π-Arene Complexes. 10.[1] Arene Distortions in π-Arene Complexes of Chromium by Ring Substituents. Crystal Structure of $(\eta^1{:}\eta^6\text{-}C_6H_5\{TiCp_2Cl\})Cr(CO)_3$

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Introduction

The interaction of ring substituents of benzene and the resulting changes in charge distributions in the ring have been the topic of many studies in physical organic chemistry.[2] While electronic disturbances in the σ-bonds originate from inductive effects, resonance effects are observed in the π-system of the ring. Ring distortions in substituted benzene derivatives, in contrast to typical bond distances of 1.397(1) Å and angles of 120° (sp^2-hybridization) in benzene,[3] are manifested in the lengthening or shortening of bonds and angular deformations especially around the *ipso*-carbon. Steric constraints caused by bulky substituents can also result in ring distortions.[4]

Benzene coordinated to chromium tricarbonyl in the η^6-fashion affords a planar ring with carbon atoms equidistant from the metal.[5] Crystal structure determinations of a number of heterobimetallic complexes with σ,π-arene bridging ligands have been recorded in our laboratories.[6,7] Small but significant distortions in the arene ring occur mainly at the *ipso*-carbon atom bonded to the transition metal fragment.

Recently Hunter and co-workers[8] discussed ring distortions of analogous complexes solely on the basis of π-interaction between the transition metal substituent and the π-system of the arene ring. Significant π-donation from FeCp(CO)$_2$ substituents in bi- and trimetallic π-arene complexes of chromium was recorded. We have observed similar ring distortions in the structural data for the bimetallic complexes $(\eta^1{:}\eta^6\text{-}o\text{-}C_6H_4R\{TiCp_2Cl\})Cr(CO)_3$ (R = H (**1**), F[6] (**2**), OMe[9] (**3**)). Little evidence of multiple-bonding interactions between the *ipso*-carbon and the σ-bonded transition metal was observed in the titanium–carbon bond distances of **1**–**3**. Furthermore, titanium is formally in a +4 oxidation state in these complexes, which implies empty d orbitals and rules out any π-donation from the metal. Therefore, to obtain a more complete picture of arene distortions in σ,π-coordinated bimetallic complexes, we wish to discuss distortions on the premise that they could also originate from inductive charge effects in the σ-frame of the arene ring.

Table 1. Crystallographic Data for $(\eta^1{:}\eta^6\text{-}C_6H_5\{TiCp_2Cl\})Cr(CO)_3$

formula	$C_{19}H_{15}O_3ClCrTi$	V, Å^3	1724.8(5)
mol wt	426.65	d_{calc}, g cm^{-3}	1.64
space group	$P2_1/n$ (No. 14)	μ(Mo Kα), cm^{-1}	11.82
cryst syst	monoclinic	$F(000)$	864
a, Å	10.493(2)	no. of data measd	2739
b, Å	12.249(2)	no. of data used ($I > \sigma_I$)	2616
c, Å	13.975(2)	no. of parms refined	227
β, deg	106.21(1)	R^a	0.049
Z	4	$R_w{}^b$	0.034

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

We have also investigated the effect of organic substituents with different electronegativities, *ortho* to the titanium moiety, on the magnitude of the angular deviation around the *ipso*-carbon atom bonded to titanium.

Experimental Section

The reaction and subsequent manipulations were performed by using conventional techniques for the handling of air-sensitive compounds.[10] Solvents were purified, degassed, and dried according to standard procedures.[11] The column packing for liquid column chromatography consisted of SiO$_2$ (0.063–0.200 mm), and the separation was performed on a column cooled by recycling cold methanol (−20 °C) through the column jacket. Prior to use, dichloromethane was distilled from P$_2$O$_5$; hexane and benzene were distilled from sodium wire, while tetrahydrofuran was freshly distilled from sodium–benzophenone ketyl under inert atmosphere. The chromium precursor $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ was prepared according to the published procedure[12] and was lithiated according to the method described by Card and Trahanovsky.[13] The bimetallic complex $(\eta^1{:}\eta^6\text{-}C_6H_5\{TiCp_2Cl\})Cr(CO)_3$ (**1**) was synthesized by modifying a procedure reported earlier[6] and checked against an authentic sample.

