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New 2,4,6-Triisopropylphenyl-Substituted Disilenes

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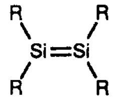
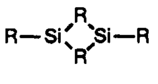
Two new substituted disilenes, of the type IsRSi=SiIsR (Is = 2,4,6-triisopropylphenyl; R = Me_3Si (**1**), *t*-Bu (**2**)), were synthesized by photolysis of the corresponding polysilanes $IsRSi(SiMe_3)_2$ (**3**, **4**). Compound **1** is the first stable disilene substituted with a non-first-row element. X-ray crystal structures are reported for the *E* isomers for disilenes **1** and **2** and for tetrasilane **3**. Both disilenes are triclinic and have space group $P\bar{1}$. The unit cell dimensions for (*E*)-**1** are a = 10.046 (3) Å, b = 10.221 (3) Å, c = 10.307 (3) Å, α = 67.73 (2)°, β = 86.36 (3)°, and γ = 84.47 (3)°. For (*E*)-**2** a = 9.387 (2) Å, b = 9.870 (3) Å, c = 11.457 (3) Å, α = 76.54 (2)°, β = 76.16 (2)°, and γ = 64.54 (2)°. Tetrasilane **3** is monoclinic, having $P2_1/n$ as space group with cell dimensions a = 9.380 (3) Å, b = 28.676 (9) Å, c = 10.862 (3) Å, and β = 97.47 (2)°. Trisilanes $Is(X)Si(SiMe_3)_2$ (X = H, Cl, F, 1-pyrrolyl) were synthesized and photolyzed at 254 nm.

Introduction

Bulky disubstituted silylenes have been known for more than 10 years to form stable dimers which posses disilene structures of type A.[1] The variety in substituents, however, is rather limited; only alkyl-, aryl-, and $(Me_3Si)_2N$-substituted compounds have been thus far isolated. Little is known of the effects of heteroatom substitution on the properties of the silicon–silicon double bond. Recent calculations suggest that electron-releasing substituents, including the trimethylsilyl group, should stabilize disilenes, whereas halides and amino groups are predicted to destabilize the double bond with respect to individual silylenes.[2] In fact, the latter class of substituents might even favor the bridged type structure B, without a formal silicon–silicon bond, rather than the classical disilene structure A.[3]



A

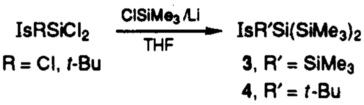


B

In this paper we report the synthesis of *E* and *Z* isomers of the first silyl-substituted disilene, 1,2-bis(trimethylsilyl)-1,2-bis(2,4,6-triisopropylphenyl)disilene (**1**), as well as the analogous *tert*-butyl compounds (*E*)-**2** and (*Z*)-**2**. In addition, the synthesis of several heteroatom-substituted trisilanes, $Is(X)Si(Me_3Si)_2$, is reported, along with results of photolysis of these compounds.

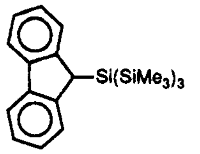
Results and Discussion

Synthesis of 3 and 4 and Crystal Structure of 3. Compounds **3** and **4** were obtained in good yield from coupling of the corresponding chlorosilanes $IsSiCl_3$ and $Is(t\text{-}Bu)SiCl_2$[4] with chlorotrimethylsilane in THF using lithium metal as reducing agent (eq 1). Compound **3** had previously been prepared from $IsSiCl_3$ and Me_3SiCl with magnesium metal and hexamethylphosphoric triamide.[5] Our procedure resulted in a comparable or higher yield without the use of HMPT.



$$\underset{R\,=\,Cl,\ t\text{-}Bu}{IsRSiCl_2} \xrightarrow[THF]{ClSiMe_3/Li} \underset{\substack{\mathbf{3},\ R' = SiMe_3\\ \mathbf{4},\ R' = t\text{-}Bu}}{IsR'Si(SiMe_3)_2} \qquad (1)$$

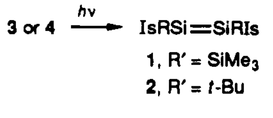
Structural analysis of **3** was undertaken to assess the effect of a hindering 2,4,6-triisopropylphenyl group on both the bond angles and the bond lengths of a 2,2-disubstituted polysilane. As expected, the structure exhibits some distortion from normal bond lengths and angles. The molecular geometry of **3** is shown in Figure 1. The structure of **3** can usefully be compared with that of the closely related fluorenyl tetrasilane **5**.[6] Compound **5** exhibits a rather long C–Si bond distance of 194.7 pm, but otherwise the molecule is essentially normal with the average of the Si–Si bond lengths being 236.6 pm. All of the Si–Si–Si and C–Si–Si bond angles are nearly tetrahedral, the average Si–Si–Si bond angle being 109.3° and the average fluorenyl-Si–Si bond angle 109.7°.



5

The geometry of **3** is somewhat more severely distorted around the central silicon atom. The long (194.8 pm) Si–C bond distance is similar to that in **5**, and the Si–Si bond lengths are only slightly larger, averaging 237.8 pm. Significant distortion is evident, however, from the bond angles in **3**: 100.0, 103.2, and 116.2° for Si–Si–Si and 103.9, 112.7, and 116.2° for C–Si–Si.

Synthesis of Disilenes. Disilenes **1** and **2** were synthesized by low-temperature photolysis (254 nm) of polysilanes **3** and **4** (eq 2). The crude photolysis mixtures



$$\mathbf{3}\ \text{or}\ \mathbf{4} \xrightarrow{h\nu} \underset{\substack{\mathbf{1},\ R' = SiMe_3\\ \mathbf{2},\ R' = t\text{-}Bu}}{IsRSi{=}SiRIs} \qquad (2)$$

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[1] Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, pp 1015–1142. Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. West, R. *Pure Appl. Chem.* **1984**, *56*, 163. West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201 and references cited in these reviews.

[2] (a) Karni, M.; Apeloig, Y. *J. Am. Chem. Soc.* **1990**, *112*, 8589. (b) Maxka, J.; Apeloig, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 737. (c) Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125.

