Organometallics **1996,** *15,* 2465−2468

Bis(triphenylphosphine)palladium Cycloheptadienynylium Tetrafluoroborate: A Palladium Complex of Tropyne

Jerzy Klosin,[†] Khalil A. Abboud, and W. M. Jones*

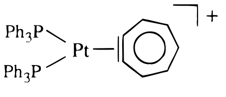
Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received January 22, 1996[⊗]

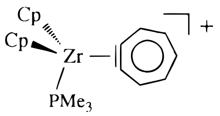
Palladium complexes of cyclohepta-3,5-dien-1-yne (**4**) and cyclohepta-1,5-dien-3-yne (**5**) have been prepared and converted to a palladium complex of tropyne (**6**) by treatment with triphenylcarbenium tetrafluoroborate.

Introduction

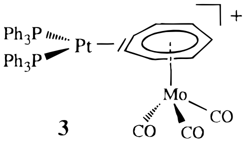
Transition metal complexes containing six-membered arynes in their coordination sphere have generated considerable interest in recent years due to their rich chemistry and unique structural features.[1] We have been interested for some time in complexes containing seven-membered ring arynes as ligands which led to the preparation of a platinum tropyne complex **1**,[2] its dibenzannelated analogue,[3] a zirconium tropyne complex **2**,[4] and a Pt−Mo bimetallic tropyne complex **3**.[5]



1



2

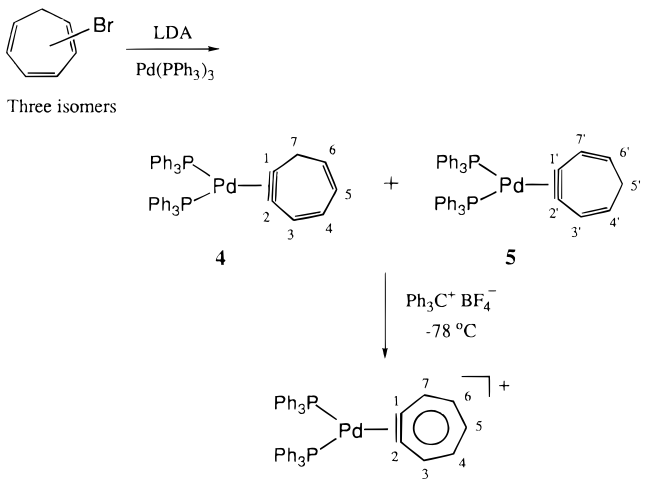


3

As a continuation of our work in this area we report at this time the synthesis of a palladium tropyne complex and its characteristics.

Results and Discussion

Scheme 1



Palladium cycloheptadienyne complexes **4** and **5** were prepared (as a 7:1 mixture) from a mixture of 1-, 2-, and 3-bromocycloheptatrienes by dehydrobromination with lithium diisopropylamide in the presence of tris(triphenylphosphine)palladium in THF solution (Scheme 1). The mixture of complexes was characterized by multinuclear spectroscopy, HRMS, IR, elemental analysis, and, in the case of **4**, single-crystal X-ray analysis. In the ^{1}H NMR of the mixture of **4** and **5**, the hydrogens attached to the sp^{3} carbon of the seven-membered rings appear as a doublet at δ 3.67 (H7, $^{3}J_{H7-H6} = 3.6$ Hz) for **4** and a triplet at δ 2.6 (H5′, $^{3}J_{H5'-H4'/H6'} = 6.3$ Hz) for **5**. Chemical shift assignments to the vinyl hydrogens of each isomer are based on a 2D COSY experiments. The $^{31}P\{^{1}H\}$ NMR of the mixture of **4** and **5** exhibits two high intensity doublets at δ 31.20 and 30.77 ($^{2}J_{P-P} = 4.6$ Hz) for **4** and a singlet at δ 31.52 for **5** as expected for complexes with C_1 and C_s symmetry, respectively. The IR spectrum of the mixture shows a peak of medium intensity at 1769 cm^{-1} which is assigned to the coordinated triple bond of **4**. The corresponding peak in the platinum analogue[6] appears at 1712 cm^{-1}. The significantly lower value for the stretching frequency of the coordinated triple bond in the platinum complex presumably results from a stronger bond between the platinum and the alkyne ligand. A similar trend in stretching frequencies is seen in palladium and platinum complexes of cyclohexyne (1780 vs 1721 cm^{-1}) and cycloheptyne (1848 vs 1770 cm^{-1}).[7] The triple bond stretching frequency of **4** (1769 cm^{-1}) is also consider-

---

[†] Present address: The Dow Chemical Co., Central Research & Development, Catalysis Laboratory, Midland, MI 48674.