Synthesis. Preparation of $(\eta^1{:}\eta^6\text{-}C_6H_5\{TiCp_2Cl\})Cr(CO)_3$. A cooled solution (−70 °C) of 0.64 g (3 mmol) of (η^6-benzene)tricarbonylchromium(0) in 30 mL of THF was treated dropwise with 2.1 mL of a 1.6 mol/dm^3 solution of butyllithium (3.3 mmol). The mixture was stirred for 20 min while the temperature was raised to −30 °C. This freshly prepared (η^6-lithiobenzene)tricarbonylchromium(0) solution was cooled to −50 °C and added to an equimolar solution of Cp$_2$TiCl$_2$ (0.78 g, 3 mmol) in THF (30 mL) at −78 °C. After being stirred for 30 min, the reaction mixture was allowed to warm to room temperature and stirring was continued for 1 h. Removal of the solvent under reduced pressure gave a black-green solid, which was subjected to column chromatography on silica gel. Elution with a dichloromethane–hexane mixture (1:1) yielded a yellow fraction, which was identified as the unreacted chromium starting material, followed by a blue-green zone containing $(\eta^1{:}\eta^6\text{-}C_6H_5\{TiCp_2Cl\})Cr(CO)_3$ (**1**). In addition, a number of other bands observed in low yield were not collected and identified. After removal of the solvent, the residue was dissolved in a minimum of dichloromethane, and the solution was filtered through a plug of Celite, after which an equal volume of hexane was carefully layered on top of the filtrate. The Schlenk tube was left undisturbed at −4 °C for several days, after which the mother liquor was decanted and the remaining crystals were dried *in vacuo*. Yield: 0.44 g (69%).

X-ray Crystallographic Analysis. Crystallographic data for $(\eta^1{:}\eta^6\text{-}C_6H_5\{TiCp_2Cl\})Cr(CO)_3$, measured at 294 K, are listed in Table 1. Accurate unit cell parameters were obtained by least-squares methods from the positions of 25 carefully selected centered reflections (15° < θ < 18°), using a black crystal with approximate dimensions 0.15 × 0.16 × 0.17 mm^3. By application of ω–2θ scan techniques and the use of monochromated Mo Kα radiation (λ = 0.7107 Å) on an Enraf-Nonius CAD4 diffractometer with an aperture of 1.3 × 4.0 mm^3, the intensity data for h = 0, +13, k = −15, 0, and l = −17, +17 were collected in the

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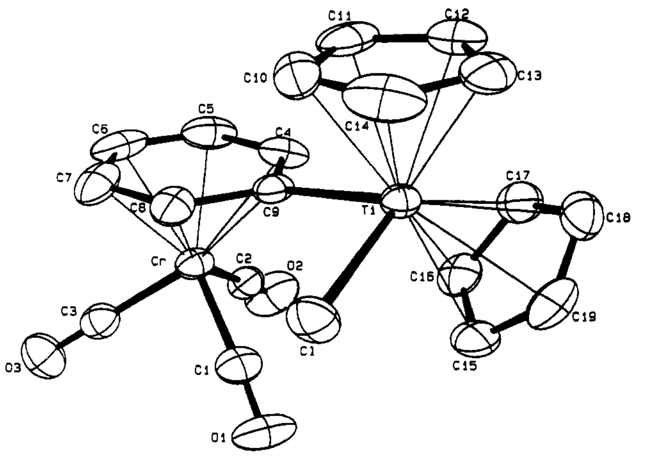

Figure 1. Perspective drawing of the molecular structure of **1**.

