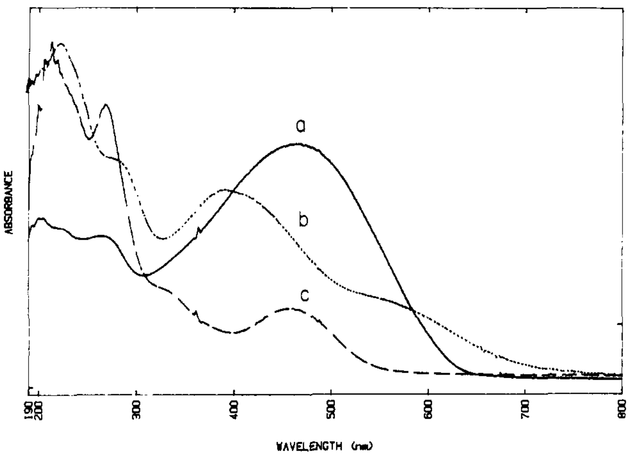

Figure 1. The UV-visible spectra of (a) **1**, (b) **3**, and (c) $[CpFe(CO)_2(3\text{-methylthiophene})]BF_4$ (**6**).

pressed from this material was of the order of $10^{-3}\ \Omega^{-1}\ cm^{-1}$.

The new material exhibits two strong bands in the carbonyl stretching region of its IR spectrum consistent with the presence of the $[CpFe(CO)_2]^+$ residue.[8,9a,10] Integration of the aryl and alkyl regions of the NMR spectrum[9b] of **3** relative to that of the Cp region suggests that 7% of the thiophene rings are attached to the organoiron cation. Treatment of **3** in CH_2Cl_2 with NaI gave, upon evaporation of solvent, a nonconducting residue whose NMR spectrum ($CDCl_3$) and IR spectrum in the carbonyl stretching region was characteristic[3] of $CpFe(CO)_2I$ (**4**),[9c] embedded in **1**. Heating solid **3** to 100 °C gave a nonconducting material whose IR spectrum was characteristic of $[CpFe(CO)_3]BF_4$ (**5**),[9d] in the carbonyl stretching region; consistent with the reported[8] behavior of $[CpFe(CO)_2(\text{thiophene})]BF_4$. In both cases the dark red color of the original **1** had returned. The preparation of **3** and its subsequent transformations are depicted in Scheme I. The similarity of the NMR and infrared spectra and reactivity of **3** to that of model compounds such as $[CpFe(CO)_2(\text{thiophene})]BF_4$ and $[CpFe(CO)_2(3\text{-methylthiophene})]BF_4$ (**6**)[10] leads to the conclusion that $[CpFe(CO)_2]^+$ residues bind to the sulfur atoms of some of the thiophene rings of the polymer backbone of **3**.

Changing the ratio of **1** and **2** in the preparation of **3** changes the percentage of iron-functionalized thiophene rings; however, the conductivity reaches its maximum value at quite low loadings ($10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 1%, $10^{-3}/\Omega^{-1}\ cm^{-1}$ at 3-20% loadings). The conductivity is constant for over 2 months when samples were stored in vacuo and increased slightly when stored in air. Comparison of the UV-visible spectra of **1**, **3**, and $[CpFe(CO)_2(3\text{-methylthiophene})]BF_4$ (**6**) (Figure 1) reveals that the single broad band at 470 nm observed for **1** is split into two bands at 400 nm and approximately 570 nm upon complexation (i.e., **3**). It is important to note here that disks composed of pure **2** or **6** or a "solid solution"[3] of **6** in **1** are nonconducting ($<10^{-6}\ \Omega^{-1}\ cm^{-1}$).[11,12] Clearly the covalent attachment of the organoiron cation to **1** perturbs the electronic configuration of the polymer.[1a]

The $[CpFe(CO)_2]^+$ residue may be regarded as mimicking the action of I_2 on **1** by introducing charge anomalies in the conjugated system leading to improved electrical conduction. However, **3** may also be viewed as a collection of complexes connected by long conjugated ligands which fulfil the requirement for inner-sphere electron transfer.[13] Since **3** is a polythiophene matrix, each "ligand" is in intimate contact with several other ligands, thus fulfilling the requirement for outer-sphere electron transfer. Conduction could occur via a combination of inner- and outer-sphere redox reactions[14] involving the Fe(II)/Fe(III) couple. The implications of these concepts are under study.