[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1996.

(1) (a) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1320. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (c) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1991**, *111*, 3404. (d) Cockcroft, K. J.; Gibson, C. V.; Howard, J. A. K.; Poole, A. D.; Siemeling, U.; Wilson. C., *J. Chem. Soc., Chem. Commun.* **1992**, 1668. (e) Houseknecht, K. L.; Stockman, K.. E.; Sabat, M.; Finn, M. G.; Grimes, R. N., *J. Am. Chem. Soc.* **1995**, *117*, 1163. (f) Bennett, M. A.; Wenger, E. *Organometallics* **1995**, *14*, 1267. (g) Bennett, M. A.; Hockless, D. C. R.; Wenger, E. *Organometallics* **1995**, *14*, 2091. (h) Mashima, K.; Tanaka, Y.; Nakamura, A. *Organometallics* **1995**, *14*, 5642.

(2) Lu, Z.; Abboud, K. A.; Jones, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10991.

(3) Lu, Z.; Jones, W. M. *Organometallics* **1994**, *13*, 1539.

(4) Klosin, J.; Abboud, K. A.; Jones, W. M. *Organometallics* **1995**, *14*, 2892.

(5) Klosin, J.; Abboud, K.; A.; Jones, W. M. *Organometallics* **1996**, *15*, 596.

(6) Lu, Z.; Abboud, K. A.; Jones, W. M. *Organometallics* **1993**, *12*, 1471.

(7) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.

S0276-7333(96)00039-8 CCC: $12.00

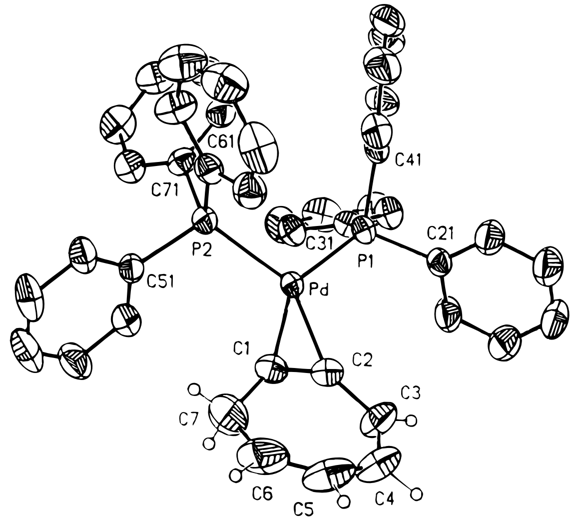


Figure 1. Structure and labeling scheme for **4** with 40% probability of thermal ellipsoids.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

	Bond Lengths (Å)		
Pd−P1	2.305(1)	Pd−P2	2.313(1)
Pd−C1	2.031(4)	Pd−C2	2.039(4)
P1−C21	1.834(4)	P2−C51	1.832(3)
P1−C31	1.838(4)	P2−C61	1.827(4)
P1−C41	1.826(4)	P2−C71	1.833(4)
C1−C2	1.258(6)	C2−C3	1.438(8)
C3−C4	1.364(8)	C4−C5	1.398(9)
C5−C6	1.360(11)	C6−C7	1.407(10)
C7−C1	1.458(7)		
	Bond Angles (deg)		
P1−Pd−P2	109.53(4)	P1−Pd−C1	146.3(1)
P2−Pd−C1	104.0(1)	P2−Pd−C2	139.7(1)
C1−Pd−C2	36.0(2)	C2−Pd−P1	110.3(1)
C(1)−C7−C6	112.5(5)	C1−C2−C3	134.4(4)
C2−C1−C7	134.7(5)	C4−C3−C2	117.4(5)
C5−C4−C3	128.1(6)	C6−C5−C4	132.8(6)
C7−C6−C5	130.0(6)		