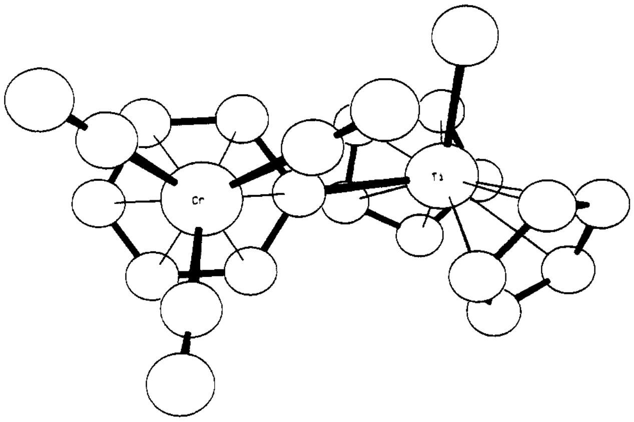

Figure 2. View of **1** along the Cr–arene bond.

range $3 \le \theta \le 27°$. There was no significant crystal decay, as indicated by monitoring the intensities of three standard reflections throughout the data collections. The data were corrected for absorption (empirical, based on the azimuthal scans for nine reflections of the crystal), as well as for Lorentz-polarization effects. The maximum, minimum, and average transmission factors were 1.000, 0.980, and 0.993, respectively. Equivalent reflections were merged (R_{int} = 0.020).

The structure was solved by conventional Patterson and Fourier techniques using SHELX86.[14] All the non-hydrogen atoms were refined anisotropically,[15] and the hydrogen atoms were placed in calculated positions and refined with a common isotropic thermal parameter that converged to U_{iso} = 0.060(4) Å^2. Perspective drawings of the molecule shown in Figure 1, illustrating the crystallographic numbering scheme used, and Figure 2, a projection on the benzene plane displaying the relative conformation of the (arene)Cr(CO)$_3$ moiety, were prepared with ORTEP.[16] Atomic scattering factors were taken from the literature.[17] There were no corrections for the presence of extinctions made. Final atomic coordinates and equivalent isotropic thermal parameters and selected bond lengths and angles appear in Tables 2 and 3, respectively.

Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Thermal Factors (×10^3 Å^2) for (η^1:η^6-C_6H_5{TiCp$_2$Cl})Cr(CO)$_3$

atom	*x/a*	*y/b*	*z/c*	U_{eq}[a]
Cr	–3347(1)	1460(1)	2168(1)	30(1)
C1	–3107(5)	729(4)	1071(3)	38(1)
O1	–2992(4)	254(3)	402(2)	62(1)
C2	–4395(5)	2498(4)	1354(3)	36(1)
O2	–5084(4)	3125(3)	859(3)	63(1)
C3	–4858(5)	647(4)	1985(3)	37(1)
O3	–5817(4)	148(3)	1861(3)	61(1)
C4	–1738(5)	2657(4)	2881(3)	38(1)
C5	–2747(5)	2712(5)	3362(4)	48(1)
C6	–3147(5)	1780(5)	3773(3)	51(1)
C7	–2557(5)	765(5)	3673(3)	44(1)
C8	–1554(4)	711(4)	3198(3)	36(1)
C9	–1081(4)	1664(4)	2799(3)	29(1)
Ti	804(1)	1524(1)	2371(1)	26(1)
C10	1300(5)	1760(5)	818(3)	47(1)
C11	1635(5)	2697(5)	1328(3)	47(1)
C12	468(5)	3145(4)	1442(3)	43(1)
C13	–580(5)	2467(4)	975(3)	39(1)
C14	2652(5)	879(5)	3676(4)	55(1)
C15	–79(5)	1576(4)	586(3)	42(1)
C16	3012(5)	1885(4)	3350(3)	44(1)
C17	2211(5)	2683(4)	3585(3)	43(1)
C18	1363(5)	2185(5)	4041(3)	47(1)
C19	1621(5)	1058(5)	4101(3)	52(1)
Cl	589(1)	–350(1)	2029(1)	41(1)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j(\mathbf{a}_i \cdot \mathbf{a}_j)$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**