[3] The marginally stable dimer of (pentamethylcyclopentadienyl)fluorosilylene, reported by Jutzi and co-workers, may have a structure of type B. See: Jutzi, P.; Holtman, U.; Bogge, H.; Muller, A. *J. Chem. Soc., Chem. Commun.* **1988**, 305. See also ref 2b.

[4] Smit, C. N.; Bickelhaupt, F. *Organometallics* **1987**, *6*, 1156.

[5] Puranik, D. B.; Johnson, M. P.; Fink, M. J. *Organometallics* **1989**, *8*, 770.

[6] Rengstl, A.; Schubert, U. *Chem. Ber.* **1980**, *113*, 278.

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Table I. Experimental Crystallographic Data for 3, (*E*)-1, and (*E*)-2

	ISSi(SiMe$_3$)$_3$ (3)	(*E*)-Is$_2$(SiMe$_3$)$_2$Si$_2$ ((*E*)-1)	(*E*)-Is$_2$(*t*-Bu)$_2$Si$_2$ ((*E*-2)
empirical formula	$C_{24}H_{50}Si_4$	$C_{36}H_{64}Si_4$	$C_{38}H_{64}Si_2$
fw	450.98	608.41	576.45
cryst size, mm	0.2 × 0.5 × 0.5	0.08 × 0.20 × 0.35	0.1 × 0.25 × 0.4
temp, K	113 (2)	123 (2)	113 (2)
cryst syst	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
unit cell dimens			
a, Å	9.380 (3)	10.046 (3)	9.387 (2)
b, Å	28.676 (9)	10.221 (3)	9.870 (3)
c, Å	10.862 (3)	10.307 (3)	11.457 (3)
α, deg		67.73 (2)	76.54 (2)
β, deg	97.47 (2)	86.36 (3)	76.16 (2)
γ, deg		84.47 (3)	64.54 (2)
V, Å^3	2896.9 (16)	974.4 (5)	920.3 (4)
Z	4	1	1
density (calcd), g cm^{-3}	1.034	1.038	1.041
abs coeff, mm^{-1}	0.208	1.566	1.04
2θ range, deg	3.5–50	4.0–114.0	4.0–114.0
scan type	Wyckoff	Wyckoff	Wyckoff
scan speed, deg/min in ω	variable (2–20)	variable (2–20)	variable (2–20)
scan range (ω), deg	0.90	0.50	0.60
no. of obsd reflns ($F > 4.0\sigma(F)$)	3977	1991	2167
data to param ratio	13.3/1	10.9/1	7.1/1
largest diff peak, eÅ^{-3}	0.41	−0.34	−0.48
largest diff hole, eÅ^{-3}	−0.58	−0.39	−0.40
R, %	4.51	6.39	6.00
R_w, %	5.16	7.18	8.17
goodness of fit	1.60	1.87	2.49

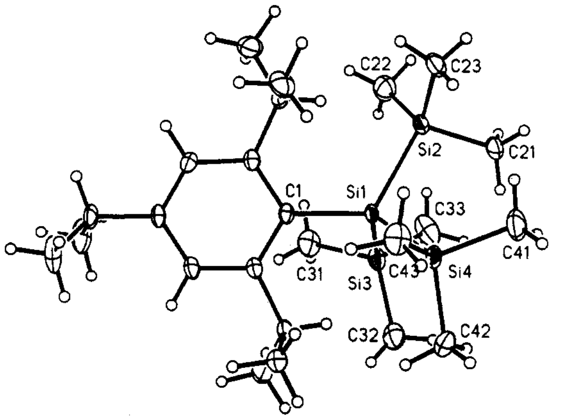

Figure 1. (1) Thermal ellipsoid drawing of IsSi(SiMe$_3$)$_3$ (3).

contain both cis and trans isomers of each disilene, with the cis isomer formed in greater yield. The trans isomers, which are much less soluble, partially precipitate from the reaction mixture as air-sensitive yellow crystalline solids. The solutions after filtration contain mainly the cis isomers. Heating of the mother liquors can be used to convert the cis isomers into the more thermodynamically stable trans isomers.

In the proton NMR of compound (*E*)-1 (see Experimental Section), all the isopropyl protons are shifted downfield as compared to those in the (*Z*)-1 isomer, but the trimethylsilyl protons are shifted upfield with respect to those in the *Z* isomer. The ^{29}Si NMR resonances for *trans*-disilene isomers normally lie upfield of those for cis isomers,[1] but for 1 the resonance for the trans isomer (^{29}Si NMR δ +97.75) is slightly downfield from that of the cis isomer (^{29}Si NMR δ +97.68).

Unlike (*E*)-1, the proton NMR of (*E*)-2 (see Experimental Section) shows both the isopropyl and the *tert*-butyl group protons to be shifted downfield as compared to those in the cis isomer. The trans isomer of (*E*)-2 (^{29}Si NMR δ +87.39) is consistent with other *trans*-disilenes, showing an upfield ^{29}Si shift as compared to the cis isomer (^{29}Si NMR δ +96.93).

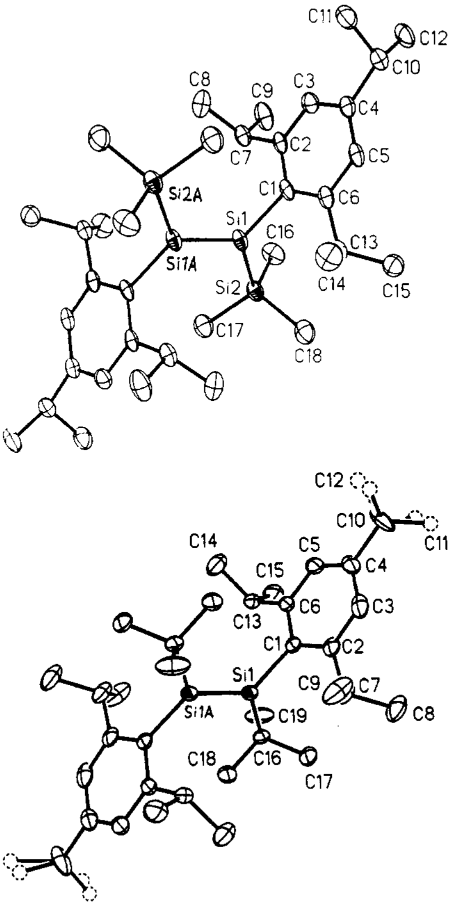

Figure 2. Thermal ellipsoid drawings of (a, top) (*E*)-Is$_2$(SiMe$_3$)$_2$Si$_2$ ((*E*)-1) and (b, bottom) (*E*)-Is$_2$(*t*-Bu)$_2$Si$_2$ ((*E*)-2).