Acknowledgment. This work was supported by the National Sciences and Engineering Council of Canada and the Quebec Department of Education. J.P.G. acknowledges the award of a McGill University predoctoral fellowship and support from the Laboratory for Inorganic Materials (Concordia University).

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[9] (a) **3**: IR (solid state) ν(CO) 2065, 2021 cm^{-1}; IR (CH_2Cl_2) 2071, 2025 cm^{-1}. (b) **3**: ^1H NMR ($CDCl_3$) [δ, (multiplicity, relative intensity, assignment)] 7.1-6.7 (s, 2, CH); 5.5-5.0 (br, 0.6-1.0, C_5H_5); 2.8-2.2 (m, 5, alkyl); 1.67-0.96 (m, 11, alkyl). (c) **4**: IR (solid state) ν(CO) 2036, 1933 cm^{-1}. (d) **5**: IR (solid state) ν(CO) 2123, 2068, 2006 cm^{-1}.

[10] Compound **2** was similarly treated with 3-methylthiophene to give $[CpFe(CO)_2(3\text{-methylthiophene})]BF_4$ (**6**). **6**: IR (solid state) ν(CO) 2069, 2016 cm^{-1}; IR (CH_2Cl_2) 2072, 2031 cm^{-1}.

[11] The failure of the solid solution of **6** in **1** to conduct and the persistence of the conductivity of **3** under DC conditions rules out ionic conduction[12] as the source of the improved conductivity.

[12] Pollock, D. D. In *Electrical Conduction In Solids: An Introduction*; American Society for Metals: Metals Park, Ohio, 1985; p 265.

[13] Cotton, F. A.; Wilkinson, T. In *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: Toronto, 1988; pp 1307-1316.

[14] Thus a Fe(III) center generated near the anode could be propogated to the cathode by intra- and interchain electron transfer. Such a process would be a type of "electron hopping" mechanism (Böltger, H.; Bryskin, V. V. In *Hopping Conduction in Solids*; VCH Verlagsgesellschaft: Akademie-Verlag, Berlin, 1985; Chapter 1).

A Homogeneous Iron(II) System Capable of Selectively Catalyzing the Reduction of Terminal Alkynes to Alkenes and Buta-1,3-dienes

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Received April 12, 1989

Summary: Terminal alkynes are selectively hydrogenated to alkenes by the iron(II) catalyst precursors $[(PP_3)FeH(N_2)]BPh_4$ and $[(PP_3)FeH(H_2)]BPh_4$ in THF under very mild conditions $[PP_3 = P(CH_2CH_2PPh_3)_3]$. The catalytic reductive dimerization of $HC{\equiv}CSiMe_3$ to 1,4-bis(trimethylsilyl)butadiene prevails over alkene formation at reflux temperature.

Few iron complexes have been reported to be efficient hydrogenation catalysts.[1] We describe here a homogeneous iron(II) system which brings about the selective reduction of terminal alkynes to the corresponding alkenes under mild conditions and at good rates. Interestingly, by an appropriate choice of the alkyne substituent, the reductive dimerization to 1,4-disubstituted butadienes can be made to prevail over hydrogenation.

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[1] Spencer, A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 6, p 231.

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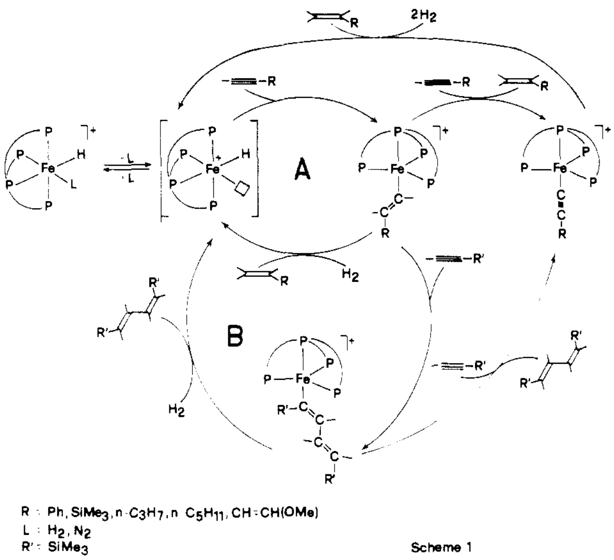
Scheme I