	Bond Distances		
Cr–C1	1.852(2)	Ti–C(cpA)	2.376(5)[a]
Cr–C2	1.850(5)	Ti–C(cpB)	2.390(5)[a]
Cr–C3	1.829(5)	C9–C4	1.418(6)
Cr–C(arene)	2.239(5)[a]	C4–C5	1.405(6)
C1–O1	1.137(5)	C5–C6	1.394(7)
C2–O2	1.146(5)	C6–C7	1.413(7)
C3–O3	1.148(5)	C7–C8	1.395(6)
Ti–C9	2.228(4)	C8–C9	1.439(6)
Ti–Cl	2.343(1)		
	Bond Angles		
C1–Cr–C2	91.0(2)	C8–C9–C4	115.9(4)
C2–Cr–C3	86.9(2)	C9–C4–C5	121.9(5)
C3–Cr–C1	86.2(2)	C4–C5–C6	120.8(5)
Cr–C1–O1	177.5(5)	C5–C6–C7	119.3(5)
Cr–C2–O2	177.4(5)	C6–C7–C8	119.9(5)
C4–C3–O3	179.0(4)	C7–C8–C9	122.2(5)
Ti–C9–C4	125.1(3)		

[a] The averaged value.

Results and Discussion

The general features of the molecular structure of (η^1:η^6-C_6H_5{TiCp$_2$Cl})Cr(CO)$_3$ (**1**) are consistent with those recorded for (η^1:η^6-C_6H_4R{TiCp$_2$Cl})Cr(CO)$_3$ (R = *o*-F, *p*-Me).[6] The Cr–C(arene) distances of **1** are identical within experimental error (Cr–C(arene) = 2.239(5) Å averaged), and the Cr–Ph(center)–C9 and Cr–Ph(center)–C6 angles of 92.2 and 89.2°, respectively, indicate that the Cr–Ph vector is almost normal to the approximate plane of the arene ring. The planar benzene ring indicates that the Cr(CO)$_3$ moiety is bonded to the π-cloud of the bridging arene ligand which is also σ-bonded to the TiCp$_2$Cl unit. The titanium is in a distorted tetrahedral environment of ligands.

The Ti–C9 distance of 2.228(4) Å does not differ significantly from the reported distances of 2.21 Å for the Ti–C(sp^3, methyl) bond in (η^5-C_9H_7)$_2$Ti(CH$_3$)$_2$,[18] the 2.216 Å distance for the Ti–C(sp^2, phenyl) bond in (η^5-Cp)$_2$Ti(*p*-$C_6H_4CH_3$)$_2$,[19] and the corresponding distances of 2.217(8) and 2.213(6) Å for (η^1:η^6-C_6H_4R{TiCp$_2$Cl})Cr(CO)$_3$ where R = *o*-F (**2**) and *p*-CH$_3$,[6] respectively. In contrast, Ti–C distances with perceivable π-interaction contributions between the titanium and a carbon atom are significantly shorter and fall in the range 2.00–2.10 Å.[20] Therefore, the Ti–C(arene) bond lengths in the bimetallic

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Table 4. Orientation of the Carbonyl Ligands with Respect to the $TiCp_2Cl$ Substituent (deg)

angle[a]	1	2[b]	3[c]
ψ_1	98.6	92.2	67.8, 41.5
ψ_2	216.9	211.7	188.3, 159.8
ψ_3	334.5	327.6	308.1, 280.6

[a] ψ_n measured in a clockwise direction from the Ti substituent to the *n*th carbonyl. [b] Reference 6. [c] Two Nonequivalent molecules in the unit cell. Reference 9.

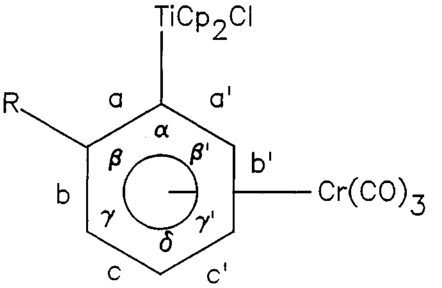

Figure 3. Labels used for bond distances and angles of **1**–**3**.

compounds (**1**–**3**) suggest little, if any, multiple bonding interaction between the titanium and the arene carbon atom.

