Probing the Effect of Organic and Organometallic Functionalization on [1,5]-Silicon Shifts in Indenylsilanes

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Received August 12, 1999

Indenylsilanes bearing organic and organometallic substituents have been prepared in order to probe the effect of substitution on the rate of [1,5]-silicon shifts in this class of compounds. In an attempt to prepare 1,1,3-tris(trimethylsilyl)indene (**7**), the hitherto unknown silicon-functionalized bis(trimethylsilyl)dibenzo[*a,d*]fulvalene (**9**) was unexpectedly generated; this species was characterized by use of both NMR spectroscopy and X-ray crystallography and was rationally prepared in 68% yield from 3,3′-bis(1-(trimethylsilyl))-indene (**16**). The molecular dynamics of 1,3-dimethyl-1-(trimethylsilyl)indene (**18**) and the crystallographically characterized chromium complex (η^6-1,3-dimethyl-1-*exo*-(trimethylsilyl)-indene)tricarbonylchromium (**22**) were examined by use of 1D-selective inversion and 2D-EXSY NMR techniques; surprisingly, the presence of chromium and methyl substituents has a negligible effect on the rate of [1,5]-silicon shifts ($\Delta G^{\ddagger} = 23-24$ kcal mol^{-1}) versus the parent compound 1-(trimethylsilyl)indene (**3**) ($\Delta G^{\ddagger} \approx 24$ kcal mol^{-1}). In the case of **18**, the intermediate isoindene **18-*iso*** was intercepted with tetracyanoethylene as the crystallographically characterized [4 + 2] cycloadduct 5,6-benzo-2,2,3,3-tetracyano-1,4-dimethyl-7-(trimethylsilyl)bicyclo(2.2.1)hept-5-ene (**19**).

Introduction

Although quasi-fluxional molecules of the type (1-indenyl)$_n$ER$_{4-n}$ (E = Si, Ge, Sn) have been known for over 3 decades,[1] the widespread use[2] of these and related main-group species as ligands in the preparation of chiral *ansa*-metallocene precatalysts has brought about renewed interest in this class of molecules.[3] The dynamic behavior of these stereochemically nonrigid σ-indenyl compounds can be rationalized in terms of symmetry-allowed, suprafacial [1,5]-sigmatropic shifts.[4] In several cases, Diels−Alder trapping with reactive dienophiles such as tetracyanoethylene (TCNE), yielding adducts analogous to **2**, has been advanced as evidence[1d,e] in support of the existence of transient isoindenes (**1-*iso***).[5] Indeed, in the course of studying the molecular dynamics and reactivity of main-group and transition-metal σ-indenyl complexes, we have crystallographically characterized several such [4 + 2] cycloadducts (Scheme 1).[6]

Kinetic data obtained for the interconversion of **1-*S*** and **1-*R*** (via **1-*iso***) in a variety of simple 1-trialkylsilyl-indenes, including 1-(trimethylsilyl)indene (**3**) suggest that the nature of the alkyl substituents on silicon has little effect on the barrier to [1,5]-silicon shifts ($\Delta G^{\ddagger} \approx$ 24 kcal mol^{-1}),[1,6] a trend that has also been noted in the related cyclopentadienyl series.[7] However, Rakita et al. noted that the introduction of methyl substituents

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(3) For a recent examination of the dynamic behavior of *ansa*-bridged group IV metallocenes, see: Miyake, S.; Henling, L. M.; Bercaw, J. E. *Organometallics* **1998**, *17*, 5528.

(4) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 2511.

(5) A crystallographically characterized metallocene arising from the intramolecular trapping of an isoindene by a metal center has been reported: Christopher, J. N.; Jordan, R. F.; Young, V. G. *Organometallics* **1997**, *16*, 3050.

