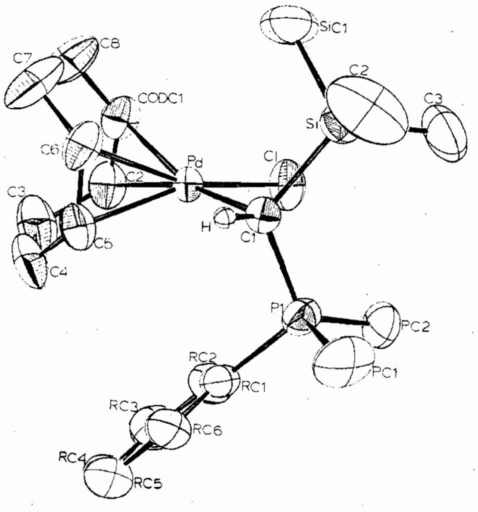

Figure 1. A perspective view of the $Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl^+$ cation.

Table II. Selected Bond Distances and Angles of the $Pd(C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl^+$ Cation

Distances (Å)

Pd–Cl	2.316 (2)	P(1)–PC(1)	1.818 (6)
Pd–C(1)	2.097 (5)	P(1)–PC(2)	1.805 (7)
Pd–CODC(1)	2.317 (6)	P(1)–RC(1)	1.814 (6)
Pd–CODC(2)	2.306 (6)	Si–SiC(1)	1.873 (7)
Pd–CODC(5)	2.178 (6)	Si–SiC(2)	1.893 (7)
Pd–CODC(6)	2.198 (6)	Si–SiC(3)	1.888 (8)
C(1)–P(1)	1.780 (6)	CODC(1)–CODC(2)	1.327 (10)
C(1)–Si	1.916 (6)	CODC(5)–CODC(6)	1.370 (9)
C(1)–C(1)H	0.95 (5)		

Angles (deg)

C(1)–Pd–Cl	92.8 (2)	CODC(1)–Pd–CODC(2)	33.4 (2)
C(1)–Pd–CODC(1)	160.6 (2)	CODC(5)–Pd–CODC(6)	36.5 (2)
C(1)–Pd–CODC(2)	165.3 (2)	Pd–C(1)–P(1)	112.5 (3)
C(1)–Pd–CODC(5)	90.7 (2)	Pd–C(1)–Si	109.8 (2)
C(1)–Pd–CODC(6)	92.2 (2)	Pd–C(1)–C(1)H	103 (3)
Cl–PD–CODC(1)	90.2 (2)	P(1)–C(1)–Si	120.4 (3)
Cl–Pd–CODC(2)	91.3 (2)	P(1)–C(1)–C(1)H	104 (3)
Cl–Pd–CODC(5)	159.2 (2)	Si–C(1)–C(1)H	106 (3)
Cl–Pd–CODC(6)	163.2 (2)		

cell contains both enantiomeric forms of the molecule. The chiral ylide carbon atom C(1) is bonded to the Pd(II) metal ion with a Pd–C(1) length of 2.097 (5) Å. This value is well within the range of lengths reported for previous structures containing alkyl ligands.[4] Phosphorus–carbon bond lengths to the phosphonium center P(1) are essentially equivalent with the bond to C(1) slightly shorter (1.780 (6) Å) than other values. Trimethylsilyl and dimethylphenylphosphonium substituents are oriented above and below the plane of the complex with the Pd, Cl, C(1) and C(1), P(1), Si planes forming a dihedral angle of 87.8 (1)°. Bond angles about P(1) are typical of sp³-hybridized phosphorus. The phenyl substituent of the phosphonium group is located atop one face of the planar complex, blocking one of the additional coordination sites of the metal. Completing the tetrahedron about ylide carbon C(1) is a hydrogen atom which is contained within the Pd, Cl, C(1) plane and is 2.48 Å from the metal.