Terminal alkynes are selectively converted to alkenes at 1 atm of H_2 by the catalyst precursors $[(PP_3)FeH(N_2)]BPh_4$[2] (1) and $[(PP_3)FeH(H_2)]BPh_4$[3] (2), octahedral iron(II) complexes which interconvert upon treatment with H_2 or N_2, respectively [$PP_3 = P(CH_2CH_2PPh_2)_3$]. Both compounds (THF, room temperature) react with terminal alkynes (but not with disubstituted alkynes) in the absence of hydrogen to give σ-alkenyl products which may or may not be isolated depending on the alkyne substituent.

In particular, $HC{\equiv}CSiMe_3$ reacts with **1** or **2** to yield the σ-alkenyl derivative (*E*)-$[(PP_3)Fe\{CH{=}CH(SiMe_3)\}]BPh_4$[4] (**3**) as the predominant product together with some σ-acetylide complex $[(PP_3)Fe(C{\equiv}CSiMe_3)]BPh_4$[5] (**4**) and free vinyltrimethylsilane (10–15%). (At least a twofold excess of alkyne must be used in the reaction with **2** as 1 equiv is hydrogenated to $H_2C{=}CH(SiMe_3)$). The trans insertion of $HC{\equiv}CSiMe_3$ across the Fe—H bond has been established by ^1H NMR spectroscopy[6] on the diamagnetic, octahedral derivative $[(PP_3)Fe(CO)\{CH{=}CH(SiMe_3)\}]BPh_4$,[7] prepared by treating **3** in THF with 1 atm of CO. By treatment of **3** with further $HC{\equiv}CSiMe_3$, **4** and $H_2C{=}CH(SiMe_3)$ are obtained quantitatively (Scheme I). At reflux temperature, both reactions produce a small amount of free 1,4-bis(trimethylsilyl)butadiene, $(Me_3Si)HC{=}CHCH{=}CH(SiMe_3)$ (2–3%).[8]

Table I. Catalytic Hydrogenation[a] of Terminal Alkynes by the Catalyst Precursors 1 and 2

substrate HC≡CR	T, °C	product[b] rate[c] $H_2C{=}CH(R)$	$(R)HC{=}CHCH{=}CH(R)$
Ph	20	3.2	
	66	19.2	
$SiMe_3$	20	3.2	
	66	2.2	9.8
n-C_3H_7	20	3.1	
	66	14.7	
n-C_5H_{11}	20	2.7	
	66	9.5	
$CH{=}CH(OMe)$	20	1.2	
	66	8.2	

[a] Reaction conditions: H_2 pressure, 1 atm; alkyne, 0.9 mmol; catalyst, 0.03 mmol; time, 3 h; THF (solvent), 10 mL. [b] Products quantified and identified by GC and GC-MS. [c] Rate is reported as moles of substrate transformed per mole of catalyst per hour.

Other terminal alkynes such as $HC{\equiv}CPh$ or $HC{\equiv}C\text{-}C_3H_7$ directly give σ-acetylide complexes $[(PP_3)Fe(C{\equiv}CR)]BPh_4$ [R = Ph (**5**),[9] *n*-C_3H_7 (**6**)][10] and the corresponding alkenes with no formation of any stable σ-alkenyl complex or free butadiene. Most likely, this occurs because of a faster reaction of the σ-alkenyl intermediate with the alkyne as compared to alkenyl formation. Alkene formation is observed also when the σ-acetylide compounds are treated with H_2 in THF. All of the isolated compounds are paramagnetic with magnetic moments corresponding to two unpaired spins, typical of trigonal-bipyramidal (TBP) PP_3 complexes of iron(II).[11] Indeed, a preliminary X-ray analysis on the phenyl acetylide derivative **5** has shown that the complex is trigonal-bipyramidal with the alkynyl ligand located trans to the bridgehead phosphorus atom of PP_3.[12] Not all the paramagnetic compounds are ESR active; when they are (**4**, **5**, and **6**), the X-band spectra of THF glasses consist of broad bands with no hyperfine structure. In general, the σ-acetylide complexes exhibit very weak IR $\nu(C{\equiv}C)$ bands which, in some cases, are matched by strong Raman absorptions.