A view from above the arene plane is shown in Figure 2. The $Cr(CO)_3$ fragment lies in a nearly staggered conformation, experiencing a 25.5° anticlockwise rotation from the fully *syn*-eclipsed conformation and a 34.5° clockwise rotation from the alternate *anti*-eclipsed structure. A *syn*-eclipsed geometry is the preferred structure for monosubstituted (η^6-arene)$Cr(CO)_3$ molecules with electron-donating functional groups, and an *anti*-eclipsed conformation is favored for electron-withdrawing groups.[5] In Table 4 carbonyl orientations with respect to the titanium substituent are compared. Conformational analysis of $Cr(CO)_3$ tripod orientations for **1**–**3** suggests that the titanium fragment can best be described as a electron-donating substituent. Spectroscopic and structural data[6] of **1**–**3** indicate a polarized Ti–C(arene) σ-bond in which the electron density is shifted toward the arene ring. Deviations from a fully *syn*-eclipsed orientation in **1** are ascribed to steric factors.

Small deviations from ideal benzene bond distances and angles[3] are observed around the *ipso*-carbon atom of **1**. The endocyclic bond angle, α, is reduced to 115.9° ($\Delta\alpha = -4.1°$) and the adjacent bonds, *a* and *a'*, are lengthened by 0.025 Å (1.429(6) Å averaged) compared with the remaining four distances (1.404(7) Å, average of *b*, *b'*, *c*, and *c'*; see Figure 3). The adjacent angles, β and β' (121.9 and 122.2°), are on average increased by $-\Delta\alpha/2$ to reduce the ring strain caused by these distortions. Coulson and coworkers[21] reported a linear dependency of the endocyclic bond angles on the Pauling's electronegativity values of substituents in monosubstituted benzene derivatives. They also suggested that the deviation for the β angles was close to $-\Delta\alpha/2$ and that the deviation of the γ angles was approximately 0°. A method developed by Norrestam and Schlepper[22] for estimating deviations in substituted benzene derivatives was based on a set of deformation parameters and confirmed conclusions made by Coulson and co-workers. The fact that a similar correlation was found for **1** suggests that the deformation of the arene ring is dependant not on the π-coordination of the arene ring to the $Cr(CO)_3$ fragment but solely on inductive electronic and steric properties of the σ-coordinated substituent.

Table 5. Arene Distortions[a] of (η^1:η^6-$C_6H_4R\{TiCp_2Cl\}$)$Cr(CO)_3$ (R = 1 (**1**), F (**2**), OMe (**3**))

	1	2	3[b]
	Bond Lengths (Å)		
a	1.418(6)	1.396(11)	1.401(8)
a'	1.439(6)	1.431(11)	1.443(8)
b	1.405(6)	1.393(12)	1.404(8)
b'	1.395(6)	1.390(12)	1.400(8)
c	1.394(7)	1.381(12)	1.387(9)
c'	1.413(7)	1.395(12)	1.387(9)
	Bond Angles (deg)		
α	115.9(4)	111.3(7)	113.4(6)
β	121.9(5)	126.3(9)	124.2(6)
β'	122.2(5)	122.9(9)	123.5(6)
γ	120.8(5)	120.7(9)	119.5(7)
γ'	119.9(5)	122.8(9)	119.3(7)
δ	119.3(5)	115.7(9)	120.1(7)
	Distances from Plane[c] (Å) and Angles between Planes (deg)		
plane defined	C4–C5–C6–C7	C5–C6–C7–C8	C5–C6–C7–C8
δ, δ_{Ti}	0.509(7)	0.546(2)	0.405(12)
δ_{C9}	0.038(8)	0.069(8)	0.040(14)
δ_R		0.129(6)	0.216(14)
δ_{C4}		0.039(10)	0.063(14)
θ[d]	2.7(4)	3.7(8)	2.0(5)
	Dihedral Angle (deg)		
C8–C9–Ti–Cl	27.4(3)	22.5(6)	21.8(4)

[a] Numbering of bond distances and angles according to Figure 3. [b] Average value of two nonequivalent molecules in the unit cell. [c] Magnitude of the displacement of the atom from the defined plane. [d] Angle between the C4–C9–C8 plane and the defined plane.