Table 2. Crystallographic Data for Complex 4

A. Crystal Data (298 K)	
a, Å	13.543(3)
b, Å	17.244(2)
c, Å	16.124(2)
β, deg	107.82(1)
V, Å^3	3585(1)
d_{calc}, g cm^{-3} (298 K)	1.336
empirical formula	$C_{43}H_{36}P_2Pd$
fw	721.06
cryst system	monoclinic
space group	$P2_1/c$
Z	4
F(000), electrons	1480
cryst size, mm^3	0.76 × 0.23 × 0.23
B. Data Collection (298 K)	
radiation, *λ* (Å)	Mo Kα, 0.710 73
mode	*ω*-scan
scan range	symmetrically over 1.2° about $K\alpha_{1,2}$ max
bkgd	offset 1.0 and -1.0 in *ω* from $K\alpha_{1,2}$ max
scan rate, deg min^{-1}	3−6
2*θ* range, deg	3−50
range of *hkl*	$0 \leq h \leq 0$ $-0 \leq k \leq 0$ $-0 \leq l \leq 0$
tot reflcns measd	6827
unique reflcns	6299
abs coeff/*μ*(Mo Kα), cm^{-1}	0.64
min, max transm	0.852, 0.902
C. Structure Refinement	
S, goodness-of-fit	1.477 08
reflcns used, $I > 2\sigma(I)$	5010
no. of variables	415
R, w*R*, %[a]	4.11, 4.68
R_{int}, %	0.0000
max shift/esd	0.0000
min peak in diff Fourier map, e Å^{-3}	-0.3
max peak in diff Fourier map, e Å^{-3}	0.4

[a] Relevant expressions are as follows, where in the footnote F_o and F_c represent, respectively, the observed and calculated structure-factor amplitudes. Function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$. $R = \Sigma(||F_o - |F_c||)/\Sigma|F_o|$. $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$. $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

ably lower than that of the corresponding palladium complex of cycloheptyne (1848 cm^{-1}), which, presumably, reflects both greater ring strain in cycloheptadienyne relative to cycloheptyne (MMX calculations predict 3,5-cycloheptadien-1-yne to be about 5 kcal/mol more strained than cycloheptyne) and conjugation with the double bonds.

For the X-ray crystal structure analysis, complex **4** was crystallized from a toluene/hexane mixture at −16 °C. It crystallizes in a monoclinic $P2_1/c$ space group. The structure of **4** is isomorphic with that of the corresponding platinum complex.[6] The thermal ellipsoid drawing of **4** is displayed in Figure 1, while selected bond lengths and angles are listed in Table 1. Crystal structure data are provided in Table 2. The coordination geometry around the palladium atom in **4** is square planar. The alkyne bond distance (C1−C2) in **4** is 1.258(6) Å and is equal, within experimental error, to alkyne distances in platinum complexes of cycloheptyne[8] [1.283(5) Å], 3,5-cycloheptadien-1-yne[6] [1.31(2) Å], and cyclohexyne[8] [1.297(8) Å]. Consistent with two double bonds, the bond lengths of C3−C4 and C5−C6 are 1.364(8) and 1.360(11) Å, respectively. The bond angle of 112.5(5)° for C1−C7−C6 is consistent with sp^3 hybridization for C7. The seven-membered ring has the shape of a shallow boat as shown by a small dihedral angle [35.0(6)°] between planes C1−C7−C6 and C2−C3−C4−C5. Corresponding dihedral angles in cycloheptatriene derivatives are much larger [for example, 93.1° for 2,5-dimethyl-3,4-diphenyl-1,3,5-cycloheptatriene[9] and 98.3° for 3-anilino-2-(2,4,6-cycloheptatrien-1-yl)-2-propenal].[10] This difference in dihedral angle values is presumably caused by significant sp character at the alkyne carbons of **3** which increases bond angles C7−C1−C2 [134.7(5)°] and C1−C2−C3 [134.4(4)°]. This distortion, in turn, leads to a flattening of the seven-membered ring.