The ylide alkyl bond of $Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl^+$ exerts a strong trans influence on the opposite cyclooctadiene olefin bond. Lengths to 1,5-COD carbon atoms C(1) and C(2) are 0.12 Å longer than lengths to C(5) and C(6). Palladium–carbon lengths in $Pd(1,5\text{-}C_8H_{12})Cl_2$ average to 2.20 Å in close agreement with the values of the present structure at the site trans to the chloro ligand.[5] Olefinic carbon–carbon lengths also reflect the difference in bond strength to the metal with the C(5)–C(6) length increased to 1.370 (9) Å while the C(1)–C(2) length is essentially that of a free olefin, 1.327 (10) Å. A similar trans effect was found for the closely related complex molecule $Pd(1,5\text{-}C_8H_{12})(CH_2(SO_2Ph))Cl$.[5] The inner coordination geometry in this case is quite similar to that of $Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl^+$ with an alkyl Pd–C length of 2.042 (5) Å, a Pd–Cl length of 2.314 (2) Å, lengths of 2.182 (5) and 2.187 (5) Å to olefin carbons trans to the chloro ligand and lengths of 2.311(6) and 2.352 (6) Å to olefin carbons trans to the alkyl carbon atom. This similarity together with other structural features of the complex cation shows that the ylide ligand of $Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl^+$ bonds in the manner of a simple alkyl zwitterion.

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Registry No. $[Pd(1,5\text{-}C_8H_{12})(CH(PPhMe_2)(SiMe_3))Cl]PF_6$, 71425-94-0.

Supplementary Material Available: A listing of structure factor amplitudes (×10) (11 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry,
University of Notre Dame, Notre Dame, Indiana 46556, and
University of Southern California, Los Angeles, California 90007

Stereochemistry of Low-Spin Bis(pyridine)(*meso*-tetraphenylporphinato)chromium(II)

W. Robert Scheidt,*[1a] A. C. Brinegar,[1a] J. F. Kirner,[1a]
and Christopher A. Reed*[1b]

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We have been recently interested in the synthesis and definitive characterization of early and middle transition metalloporphyrin complexes both as precursors to dioxygen complexes[2] and also in determining the trends in their spin-state stereochemical relationships.[3] We report herein the structural characterization of the low-spin bis(pyridine)(*meso*-tetraphenylporphinato)chromium(II) complex, abbreviated $Cr(py)_2(TPP)$. This complex is known to react irreversibly with dioxygen.[2] Comparison of the molecular stereochemistry of low-spin $Cr(py)_2(TPP)$ with the high-spin d^4 metalloporphyrin derivatives $Cr(TPP)\cdot 2(toluene)$[4] and several Mn(III) derivatives reveals bond length differences which can be qualitatively rationalized by consideration of the formal d-orbital occupancies.

Experimental Section

The preparation of $Cr(py)_2(TPP)$ has been described.[5] Single crystals were prepared from toluene and obtained as the toluene solvate. Crystals were mounted in thin-walled glass capillaries in a nitrogen-filled drybox to prevent oxidation of the sample. Preliminary examination established a centered monoclinic unit cell whose systematic absences were consistent with the space groups *Ic* or *I*2/*c*, a nonstandard setting of *Cc* or *C*2/*c*. Lattice constants $a = 16.521$ (6) Å, $b = 35.090$ (8) Å, $c = 19.325$ (6) Å, and $\beta = 119.14$ (3)° (λ 0.71073 Å) came from a least-squares refinement that utilized the setting angles of 60 reflections given the automatic centering routine supplied with the Syntex $P\bar{1}$ diffractometer. These constants led to a calculated density of 1.242 g/cm^3 for a cell content of eight molecules. The experimental density was not measured because of the air sensitivity of the sample. All measurements were made at the ambient laboratory temperature of 20 ± 1 °C. The crystal used in all measurements was a needle with approximate dimensions of 0.13 × 0.30 × 0.67 mm.