Solid-State Structures of (*E*)-1 and (*E*)-2. Thermal ellipsoid diagrams indicating the molecular structure are shown in Figure 2a for (*E*)-1 and Figure 2b for (*E*)-2, and the data collection for these structures as well as for 3 is summarized in Table I. The structures of (*E*)-1 and (*E*)-2 are similar to that for (*E*)-Mes(*t*-Bu)Si═Si(*t*-Bu)Mes

Table II. Selected X-ray Data for Disilenes (*E*)-1, (*E*)-2, and (*E*)-6

	(*E*)-Is_2-$(SiMe_3)_2Si_2$ ((*E*)-1)	(*E*)-Is_2(*t*-$Bu)_2Si_2$ ((*E*)-2)	(*E*)-Mes_2(*t*-$Bu)_2Si_2$ ((*E*)-6)
$r_{Si=Si}$, pm	215.2 (3)	215.7 (2)	214.3 (1)
$r_{Si-C_{aryl}}$, pm	189.8 (5)	188.0 (3)	188.4 (2)
$R_{Si-C_{alkyl}}$, pm		191.8 (4)	190.4 (3)
$r_{Si-Si_{silyl}}$, pm	233.4 (2)		
twist, deg[a]	0	0	0
pyram, deg[b]	0	0	0
ring orientn, deg[c]	89.2	90.0	88.0

[a] The twist angle is taken as the dihedral angle between the C–Si–C and C′–Si′–C′ planes (for (*E*)-2 and (*E*)-6) or Si_{silyl}–Si–C and Si'_{silyl}–Si′–C′ planes (for (*E*)-1. [b] The pyramidalization is gauged by the angle formed between the C–Si–C plane (for (*E*)-2 and (*E*)-6) or Si–Si–C plane (for (*E*)-1) and the Si–Si vector. [c] Angle between the aromatic ring plane and the corresponding C_{aryl}–Si–Si plane (for (*E*)-2 and (*E*)-6) or Si_{silyl}–Si–Si plane (for (*E*-1).

((*E*)-6),[7a] and important structural parameters for these three compounds are listed in Table II.

Compounds (*E*)-1, (*E*)-2, and (*E*)-6 each possess a crystallographic center of symmetry midway between the silicon atoms. In all three compounds the silicon–silicon double bond has a planar, untwisted geometry, with no pyramidalization at silicon. In these features these three compounds differ from most other disilenes, which exhibit slight twisting at the Si=Si bond, pyramidalization at silicon, or both. Finally, in all three compounds the aromatic rings are perpendicular to the plane of the Si=Si double bond, or nearly so (see Table II).[7b]

The silicon–silicon distances in (*E*)-1 and (*E*)-2 are slightly longer than for (*E*)-6, perhaps reflecting greater hindrance in the 2,4,6-triisopropylphenyl-containing disilenes. The Si–C(alkyl) and Si–C(aryl) bond lengths are also slightly longer than in (*E*)-6. The Si–Si single-bond length in (*E*)-1 of 233.4 pm is shorter than the usual Si–Si single-bond distance of 234–236 pm. This decrease is expected for a bond from an "sp^2 hybridized" silicon atom and was observed earlier for a trimethylsilyl-substituted silene.[8]

UV/Visible Spectroscopy of 1 and 2. The electronic absorption spectra for disilenes 1 and 2 are shown in Figure 3. Selected UV/vis data for these compounds as well as for (*E*)-6 are summarized in Table III. It has been mentioned before that (*E*)-1, (*E*)-2, and (*E*)-6 are structurally very similar, and one might have expected to find close resemblances in their electronic spectra as well. Indeed, (*E*)-2 and (*E*)-6 show main absorptions, due to $\pi \rightarrow \pi^*$ transitions, that differ only slightly; for (*E*)-1, on the other hand, λ_{max} lies at much lower energy, shifted by almost 60 nm. In all three trans isomers, none of the aryl groups are in positions suitable for conjugation with the silicon–silicon double bond (see Table II). Therefore, the large red shift observed for (*E*)-1 as compared to (*E*)-6 must be due to the electronic effect of the Me_3Si substituents. Since the silicon atom is much more electropositive than carbon, it may inductively release electrons to the sp^2 silicon through the σ system, raising the energy of the π HOMO. In addition, and perhaps more important, the silyl substituent may delocalize electrons from the π^* excited state by mixing of C–Si σ^* orbitals.