The tropyne complex **6** was prepared by treating a CD_2Cl_2 mixture of **4** and **5** with triphenylcarbenium tetrafluoroborate at −78 °C (Scheme 1). Similar to the platinum analogue,[2] reaction occurred rapidly to give a deep red solution. After 1 h at −78 °C, multinuclear NMR spectra revealed clean formation of the palladium tropyne complex **6** and triphenylmethane. With the exception of no coupling to Pd which has no magnetically active isotope, the ^{1}H NMR of **5** is almost identical to that of the platinum tropyne complex **1**. As in the

---

[8] Robertson, G. B.; Whimp, P. O. *J. Am. Chem. Soc.* **1975**, *97*, 1051.

[9] Stegemann, J.; Lindner, H. J. *Acta Crystallogr., Sect. B* **1979**, *35*, 2161.

[10] Reichardt, C.; Yun, K.-Y.; Massa,W.; Birkhahn, M.; Schmidt, R. E. *Liebigs Ann. Chem.* **1985**, 1969.

platinum analogue, all of the remote ring hydrogens are shifted significantly upfield from the tropylium ion (δ 9.55) with the hydrogens on C5 and C4/C6 appearing as a triplet at δ 8.52 ($^3J_{\mathrm{H5-H4/H6}} = 9.6$ Hz) and a multiplet at δ 8.32, respectively, and the C3/C7 hydrogens appearing as a doublet at δ 7.83 ($^3J_{\mathrm{H3/H7-H4/H6}} = 6.3$ Hz). The chemical shift assignment for the C5 hydrogen is based on its area (one-half that of the other two), and further chemical shift assignments are based on decoupling experiments. The corresponding resonances for the remote ring hydrogens in the platinum complex appear at δ 8.64, 8.34, and 7.66, respectively.[2] From these proton chemical shifts, it would appear that bis(triphenylphosphine)palladium is about as effective as an electron donor as is its platinum counterpart. Resonances in the ^{13}C{^{1}H} NMR for the palladium complex are also very similar to those of the platinum analogue. Probably the most characteristic resonance is that of the carbons attached to the palladium atom which appear at δ 173.34 ppm as a doublet of doublets due to coupling with two nonequivalent phosphorus nuclei ($^2J_{\mathrm{C1/C2-P_{trans}}} = 85.3$ Hz, $^2J_{\mathrm{C1/C2-P_{cis}}} = 4.2$ Hz). The ^{31}P{^{1}H} NMR and the ^{19}F NMR exhibit singlets at δ 24.32 and -151.84, respectively.

In contrast to its platinum analogue which is stable to at least 70 °C, the palladium tropyne complex is very thermally unstable. For example, in CD_2Cl_2 it decomposes at -35 °C with a half-life of about 3 h and decomposes slowly, even at temperatures as low as -50 °C.

Attempts to effect productive reactions with **6** failed. Treatment of **6** with $KBEt_3H$ or LiAl(O-*t*-Bu)$_3$H at -78 °C followed by slow warming to room temperature showed no detectable amount of **4** or **5**; only a complex mixture was formed from which no single product could be characterized. Both of these reagents reduce **1** to its cycloheptadienyne precursors.[2] Similarly, treatment of **6** with HBr at -78 °C followed by warming gave no σ complex comparable to the platinum analogue. And, finally, on the chance that the reason for decomposition might be low-temperature dissociation of the tropyne moiety from the metal center, a CD_2Cl_2 solution of **6** was warmed in the presence of cyclopentadiene which would be expected to trap the electorphilic tropyne dienophile. Again, only decomposition was observed.