The Hunter model[8] predicted the direction of deviation in substituted π-arene complexes of chromium on the basis of the resonance effects of known organic π-donor and π-acceptor substituents. In contrast, an approach based on the inductive effects of the more electropositive titanium substituent in the bimetallic complexes **1**–**3** can be applied satisfactorily to account for observed distortions. Furthermore, it has become an accepted practice in organic chemistry to treat σ- and π-effects of substituted benzene derivatives independently.[2b,23]

The electropositive Ti substituent will interact with a sp^2-hybrid orbital of the phenyl ring with relatively more s and less p character to form the Ti–C(arene) σ-bond. As a result, the remaining two sp^2-hybrid orbitals of the *ipso*-carbon, which form the σ-frame of the ring, will have more p and less s character. Therefore, the endocyclic angle will decrease, causing the *a* and *a'* bonds to lengthen. To relieve the resulting ring strain in the σ-system of the benzene ring, the arene ligand will distort in such a way that steric interactions are minimized. Thus, the *ipso*-carbon and titanium substituent will move away from the $Cr(CO)_3$ moiety towards the open side of the arene ring. These arguments are consistent with the structural data for **1**, where a displacement of 2.7(4)° out of the plane of the arene ring and away from the chromium tricarbonyl is recorded, and with literature references[4,21,24] describing phenyl distortions in organic molecules. The deviations from ideal benzene values are small compared to distortions of 35–45° for *ipso*-carbons of sp^3-hybridization in cyclohexadienyl complexes.[25,26]

The magnitude of the distortion is expected to correlate with the electronegativity of the substituent attached to the benzene ring. To test this assumption, we investigated the effect of an additional substituent of different electronegativity in the position *ortho* to the Cp_2TiCl substituent. Arene distortion data for the bimetallic complexes (η^1:η^6-*o*-$C_6H_4R\{TiCp_2Cl\}$)$Cr(CO)_3$ (R = H, OMe, F) are summarized in Table 5. The substituents, OMe

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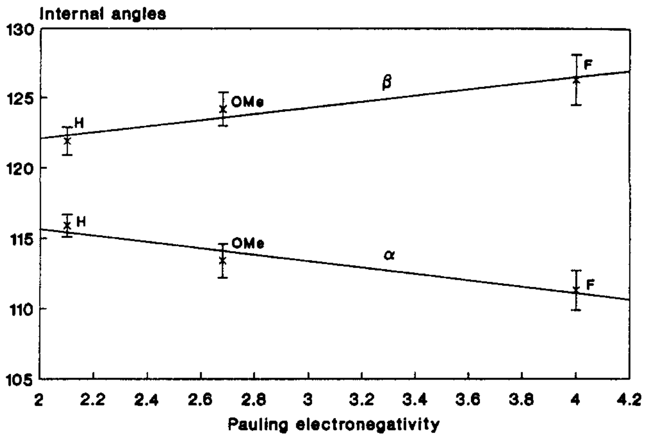

Figure 4. Endocyclic angles (α, β) *versus* Pauling electronegativities (χ). A vertical bar shows the error range (±2σ) of each point.

and F, should, because of their electron-withdrawing properties, assist in increasing the β and decreasing the α angles. Owing to the relative positions of the substituents on the arene ring, the two effects are synergic and the magnitude of the distortions will depend directly on the electronegativity of the R substituent. While the decrease in the α angle results in substantial increases in the β and β′ angles, the increases in the β angles do not affect the adjacent γ and γ′ angles significantly. Plots of the internal angles α and β *versus* Pauling's electronegativity (χ) of the organic substituent are shown in Figure 4. Although only three data points are available and their differences are small relative to the standard deviations, a definite pattern emerges. Linear correlations exist between the internal bond angles (α or β) and Pauling's electronegativities of the heteroatoms of the substituents *ortho* to the titanium fragment. The dependency of α on χ demonstrates the cooperative effect of the substituents in enhancing distortions of the planar arene ligand.

Conclusion

This study has shown that π-coordination to the $Cr(CO)_3$ fragment does not significantly affect the geometry of the planar arene ring and that distortions of the ring, irrespective of substituents being organic or transition metal fragments, are determined by the inductive properties of the σ-bonded substituent. Thus, models based on resonance[8] and inductive effects of substituents can be used to explain structural deviations of substituted benzene derivatives when they are present as ligands in organometallic chemistry.

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Supplementary Material Available: Tables of bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates, as well as an ORTEP plot of the unit cell contents (5 pages). Ordering information is given on any current masthead page.