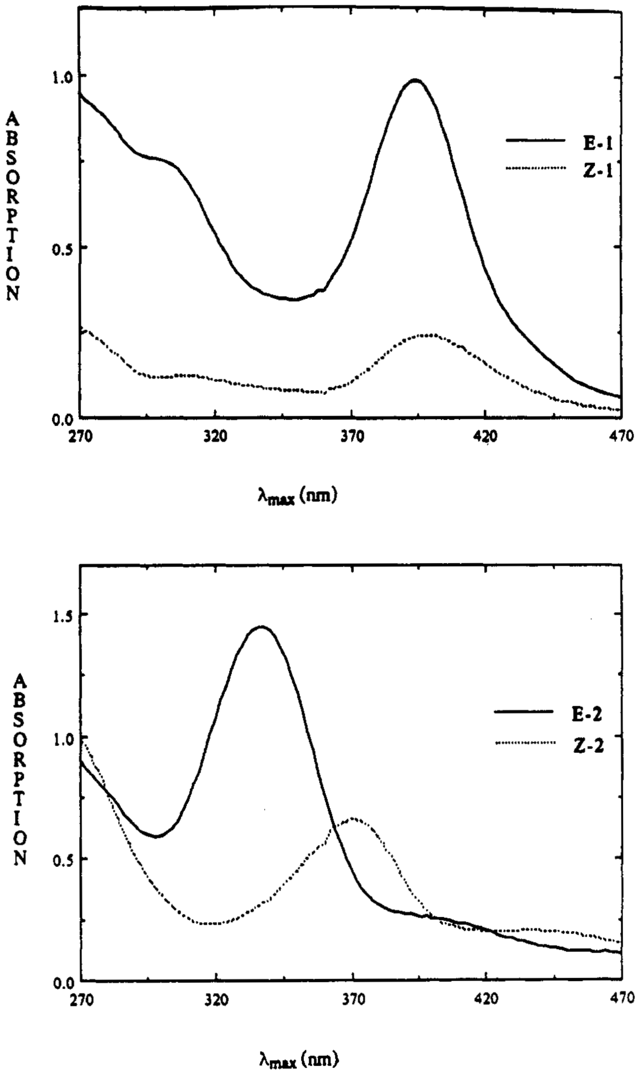

Figure 3. Electronic spectra for disilenes (a, top) $Is_2(SiMe_3)_2Si_2$ (1) and (b, bottom) Is_2(*t*-$Bu)_2Si_2$ (2).

For both 1 and 2, the *Z* isomer absorbs at lower energy than the *E* isomer, probably as a result of increased phenyl delocalization. The shift difference for 2 is considerably larger (35 nm) than for 1 (4 nm). In the latter case, the stabilization due to the silyl substituents seems to be more important than the delocalization effect from the phenyl rings.

Photolysis of (*E*)-1 and (*E*)-2. Previous studies on unsymmetrical disilenes have shown that irradiation of either the *trans*-disilene or a cis/trans mixture of disilenes eventually leads to a photostationary equilibrium mixture containing both cis and trans isomers.[9] We irradiated the pure *trans*-disilenes at 350 nm to determine the cis/trans equilibrium composition. Disilene (*E*)-2 rearranges completely (>99%) and cleanly to its *Z* isomer after 50 h of irradiation. In a comparison of the extinction coefficients at 350 nm for the cis and trans isomers (see Table III), it is not surprising that the cis isomer is favored over the trans form, since the latter absorbs three times more strongly at this wavelength. Total conversion of trans into cis, however, is unprecedented. The conversion of (*E*)-1 to (*Z*)-1 was somewhat slower, requiring 100 h for complete disappearance of the *E* isomer. Considerable (~50%) decomposition also took place, yielding what appeared to be polymeric material.

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(7) (a) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793. (b) Shepherd, B. D.; Campana, C. F.; West, R. *Heteroat. Chem.* **1990**, *1*, 1.

(8) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

(9) Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 821.

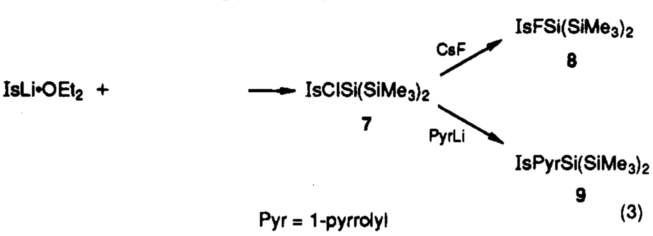
Table III. UV/Visible Data for Disilenes 1, 2, and 6[a]

	(*E*)-1	(*Z*)-1	(*E*)-2	(*Z*)-2	(*E*)-6[b]
λ_{max}, nm	294 sh, 394	304 sh, 398	337, 410 sh	372, 452 sh	338
$\epsilon\lambda_{max}$, 10^3 M^{-1} cm^{-1}	6.0, 8.4	1.0, 2.0	11, 2.0	4.8, 1.4	c
$\epsilon_{350\ nm}$, 10^3 M^{-1} cm^{-1}	2.9	0.34	8.5	3.2	c

[a] UV measured in 3-methylpentane (3mp) solutions. [b] The (*Z*)-6 isomer was not reported. [c] The ϵ value was not reported.

In addition to photolysis with a 350-nm light source, irradiation of (*E*)-1 and (*E*)-2 with 254-nm light was also examined. As expected from higher energy light, the degree of decomposition of compound 1 was more rapid, and in fact after 100 h of photolysis, no disilene, either cis or trans, was left. The rate of conversion for (*E*)-2 was slower than with 350-nm light, reflecting a smaller difference in absorption between the isomers at this wavelength; after 100 h the cis/trans ratio was found to be 6.3/1.

Synthesis and Photolysis of Heteroatom-Substituted Trisilanes. Several heteroatom-substituted trisilanes $Is(X)Si(SiMe_3)_2$ were synthesized and photolyzed, with the hope that disilenes with heteroatom substitution might be formed. Reaction of (2,4,6-triisopropylphenyl)lithium[4] with 2,2-dichlorohexamethyltrisilane produced the chloro compound 7 in 95% yield. This compound was then used to synthesize two additional trisilanes bearing a fluorine (8) or a 1-pyrrolyl group (9) (eq 3).



(3)

The hydrogen-substituted trisilane $Is(H)Si(SiMe_3)_2$ was prepared by hydrolysis of $Is(Li)Si(SiMe_3)_2$.[5] In addition, for reasons which will become apparent, dichlorodisilane $Is(SiMe_3)SiCl_2$ was made by a reaction analogous to that used for 7, using $Cl_3SiSiMe_3$ as starting material instead of $Cl_2Si(SiMe_3)_2$.