Experimental Section

General Methods. All experiments involving organometallic compounds were carried out under an atmosphere of purified N_2 using Schlenk, vacuum line, and drybox techniques. Solvents were distilled under nitrogen prior to use, toluene and THF from sodium benzophenone ketyl, hexane from sodium benzophenone ketyl/tetraglyme mixture, and methylene chloride from CaH_2. Potassium *tert*-butoxide, hydrogen bromide (30 wt % solution in acetic acid), potassium triethylborohydride (1.0 M solution in THF), lithium tri-*tert*-butoxyaluminohydride (1.0 M solution in THF), and triphenylcarbenium tetrafluoroborate were purchased from Aldrich Chemical Co. and were used as received. NMR spectra were measured on a Varian XL-300 (FT 300 MHz, ^{1}H; 75 MHz, ^{13}C; 282 MHz, ^{19}F; 121 MHz, ^{31}P). ^{1}H NMR and ^{13}C{1H} NMR spectra were referenced to the residual solvent peaks and are reported in ppm relative to tetramethylsilane. ^{19}F NMR spectra were referenced to external $CFCl_3$. ^{31}P{^{1}H} NMR spectra were referenced to external 85% H_3PO_4 in D_2O. Infrared spectra were measured in KBr pellets on a Perkin-Elmer 1600 FTIR spectrometer. Mass spectra (positive FAB) were obtained on the Finnigan Mat 95Q. Elemental analyses were performed in the microanalysis lab in the Chemistry Department at the University of Florida. Melting points were measured in open capillaries and were not corrected. The following compounds were prepared as described in the literature without any modification: Pd(PPh$_3$)$_3$;[11] bromocycloheptatrienes.[12]

Preparation of (1,2-η^2-cyclohepta-3,5-dien-1-yne)bis(triphenylphosphine)palladium (4) and (1,2-η^2-cyclohepta-1,5-dien-3-yne)bis(triphenylphosphine)palladium (5). Tris(triphenylphosphine)palladium (0.5 g, 0.56 mmol) and LDA (100 mg, 0.934 mmol) were dissolved in a minimum amount of THF (ca. 16 mL). To this solution was added very slowly (1 h) 160 mg (0.934 mmol) of bromocycloheptatriene (mixture of three isomers) in 3 mL of THF at room temperature. After addition was complete the mixture was stirred for 1 h and then the solvent was removed in vacuum. The residue was dissolved in 14 mL of toluene. To this solution 36 mL of hexane was added, and the solution was filtered through a cannula. The filtrate was set aside in the freezer (-16 °C) for 2 days to give 210 mg (52% yield) of pure **4** and **5**, mp 114–115 °C (dec). IR (KBr): 3053, 3001, 1769 (coordinated C≡C), 1478, 1433, 1307, 1181, 1093, 1026, 744, 696 cm^{-1}. ^{1}H NMR data for **4** (C_6D_6): δ 7.6–7.8 and 6.95–7.1 (m, P*Ph*$_3$), 5.96 (m, 1H, H3), 5.8 (m, 2H, H4 and H5), 5.23 (m, 1H, H6) 3.7 (d, 2H, $^3J_{\mathrm{H7-H6}} = 3.6$ Hz, H7). ^{1}H NMR data for **5** (C_6D_6): δ 7.6–7.8 and 6.95–7.1 (m, P*Ph*$_3$), 6.74 (d, 2H, $^3J_{\mathrm{H3'/H7'-H4'/H6'}} = 8.1$ Hz, H3′/H7′), 5.15 (m, 2H, H4′/H6′), 2.65 (t, 2H, $^3J_{\mathrm{H5'-H4'/H6'}} = 6.3$ Hz, H5′). ^{13}C{^{1}H} NMR (C_6D_6): δ 137.65 (m, PPh$_3$-*ipso*), 134.36, (dd, $J_{\mathrm{C-P}} = 15.1$, $J_{\mathrm{C-P}} = 4.5$ Hz, PPh$_3$), 129.11 (s, PPh$_3$), 128.26 (d, $J_{\mathrm{C-P}} = 9.4$ Hz, PPh$_3$), 127.26 (d, $J_{\mathrm{C-P}} = 9$ Hz), 126.4, 123.78 (t, $J_{\mathrm{C-P}} = 9.5$ Hz), 120.34 (m), 114.89 (m), 114.1 (d, $J_{\mathrm{C-P}} = 4$ Hz), 113.23 (d, $J_{\mathrm{C-P}} = 4.8$ Hz), 30.31, 29.72 (t, $J_{\mathrm{C-P}} = 9.4$ Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 31.52 (s, complex **5**), 31.20 (d, $^2J_{\mathrm{P-P}} = 4.6$ Hz), 30.77 (d, $^2J_{\mathrm{P-P}} = 4.6$ Hz). HRMS (FAB): calcd for $(M + 1)^+$, *m*/*e* 721.1405; found, *m*/*e* 721.1528. Anal. Calcd for $C_{43}H_{36}P_2Pd$: C, 71.62; H, 5.03. Found; C, 71.77; H, 5.07.