Under 1 atm of H_2, the reactions between **1** (or **2**) and excess alkynes are catalytic and produce only alkenes[13] (cycle A) regardless of the temperature, except for $HC{\equiv}CSiMe_3$ (Table I). In this case, the reductive dimerization[14] of the alkyne to 1,4-bis(trimethylsilyl)butadiene predominates over hydrogenation at high temperature (cycle B). In all cases, no appreciable formation of alkanes is observed even for very long reaction times (24 h). Compound **2** can be recovered almost quantitatively. Although we were not able to detect any intermediate, the dimerization reaction to butadiene probably proceeds via a TBP σ-butadienyl species. A complex of the latter type

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(3) Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1988**, *354*, C19.

(4) A mixture of $[(PP_3)FeH(N_2)]BPh_4$ (1.07 g, 1 mmol) and $HC{\equiv}CSiMe_3$ (145 μL, 1 mmol) in THF (40 mL) was stirred at room temperature for 1 h under nitrogen. Addition of ethanol (30 mL) and slow concentration of the solution led to the precipitation of yellow orange crystals in 80% yield. These contain **3** and a variable amount of **4** (10–15%). A pure sample of **3** was obtained by repeated recrystallization from THF/1-butanol mixtures: IR (Nujol mulls) 1605 cm^{-1} (m), $\nu(C{=}C)$, 850 cm^{-1} (vs), $\nu(Si{-}C)$; $\mu_{eff} = 3.35\ \mu_B$; ESR silent. Anal. Calcd for $C_{71}H_{73}BFeP_4Si$: C, 74.48; H, 6.43; Fe, 4.88. Found: C, 74.32; H, 6.36; Fe, 4.79.

(5) **4**: IR (Nujol mulls) 1990 cm^{-1} (m), $\nu(C{\equiv}C)$, 850 cm^{-1} (vs), $\nu(Si{-}C)$; $\mu_{eff} = 3.28\ \mu_B$; X-band ESR spectrum (THF glass, 100K) $\langle g \rangle = 2.018$, $\langle \Delta H \rangle = 200$ G. Anal. Calcd for $C_{71}H_{71}BFeP_4Si$: C, 74.61; H, 6.26; Fe, 4.89. Found: C, 74.44; H, 6.15; Fe, 4.78.

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(7) IR (Nujol mulls): 1980 cm^{-1} (s), $\nu(C{\equiv}O)$; 1520 cm^{-1} (m), $\nu(C{=}C)$. $^{31}P\{^1H\}$ (AM_2Q system, CD_3COCD_3, 293 K): δ_A, 172.29 ppm, td; δ_M, 79.95 ppm, dd; δ_Q 77.79 ppm, td; $J_{AQ} = 11.5$ Hz; $J_{AM} = 28.5$ Hz; $J_{MQ} = 11.7$ Hz. ^1H (CD_2Cl_2, 293 K): δ −0.73 (s, 9 H, $Si(CH_3)_3$), 5.67 (ddt, 1 H, $J_{HH} = 18.6$ Hz, $J_{HP} = 4.3$ Hz, $J_{HP} = 5.6$ Hz, $CH{=}C\mathit{H}(SiMe_3)$), 6.54 (m, 1 H, $J_{HP} = 9.00$ Hz, $J_{HP} = <4$ Hz, $C\mathit{H}{=}CH(SiMe_3)$). Anal. Calcd for $C_{72}H_{73}BFeOP_4Si$: C, 73.67; H, 6.27; Fe, 4.76. Found: C, 73.58; H, 6.24; Fe, 4.69.