When 7 was photolyzed in degassed pentane at −60 °C for 24 h, the solution gradually became a dark yellow-orange, indicative of disilene formation. The pentane was removed, and the orange solid was dissolved in benzene and examined by ^{29}Si NMR. No signal for 7 remained, but resonances at +97.78, +97.67, −10.56, and −9.98 ppm were observed. These signals match exactly those for (*E*)-1 and (*Z*)-1 (vide supra). A resonance at δ 30.5 was also observed, corresponding to trimethylchlorosilane. Thus, in this case photolysis proceeds with loss of trimethylchlorosilane instead of hexamethyldisilane (eq 4). The process does not occur thermally. This mode of silylene extrusion is related to that which occurs in the photolysis of tris(trimethylsilyl)(trimethylsiloxy)silane, in which hexamethyldisiloxane is produced.[10]

$$[IsClSi:] \xleftarrow[\times]{-Me_3SiSiMe_3} \mathbf{7} \xrightarrow[h\nu]{-Me_3SiCl} \underset{\mathbf{1}}{{}^1\!/_2 Is(SiMe_3)Si{=}SiIs(SiMe_3)} \quad (4)$$

With the intention of using this mode of silylene extrusion to our advantage, $Is(SiMe_3)SiCl_2$ was photolyzed for 36 h at −60 °C in degassed pentane. However, no reaction took place. Photolysis of $Is(H)Si(SiMe_3)_2$ also gave only starting material after 36 h of photolysis at −60 °C in pentane.

Both 8 and 9 underwent photolysis under the same conditions, to give colored solutions. However, when these solutions were examined by ^{29}Si NMR spectroscopy, the only new peak observed was that for hexamethyldisilane. The signals in the ^1H NMR spectrum were quite broad, even at elevated temperatures. It seems likely these photolyses led to polymeric products.

Experimental Section

All reactions and manipulations were conducted under a nitrogen or argon atmosphere by using standard Schlenk techniques. Routine ^1H NMR (200 MHz) spectra were collected on a Bruker WP-200 spectrometer. ^{29}Si NMR spectra were collected on either a Bruker WP-270 (53.67 MHz) or a Bruker AM-360 (71.55 MHz) spectrometer using INEPT pulse sequences and complete proton decoupling.[11] Chemical shifts are reported in parts per million from a tetramethylsilane external standard. High-resolution mass spectra were recorded on a Kratos MS-80 mass spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard (HP) 5890A gas chromatograph with an AP series 530-μm fused silica column and HP 3390A integrating recorder. Reported melting points are uncorrected.

Hydrocarbon solvents were dried and distilled over either sodium or potassium. Halogenated solvents were distilled from phosphorus pentoxide. Solvents for photolysis or UV spectroscopy were deolefinated by washing twice each with a 50% H_2SO_4–50% HNO_3 mixture, H_2SO_4, H_2O, KOH (aqueous), and H_2O, 200 mL per 600 mL of hydrocarbon. The solvents were then dried over $MgSO_4$ and distilled over CaH_2 under nitrogen.

Methyllithium–lithium bromide complex in diethyl ether (1.5 M), *n*-butyllithium in hexanes (2.5 M), zinc fluoride, and cesium fluoride (Aldrich) were purchased and used without further purification. Triethylamine and pyrrole were distilled from calcium hydride before use.

Photolyses were carried out in a Rayonet Model RPR-208 photoreactor equipped with 254-nm lamps or in a Rayonet Model RPR-100 photoreactor equipped with 350-nm lamps. Low temperatures for photolysis were maintained by the use of a quartz Dewar equipped with a liquid-nitrogen blow-off system and temperature controller.

$IsSi(SiMe_3)_3$ (3).[5] To a solution containing (2,4,6-triisopropylphenyl)trichlorosilane[4] (8.0 g, 0.024 mol) and chlorotrimethylsilane (25.7 g, 0.24 mol) in THF (150 mL) was added lithium metal (1.1 g, 0.16 mol) cut into small chunks. The solution was allowed to react at room temperature for 12 h and then refluxed for an additional 6 h, at which time GC analysis indicated the reaction to be complete. The solution was filtered to remove unreacted lithium and insoluble salts. Next, the filtrate was evaporated to a solid and 250 mL of hexane was added. The insoluble salts were removed by filtration. The filtrate was evaporated in vacuo, leaving a crude solid which was recrystallized from ethanol to yield 8.7 g (76%) of pure 3 as a white solid, mp 91–92 °C. ^1H NMR (C_6D_6): δ 6.85 (s, 2 H), 3.15 (hept, 2 H, J = 7 Hz), 2.72 (hept, 1 H, J = 7 Hz), 1.08 (d, 12 H, J = 7 Hz), 0.12 (s, 27 H). ^{29}Si NMR (C_6D_6): δ −11.32, −82.46. HRMS:[12] exact mass for $C_{23}H_{47}Si_4$ {M − CH_3} calculated *m*/*e* 435.2738, found *m*/*e* 435.2755 (4.5%); exact mass for $C_{21}H_{41}Si_3$ {M − C_3H_9Si} calculated *m*/*e* 377.2524, found *m*/*e* 377.2516 (70.7%).

Is-*t*-$BuSi(SiMe_3)_2$ (4). To a solution containing dichloro(2,4,6-triisopropylphenyl)-*tert*-butylsilane[4] (42 g, 0.012 mol) and chlorotrimethylsilane (13.0 g, 0.12 mol) in THF (150 mL) was added small chunks of lithium metal (0.35 g, 0.051 mol). The solution under argon was allowed to react at room temperature

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[10] Gaspar, P. P.; Chen, Y.-S.; Helfer, A. P.; Konieczny, S.; Ma, E. C.-L.; Mo, S.-H. *J. Am. Chem. Soc.* **1981**, *103*, 7344.

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[12] The molecular ion could not be observed.

for 12 h and the refluxed for an additional 6 h, at which time GC analysis indicated the reaction to be complete. The solution was filtered to remove unreacted lithium metal and any insoluble salts; the filtrate was then stripped and 200 mL of hexane was added. The remaining salts were removed by filtration, and the filtrate was evaporated to dryness. The resulting crude solid was recrystallized from ethanol, yielding 4.8 g (95%) of pure **4** as a white solid, mp 115–116 °C. ^{1}H NMR (C_6D_6): δ 6.90 (s, 2 H), 3.27 (hept, 2 H, J = 7 Hz), 2.74 (hept, 1 H, J = 7 Hz), 1.14 (d, 6 H, J = 7 Hz), 1.10 (d, 12 H, J = 7 Hz), 0.98 (s, 9 H), 0.28 (s, 18 H). ^{29}Si NMR (C_6D_6): δ −13.05, −26.72. HRMS:[12] exact mass for $C_{24}H_{46}{}^{28}Si_2{}^{29}Si$ {M − CH_3} calculated *m/e* 419.2903, found *m/e* 419.2873 (2.4%); exact mass for $C_{22}H_{41}Si_2$ {M − C_3H_9Si} calculated *m/e* 361.2747, found *m/e* 361.2733 (53.4%). Anal. Calcd for $C_{25}H_{50}Si_3$: C, 69.04; H, 11.59. Found: C, 66.13; H, 11.55.