Preparation of (1,2-η^2-tropyne)bis(triphenylphosphine)palladium (6). An NMR tube equipped with a joint and a stopcock (mini Schlenk tube) was charged with 70 mg (0.097 mmol) of **4** and **5**. This complex was dissolved in 0.2 mL of CD_2Cl_2, and subsequently the solution was frozen in liquid N_2. To this apparatus 33 mg (0.098 mmol) of triphenylcarbenium tetrafluoroborate dissolved in 0.4 mL of CD_2Cl_2 was added via a syringe, and this solution was frozen. While keeping the mixture under a nitrogen atmosphere, it was allowed to warm up to -78 °C. After the mixture had become homogeneous it was frozen in liquid N_2, the apparatus was evacuated and the NMR tube was sealed. This NMR tube was then warmed to -78 °C in a dry ice bath before NMR measurements which were performed at -90 °C. ^{1}H NMR (CD_2Cl_2): δ 8.52 (t, 1H, $^3J_{\mathrm{H5-H4/H6}} = 9.6$ Hz, H5), 8.32 (m, 1H, H4/H6), 7.83 (d, $^3J_{\mathrm{H3/H7-H4/H6}} = 6.3$ Hz, H3/H7), 7.0–7.5 (m, 30H, PPh$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 173.34 (dd, $^2J_{\mathrm{C4-P_{trans}}} = 85.3$ Hz, $^2J_{\mathrm{C4-P_{cis}}} = 4.2$ Hz, C1/C2), 149.67 (s, br, C4/C6), 143.05 (s, C5), 139.47 (t, $^3J_{\mathrm{C3-P}} = 10.2$ Hz, C3/C7), 133.35 (t, $J_{\mathrm{C-P}} = 6.8$, PPh$_3$), 131.91 (m, PPh$_3$-*ipso*), 130.29 (s, PPh$_3$), 128.33 (t, $J_{\mathrm{C-P}} = 4.6$, PPh$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 24.32 (s). ^{19}F NMR (CD_2Cl_2): δ -151.84 (s). The spectra for **6** are almost identical to those of the platinum analog (**1**); therefore peak assignments in the ^{13}C NMR for **6** were based on simple comparison with **1**.

Crystallographic Analysis of Complex 4. Data were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\,73$ Å). A total of 32 reflections with $20.0° \le 2\theta \le 22.0°$ were used to refine the cell parameters of each crystal. Four reflections were measured every 96 reflections to monitor instrument and crystal stability for each data

---

(11) Giannoccaro, P.; Sacco, A.; Vasapollo, G. *Inorg. Chim. Acta* **1979**, *37*, L455.

(12) Fohilsh, B.; Haug, E. *Chem. Ber.* **1971**, *104*, 2324.

set (maximum correction on I was 2%). Absorption corrections were applied on the basis of measured crystal faces using SHELXTL plus.[13] The structure was refined in SHELXTL plus using full-matrix least squares. The structure of **3** was solved by the heavy-atom method in SHELXTL plus from which the location of the Pd atoms were obtained. The rest of the non-hydrogen atoms were obtained from subsequent difference Fourier maps. All non-H atoms were refined with anisotropic thermal parameters, while positions of all of the H atoms were calculated in ideal positions and their isotropic thermal parameters were fixed. The linear absorption coefficients were calculated from values from ref 14. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann[15] with anomalous-dispersion corrections from Cromer and Liberman,[16] while those of hydrogen atoms were from Stewart, Davidson, and Simpson.[17]

Acknowledgment. Support of this research by the National Science Foundation and the Chevron Research and Technology Co. is gratefully acknowledged.

Supporting Information Available: A thermal ellipsoid drawing showing full numbering schemes and tables of atomic positions and *U* values, anisotropic thermal parameters for non-hydrogen atoms, and comprehensive bond lengths and angles (10 pages). Ordering information is given on any current masthead page.

OM9600396

---

[13] Sheldrick, G. M. SHELXTL plus, version 4.21/V, Siemens XRD, Madison, WI, 1990.

[14] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 55. (Present distributor: D. Reidel, Dordrecht, The Netherlands.)

[15] Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

[16] Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

[17] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.