(8) Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1978**, *144*, 1.

(9) **5**: IR (Nujol mulls) 2035 cm^{-1} (vw), $\nu(C{\equiv}C)$, 1580 cm^{-1}, reinforced phenyl vibration; Raman (CH_2Cl_2 solution) 2040 cm^{-1} (s), $\nu(C{\equiv}C)$; $\mu_{eff} = 3.42\ \mu_B$; X-band ESR spectrum (THF glass, 100 K) $\langle g \rangle = 2.030$, $\langle \Delta H \rangle = 175$ G. Anal. Calcd for $C_{74}H_{67}BFeP_4$: C, 77.50; H, 5.89; Fe, 4.87. Found: C, 77.34; H, 6.01; Fe, 4.82.

(10) **6**: IR (Nujol mulls) 2060 cm^{-1} (vw), $\nu(C{\equiv}C)$; $\mu_{eff} = 3.31\ \mu_B$; X-band ESR spectrum (THF glass, 100 K) $\langle g \rangle = 2.023$, $\langle \Delta H \rangle = 86$ G. Anal. Calcd for $C_{71}H_{69}BFeP_4$: C, 76.63; H, 6.25; Fe, 5.02. Found: C, 76.47; H, 6.14; Fe, 4.99.

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is likely formed when *cis*-1-ethoxy-1-buten-3-yne, $HC{\equiv}CCH{=}CH(OMe)$, is reacted with 1 to give the paramagnetic, TBP acetylide $[(PP_3)Fe\{C{\equiv}CCH{=}CH(OMe)\}]BPh_4$ (**7**)[15] as the butadiene $H_2C{=}CHCH{=}CH(OMe)$ is quantitatively liberated. Under H_2 this reaction is also catalytic, selectively hydrogenating the C–C triple bond.

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[15] 7: IR (Nujol mulls) 2015 cm^{-1} (w), ν(C═C), 1615 cm^{-1} (m), ν(C═C), 1270 cm^{-1} (s), ν(C—O—C); μ_{eff} = 3.36 μ_B; ESR silent. Anal. Calcd for $C_{71}H_{67}BFeOP_4$: C, 75.68; H, 5.99; Fe, 4.96. Found: C, 75.53; H, 5.92; Fe, 4.89.

Synthesis and Structure of Novel Antimony Thiametallacycles[†]

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Received May 25, 1989

Summary: The first examples of a new class of main-group metallacycles, 4,5-didehydro-2-thiastibolanes, have been synthesized. These compounds were prepared via transmetalation from zirconocene metallacycles. The X-ray crystal structures of the 1-chloro-4,5-dimethyl-4,5-didehydro-2-thiastibolane (**4a**) and the 1-bromo-4,5-diphenyl-4,5-didehydro-2-thiastibolane (**5b**) are reported.

Recently a dramatic resurgence of interest in the organometallic chemistry of the main group elements has occurred. To a large degree this renewed activity derives from the utility of main-group compounds in fields such as ceramics,[1] electronic[2] and thermochromic materials,[3,4] and marine antifouling compounds.[5] The development of general, efficient synthetic methods for the preparation of hitherto inaccessible main-group organometallics should greatly enhance progress in many of these fields. In this communication, we report the preparation and characterization of a new class of main-group metallacycle, 4,5-didehydro-2-thiastibolanes, via a transmetalation from zirconium.[6]

We recently reported the synthesis and a study of the reactivity of the thioformaldehyde complex of zirconocene.[7] In particular, metallacycles **2** can be prepared by treatment of either thioformaldehyde complex **1a** or **1b** with an alkyne. Following the precedent of Fagan and Nugent,[6] exposure of benzene suspensions of the thiazirconacycles to 1 equiv of $PhSbCl_2$ or SbX_3 (X = Cl, Br) results in the rapid and quantitative (by ^1H NMR) formation of the corresponding antimony metallacycles **3**–**5** and zirconocene dichloride. With the exception of **3b**, the compounds may be isolated in good yield by the removal of benzene in vacuo, extraction with hexanes/ether (ca. 10:1), and chromatography on alumina III or anhydrous $MgSO_4$.[8] The formation of **3b** can be observed by ^1H NMR,[9] and the compound is indefinitely stable either in solution or as a solid in the presence of Cp_2ZrCl_2. However, all attempts to remove Cp_2ZrCl_2 have either failed or resulted in the decomposition of **3b**. Metallacycles **3a**, **4**, and **5** are all air-stable solids and may be stored indefinitely in a dry atmosphere.