(*E*)-Disilenes (1 and 2). A solution of **3** (1.0 g, 2.2 mmol) or **4** (1.0 g, 2.3 mmol) in deolefinated pentane (40 mL) was placed in a quartz photolysis tube equipped with a fritted filter for recrystallization. The solution was degassed (three times) and photolyzed at −60 °C using a 254-nm light source. The solution changed color immediately, and precipitation of the *trans*-disilene was observed. After 48 h of photolysis, two-thirds of the volume of the solvent was removed in vacuo and the trans isomer was further precipitated at −78 °C. The trans isomer was filtered, yielding 110 mg (17%) of (*E*)-**1** (or 170 mg (25%) of (*E*)-**2**) as a (pale) yellow solid. The orange-red mother liquor contained the cis isomer and remaining impurities. The mother liquor was evaporated in vacuo and the residue then dissolved in degassed hexane (15 mL). The orange solution was placed into a Schlenk tube and heated for 1 week at 60 °C. The less soluble trans disilenes precipitated and were filtered, yielding 0.37 g (an additional 56%) or 73% total of (*E*)-**1** (or 0.36 g (an additional 58%) or 83% total of (*E*)-**2**). (*E*)-**1**: mp 233–235 °C (thermochromic, red); ^{1}H NMR (C_6D_6) δ 7.17 (s, 4 H), 4.05 (hept, 4 H, J = 6.7 Hz), 2.82 (hept, 2 H, J = 6.9 Hz), 1.53 (d, 12 H, J = 6.7 Hz), 1.42 (d, 12 H, J = 6.7 Hz), 1.25 (d, 12 H, J = 6.9 Hz), 0.11 (s, 18 H); ^{29}Si NMR (C_6D_6) δ +97.75, −10.56; HRMS exact mass for $C_{36}H_{64}Si_4$ calculated *m/e* 608.4085, found *m/e* 608.4094 (23%); UV (3-methylpentane (3mp)) λ_{max} 294 sh nm ($\epsilon = 6 \times 10^3\ M^{-1}\ cm^{-1}$), 394 nm ($\epsilon = 8 \times 10^3\ M^{-1}\ cm^{-1}$). Anal. Calcd for $C_{36}H_{64}Si_4$: C, 70.97; H, 10.60. Found: C, 70.11; H, 10.74. (*E*)-**2**: mp 250–252 °C (thermochromic, yellow-orange); ^{1}H NMR (C_6D_6) δ 7.11 (s, 4 H), 4.21 (hept, 4 H, J = 6.5 Hz), 2.76 (hept, 2 H, J = 7.0 Hz), 1.49 (d, 12 H, J = 6.5 Hz), 1.38 (d, 12 H, J = 7 Hz), 1.18 (d, 12 H, J = 7.0 Hz), 1.11 (s, 18 H); ^{29}Si NMR (C_6D_6) δ 87.39; HRMS exact mass for $C_{38}H_{64}Si_2$ calculated *m/e* 576.4546, found *m/e* 576.4504 (14.7%); UV (3mp) λ_{max} 337 nm ($\epsilon = 11 \times 10^3\ M^{-1}\ cm^{-1}$), 410 sh nm ($\epsilon = 2 \times 10^3\ M^{-1}\ cm^{-1}$). Anal. Calcd for $C_{38}H_{64}Si_2$: C, 79.09; H, 11.18. Found: C, 79.05; H, 11.40.

Photolysis of (*E*)-1 and (*E*)-2. Compound (*E*)-**1** (or (*E*)-**2**) (50 mg) in C_6D_6 (1 mL) was placed in a sealed NMR tube and photolyzed at 35 °C with a 350-nm light source. After 100 h (or 50 h) ^{1}H and ^{29}Si NMR showed complete conversion to the *cis*-disilene. By NMR, the yield of (*Z*)-**1** in the orange-red solution is about 50%, with the remaining product representing unidentified decomposition compounds. For (*Z*)-**2**, the yield is greater than 99%. Both compounds were obtained as orange, glassy, noncrystalline solids. (*Z*)-**1**: ^{1}H NMR (C_6D_6) δ 7.01 (s, 4 H), 3.95 (hept, 4 H, J = 6.8 Hz), 2.70 (hept, 2 H, J = 6.7 Hz), 1.32 (d, 12 H, J = 6.8 Hz), 1.13 (d, 12 H, J = 6.8 Hz), 1.04 (d, 12 H, J = 6.7 Hz), 0.43 (s, 18 H); ^{29}Si (C_6D_6) δ +97.68, −9.99; HRMS exact mass for $C_{36}H_{64}Si_4$ calculated *m/e* 608.4085, found *m/e* 608.4070 (1.59%); UV (3mp) λ_{max} 304 sh nm ($\epsilon = 1 \times 10^3\ M^{-1}\ cm^{-1}$), 398 nm ($\epsilon = 2 \times 10^3\ M^{-1}\ cm^{-1}$). (*Z*)-**2**: ^{1}H NMR (C_6D_6) δ 7.00 (s, 4 H), 3.78 (hept, 4 H, J = 6.8 Hz), 2.69 (hept, 2 H, J = 6.8 Hz), 1.44 (s, 18 H), 1.34 (d, 12 H, J = 6.8 Hz), 1.14 (d, 12 H, J = 6.8 Hz), 0.95 (d, 12 H, J = 6.8 Hz); ^{29}Si NMR (C_6D_6) δ 96.93; HRMS exact mass for $C_{38}H_{64}Si_2$ calculated *m/e* 576.4546, found *m/e* 576.4571 (2.1%); UV (3mp) λ_{max} 372 nm ($\epsilon = 4.8 \times 10^3\ M^{-1}\ cm^{-1}$), 452 sh ($\epsilon = 1.4 \times 10^3\ M^{-1}\ cm^{-1}$). Photolysis with a 254-nm light source was performed in essentially the same way as described above for 350 nm. This time diluted solutions—in quartz tubes—of the *E* isomers in deolefinated hexanes were irradiated. After 24 h (*E*)-**1**/(*Z*)-**1** was 1/2.7 (35% decomposition) and (*E*)-**2**/(*Z*)-**2** was 1/2.3. After 100 h the disilenes **1** were totally decomposed and (*E*)-**2**/(*Z*)-**2** was 1/6.3.