Diffracted intensities were measured by θ–2θ scanning with graphite-monochromated Mo Kα radiation. The scan range used was 0.7° below Kα_1 to 0.7° above Kα_2. Backgrounds were estimated by profile analysis.[6] All unique data to 2θ of 48.33° were measured. Four standard reflections, measured every 50 reflections, showed a small (~5%) decrease in intensity. Variable 2θ scan rates were used as previously described; the slowest was 1.0°/min and the fastest was 6.0°/min. Net intensities were reduced to relative squared amplitudes, $|F_o|^2$, with correction for absorption of X-radiation ($\mu = 0.27$ mm^{-1}).[7] Reflections having $F_o \geq 3\sigma(F_o)$ were taken to be observed. A total of 3354 unique data were obtained, 43% of the theoretical number possible in the range of $(\sin \theta)/\lambda$ examined.

The structure was solved by the heavy-atom method. Interpretation of the Patterson map in space group *I*2/*c* required positioning of the chromium atoms at 0, *y*, $^1/_4$ and $^1/_2$, 0, $^1/_2$ on a twofold axis and a center of symmetry, respectively. The structure was then essentially solved in the space group *Ic*; when the assumed pseudosymmetry was not broken, it was concluded that the symmetry was real and the true space group is *I*2/*c*. The content of the asymmetric unit of structure is thus two half-molecules of $Cr(py)_2(TPP)$, one having a required twofold axis of symmetry and the other a center of symmetry, and a toluene molecule of solvation. Owing to the large number of parameters, the phenyl groups of the porphinato ligands and the toluene molecule were refined as rigid groups. Individual isotropic temperature factors were assigned to the atoms of the groups and an occupancy factor of 0.8 was assigned to the toluene group. The geometry observed for the phenyl groups in the low-temperature Mn(TPP) structure[8] was employed for the rigid group description. The structure was refined by full-matrix least-squares techniques[9] with standard values for the atomic form factors.[10] A difference Fourier synthesis gave the approximate positions for the hydrogen atoms of the porphinato ligands; these atoms were then assigned to theoretically calculated positions (C–H = 0.95 Å), with isotropic thermal parameters fixed one unit higher than those of the associated carbon atoms, and their contributions to the calculated structure amplitudes were included in subsequent cycles of refinement. The structure was refined to convergence by using anisotropic temperature factors for the chromium atoms, the outer carbon atoms of the porphinato ligands (C_b's and C_m's), and the carbon atoms of the pyridine ligands and isotropic temperature factors for the remaining nongroup atoms.

Final least-squares refinement led to a conventional residual (R_1) of 0.120, a weighted residual (R_2) of 0.109, an error of fit of 2.39, and a final data/parameter ratio of 10.3. A final difference synthesis displayed peak density (~0.5 e/Å^3) near each chromium atom and much smaller densities (~0.3 e/Å^3) elsewhere in the asymmetric unit. The atomic coordinates and associated thermal parameters of all nongroup atoms are listed in Table I. Rigid-body parameters and the derived atomic coordinates are given in Table II (supplementary material). A listing of observed and calculated structure amplitudes is available (supplementary material).

Discussion of Results

Figure 1 presents a perspective view of the $Cr(py)_2(TPP)$ molecule (**1**) with the required twofold axis of symmetry; Figure 2 presents a view of the $Cr(py)_2(TPP)$ molecule (**2**) with the required center of symmetry. The crystallographic symmetry of both molecules requires the centering of the Cr atoms in the respective porphinato planes. The figures also illustrate the numbering scheme employed for the unique atoms. Individual bond parameters for the two molecules are presented in Tables III and IV.

The bond parameters of the porphinato cores are normal;[11] both cores show only small deviations from planarity. The out-of-plane displacements of individual atoms are shown in Figures 3 and 4 of the supplementary material. The dihedral angles between the five crystallographically independent phenyl