Compounds **4b** and **5c** were characterized by single-crystal X-ray diffraction studies,[10] and the ORTEPs are shown in Figures 2 and 3. Compound **4b** is polymeric in the crystalline state. The structure consists of a single stibacycle per asymmetric unit cell. However, the antimony and sulfur atoms of the molecule are mutually bound to the sulfur and antimony atoms of a neighboring molecule (contact distance 3.1 Å), affecting a seesaw geometry about the antimony atoms of the dimeric unit. An additional S–Sb close contact of approximately 3.5 Å gives rise to a puckered net of Sb–S parallelograms in the *ac* plane of the unit cell (see Figure 2b). The geometry about the antimony atom can best be described as a square pyramid with the long contact lying in the basal plane of the unit and the axial position occupied by an intermolecular carbon atom C(3). The sulfur atom of each stibacycle is puckered 0.26 Å out of the plane defined by Sb, C(1), C(2), and C(3) in the direction of the second antimony atom to which it is bound.

The structure of compound **5c** consists of a centrosymmetric dimer. The intermolecular Sb–S distances are in

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[†] Dedicated to our friend and colleague Professor Dietmar Seyferth on the occasion of his 60th birthday.

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[8] Compounds **3a**, **4a**, and **5a** were purified by chromatography on alumina III; compounds **4b**,**c** and **5b**,**c** were purified by chromatography on anhydrous $MgSO_4$.

[9] ^1H NMR (300 MHz, C_6D_6): δ 6.98 (dt, J = 7, 1 Hz, 1 H), 6.74 (dt, J = 7, 1 Hz, 1 H).

[10] X-ray data for **4b**: crystals from toluene-d_8 at room temperature; a colorless prism of **4b** (0.15 mm × 0.18 mm × 0.18 mm) was mounted on a glass fiber; data were collected at 23 °C on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation, λ = 0.7169 Å; orthorhombic, space group *Pbca*; a = 11.541 (2) Å, b = 19.104 (3) Å, c = 7.3483 (8) Å; V = 1620.2 (8) Å^3; Z = 8; d(calcd) = 2.11 g/cm^3. A total of 1682 reflections were collected (ω–2θ scan) to 2θ of 50.0°. The structure was solved by direct methods (SHELXS-86). Anisotropic refinement of all non-hydrogen atoms by full matrix least squares (fixed hydrogen parameters, $d_{C'-H}$ = 0.95 Å) resulted in R = 0.036 and R_w = 0.042. X-ray data for **5c**: crystals from toluene at −20 °C; a colorless block of **5c** (0.65 mm × 0.65 mm × 0.65 mm) was mounted on a glass fiber; data were collected at 23 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation, λ = 0.7169 Å; monoclinic, space group $C2/c$; a = 18.805 (2) Å; b = 7.566 (1) Å, c = 24.416 (2) Å; V = 3358 (1) Å^3; Z = 8; d(calcd) = 1.982 g/cm^3. A total of 2575 unique reflections were collected (ω–2θ scan) to 2θ of 48.8°. The structure was solved by direct methods (SHELXS-86). Non-hydrogen atoms were refined anisotropically with the exception of the solvate presumed to be toluene (vide infra): R = 0.043 and R_w = 0.051. The solvate (occupancy = 0.5) was highly disordered about the crystallographic 2-fold axis. The model used evenly distributed the toluene molecule about the 2-fold axis with the symmetry element passing through the ortho and meta carbons. Seven peaks from the difference Fourier map were assigned a total scattering power equivalent to three carbon atoms. This model precluded the location of the methyl carbons because of the large number of sites over which they were distributed.

0276-7333/89/2308-2082$01.50/0