$IsHSi(SiMe_3)_2$. To $Is(Li)Si(SiMe_3)_2$ (25 mmol, prepared from **3** and $MeLi\cdot LiBr$)[5] in THF (130 mL) was added degassed water (20 mL). Hexane (100 mL) was added, and the mixture was washed five times with water (200 mL each time). The reaction was nearly quantitative by GC. The hexane was removed, and the resulting orange-tan oil was recrystallized from methanol/ethanol/ethyl acetate (10/4/1) to yield 5.5 g of off-white waxy crystals (60% isolated yield) > 98% pure by GC: mp 51.0–53.5 °C; ^{1}H NMR (C_6D_6) δ 0.24 (s, 18 H), 1.19 (d, 6 H), 1.31 (d, 12 H), 2.78 (sept, 2 H), 3.35 (sept, 1 H), 4.31 (s, 1 H), 7.12 (s, 2 H); ^{29}Si NMR (C_6D_6) δ −13.21, −76.92; HRMS[12] exact mass for $C_{20}H_{39}Si_3$ {M − CH_3} calculated *m/e* 363.2359, found *m/e* 363.2354. Anal. Calcd for $C_{21}H_{42}Si_3$: C, 66.58; H, 11.18. Found: C, 66.27; H, 11.45.

$IsClSi(SiMe_3)_2$ (7). $IsLi\cdot OEt_2$[4] (3.2 g, 11 mmol) was added to a Schlenk flask in a drybox and then dissolved in hexane (30 mL). 2,2-Dichlorohexamethyltrisilane (2.5 mL, 10 mmol) was then added to the solution. After the mixture was refluxed for 12 h, the GC showed that the reaction had gone to completion. More hexane was added (50 mL), and the mixture was filtered into a separatory funnel. The organic layer was washed three times with 100 mL of aqueous saturated sodium bicarbonate and two times with 100 mL of water. The hexane was removed under vacuum, and the resulting colorless solid was dissolved in a minimum amount of boiling hexane. Large colorless crystals were obtained (2.9 g, 70%), mp 78.0–81.0 °C. ^{1}H NMR (C_6D_6): δ 0.31 (s, 18 H), 1.18 (d, 6 H), 1.32 (d, 12 H), 2.74 (sept, 1 H), 3.45 (sept, 2 H), 7.13 (s, 2 H). ^{29}Si NMR (C_6D_6): δ 1.22, −10.87. HRMS:[12] exact mass for $C_{20}H_{38}ClSi_3$ {M − CH_3} calculated *m/e* 397.1970, found *m/e* 397.1960. Anal. Calcd for $C_{21}H_{41}Si_3Cl$: C, 61.03; H, 10.00. Found: C, 60.67; H, 10.18.

$IsFSi(SiMe_3)_2$ (8). The chloride **7** (1.0 g, 2.4 mmol) was stirred with a suspension of cesium fluoride (3.6 g, 24 mmol) in THF (60 mL) at 25 °C. After 10 h the reaction went to completion and the fluoride **8** was obtained 90% pure by GC. Purification was difficult, since **8** would not crystallize from any solvents tried and remained an oil even after it was left under vacuum for extended periods of time. ^{29}Si NMR (C_6D_6): δ 28.18 (d, J = 322 Hz). HRMS: exact mass for $C_{21}H_{41}FSi_3$ calculated *m/e* 396.2500, found *m/e* 396.2504.

$Is(1\text{-pyrrolyl})Si(SiMe_3)_2$ (9). The lithium amide of pyrrole was formed by adding *n*-butyllithium (0.51 mL, 1.2 mmol, 2.5 M) to pyrrole (0.2 mL, 2.5 mmol) in diethyl ether (25 mL) at −78 °C. This solution was then added to the chloride **7** (0.50 g, 1.2 mmol), also at −78 °C. The solution was warmed to room temperature after 1 h. After a short time salts began to precipitate, and after 1 h **9** was formed in greater than 95% yield, as determined by GC. The reaction mixture was worked up in the same manner as for **8**. Crude **9** was isolated as a pale tan solid with a slight impurity of unreacted **7** (0.30 g, 60%). ^{29}Si NMR (C_6D_6): δ −13.70, −16.23. HRMS: exact mass for $C_{25}H_{45}NSi_3$ calculated *m/e* 443.2860, found *m/e* 443.2861. Anal. Calcd for $C_{25}H_{45}Si_3N$: C, 67.64; H, 10.22. Found: C, 67.43; H, 10.31.

$IsCl_2Si(SiMe_3)$. $IsLi\cdot OEt_2$[4] (8.7 g, 31 mmol) was stirred as a slurry in hexane (100 mL). This slurry was added over 1 h to a solution of $Cl_3SiSiMe_3$ (6.3 g, 31 mmol). Examination of the reaction by GC indicated that the reaction was nearly complete with only 4% of the trichloride remaining. All volatiles were removed under vacuum, hexane was added, and the salts were filtered. The volume of the hexane was reduced and kept at −20 °C for 12 h. Large colorless crystals were obtained (1.5 g, 15%), 100% pure by GC; mp 98–101 °C. ^{1}H NMR (C_6D_6): δ 0.35 (s, 9 H), 1.18 (d, 6 H), 1.29 (d, 12 H), 2.72 (sept, 1 H), 3.79 (sept, 2 H), 7.13 (s, 2 H). ^{29}Si NMR (C_6D_6): δ +17.85, −4.14. HRMS:[12] exact mass for $C_{17}H_{29}{}^{35}Cl_2Si_2$ {M − CH_3} calculated *m/e* 359.1185, found *m/e* 359.1155. Anal. Calcd for $C_{18}H_{32}Si_2Cl_2$: C, 57.57; H, 8.59. Found: C, 57.37; H, 8.58.

Photolysis of $IsClSi(SiMe_3)_2$ (7). The trisilane **7** (0.5 g, 1.2 mmol) solution in pentane (30 mL) was freeze–thaw–degassed four times and photolyzed at 254 nm at −60 °C for 24 h. The initially colorless solution became deep orange-red during this time. Examination by ^{29}Si NMR showed signals at δ +97.76, +97.67, −10.56, and −9.98, which match those observed for disilenes **1**, as well as a signal at δ 30.5 corresponding to trimethylchlorosilane.

Photolysis of $IsCl_2Si(SiMe_3)$. A pentane (15 mL) solution of $IsCl_2Si(SiMe_3)$ (100 mg) was photolyzed for 18 h at −60 °C.

Examination of the slightly discolored solution by ^{29}Si NMR showed that only starting material was present.

Photolysis of IsHSi(SiMe$_3$)$_2$. A pentane (15 mL) solution of IsHSi(SiMe$_3$)$_2$ (100 mg) was photolyzed for 18 h at −60 °C. Examination of the slightly colored solution by ^{29}Si NMR showed that only starting material was present.

Photolysis of IsFSi(SiMe$_3$)$_2$ (8) and Is(1-pyrrolyl)Si(SiMe$_3$)$_2$ (9). A pentane (15 mL) solution of 8 or 9 (100 mg) was photolyzed for 18 h at −60 °C. Examination of the colored solutions by ^{29}Si NMR showed only hexamethyldisilane. The signals in the ^{1}H NMR spectrum were broad, even at elevated temperatures.

Thermolysis of IsClSi(SiMe$_3$)$_2$ (7). Trisilane 7 (115 mg) was heated in refluxing benzene (20 mL) for 2 days. No change was noted. Examination of the solution by ^{29}Si NMR indicated that only trisilane 7 was present.

X-ray Data Collection. Single crystals of (*E*)-1 were grown by slow cooling of a saturated solution in C_6D_6 to 10 °C. Single crystals of (*E*)-2 were grown by heating a concentrated solution of (*Z*)-2 in hexane for 1 week, followed by slow cooling of this solution to 10 °C. Suitably sized crystals of (*E*)-1 and (*E*)-2 were taken from the solution under argon and immediately mounted on a thin glass thread with cyanoacrylate cement. Single crystals of 3 were grown by slow cooling of a saturated solution in hexane to 0 °C and mounted similarly. A thin coat of this cement was used to seal the surface of all the crystals. All studies were carried out on a Siemens P3F diffractometer equipped with Cu Kα radiation (except Mo Kα for 3) and a graphite-crystal monochromator. Unit cell parameters were obtained from least-squares refinements based on the setting angles of 25 reflections. For 3 the space group was uniquely determined by the systematic absences in the data; for (*E*)-1 and (*E*)-2 $P\bar{1}$ was assumed and confirmed by successful structure solution and refinement. Data collection and refinement parameters used for the structure determinations are summarized in Table I. Throughout data collection standard reflections were measured every 100 reflections to monitor stability. The structures were solved by direct methods using Siemens SHELXTL PLUS (VMS). *E* maps revealed the positions of the silicon and carbon atoms. For (*E*)-2, the *p*-isopropyl group is disordered. Further electron density difference maps revealed the hydrogen atoms. In the final cycles of refinement all non-hydrogen atoms were assumed to vibrate anisotropically and all hydrogen atoms were assumed to vibrate isotropically.

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Supplementary Material Available: Tables of crystal data, bond lengths, bond angles, atomic coordinates, equivalent isotropic dispacement coefficients and occupancies, anisotropic displacement coefficients, and hydrogen atom coordinates for compounds (*E*)-1, (*E*)-2, and 3 (24 pages). Ordering information is given on any current masthead page.

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^{13}C NMR Spectroscopic and EHMO Study of Slowed Tripodal Rotation in $[(\text{Benzyl})\text{Cr(CO)}_3]^+$ and (Fulvene)Cr(CO)$_3$ Systems: Metal-Stabilized Nonplanar Cations

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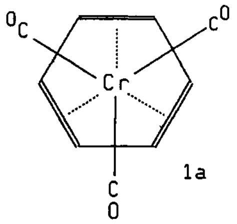
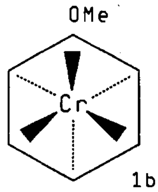
The variable-temperature ^{13}C NMR spectra of a series of methyl- and methoxy-substituted (benzyl)Cr(CO)$_3$ cations and neutral (fulvene)Cr(CO)$_3$ complexes reveal that the metal carbonyl resonances are split at low temperature; the barriers to tripodal rotation are rationalized in terms of the degree of localization of charge at the aromatic or fulvene carbons. It is shown that primary benzyl cations require greater stabilization by the tricarbonylchromium fragment than do analogous secondary or tertiary benzyl cations. These experimental results are complemented by molecular orbital calculations at the extended Hückel level.

Introduction

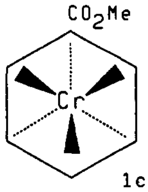
In complexes of the type (arene)Cr(CO)$_3$, the question of slowed tripodal rotation on the NMR time scale has aroused much controversy for nearly 20 years.[1] The favored conformations in the solid state were enunciated by Carter, McPhail, and Sim as the result of a series of X-ray crystallographic determinations.[2] While the staggered isomer **1a** is found for (benzene)Cr(CO)$_3$ itself,[3] incorporation of electron-donating or electron-withdrawing substituents yields the eclipsed rotamers **1b** and **1c**, respectively. The rationale offered to account for structure **1b** is that the electron-donating group, e.g., Me$_2$N or MeO, polarizes the charge distribution in the ring so as to render the ortho and para carbons relatively electron-rich. This makes the C(2), C(4), and C(6) positions better donors to the metal atom and, maintaining the preferred octahedral geometry at chromium, the carbonyl ligands are found to eclipse the C(1), C(3), and C(5) sites.[4] Conversely, com-



1a



1b



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