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Scheme 1. [1,5]-Sigmatropic Shifts and Isoindene Cycloaddition Chemistry of Metalloindenes
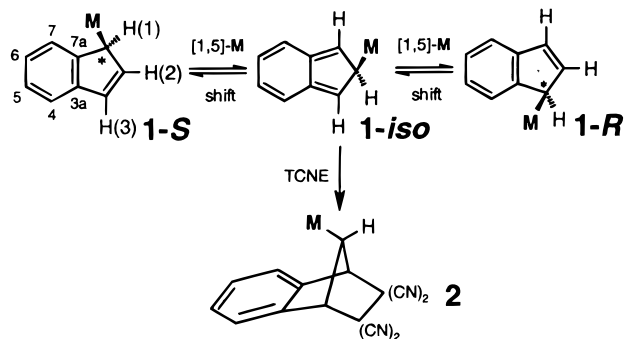
Chart 1

at the C(4) and C(7) positions on the indene framework in **4a** (Chart 1) modestly reduces this barrier (21.8 kcal mol^{-1}), while the presence of a C(2) methyl group leads to a slightly increased barrier to silicon migrations (26.5 kcal mol^{-1}). On the basis of data obtained from extended Hückel calculations, these workers postulated that the reduced barrier in **4a** arises as a result of electronic stabilization of the [1,5]-silicon shift transition-state structure.[8] More recently, we have demonstrated that such silatropic shifts are also electronically facilitated by the incorporation of fused benzo rings in **4b** (22 kcal mol^{-1}) and **4c** (18 kcal mol^{-1}), presumably attributable to an increase in the aromatic character of the transition-state species.[9] In continuation of these studies, we report herein on our attempts to examine the effect on the rate of [1,5]-silicon shifts of incorporating carbon, silicon, and transition-metal substituents[6d] into the indenylsilane architecture.

Results and Discussion

In Search of the Sterically Loaded Isoindene Tris(trimethylsilyl)isoindene (8). In an extension of the work of Rakita et al., metalloindenes comprising sterically demanding functionalities at the C(1) and C(3) positions, rather than at the C(4) and C(7) sites, were sought. Our initial approach in this regard was to create a system in which the bulky C(1) and C(3) substituents were identical with the migrating fragment, so as to facilitate the generation of sterically loaded isoindenes, while avoiding complications arising due to the generation of complex isomeric mixtures. Toward this end, 1,1,3-tris(trimethylsilyl)indene (**7**) was identified as an attractive synthetic target, in which steric interactions between the trimethylsilyl groups on C(1) could facilitate isomerization to the corresponding tris(trimethylsilyl)isoindene **8** (Scheme 2). The choice of **7** appeared especially judicious in light of the fact that the logical synthetic precursors, 1,1- and 1,3-bis(trimethylsilyl)-indene (**5** and **6**), are known[1c] and because the exchanging trimethylsilyl environments in **8**, arising due to [1,5]-silatropic shifts, could be readily monitored by use of 2D-EXSY NMR.[10]
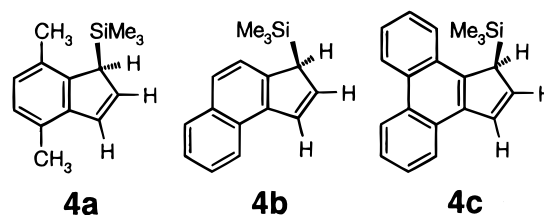
In an attempt to prepare the target compound **7**, the standard synthetic approach involving the reaction of a carbanion with an appropriate chlorosilane was employed. Unfortunately, all attempts, either via three consecutive additions of base, each followed by quenching with chlorotrimethylsilane (Scheme 3), or directly from a mixture of **5** and **6**, did not produce the desired product **7**, the isoindene **8**, or any other dimerization product derived from these species. However, careful chromatographic separation of the products in these reactions consistently yielded the bright red solid product **9**, in low yield. Although the simplicity of the ^{1}H, ^{13}C, and ^{29}Si NMR spectral data suggested the presence of one indene and one silicon environment in this compound, mass spectrometric data for **9** indicated a dimeric structure, comprised of two (SiMe$_3$)C$_9$H$_5$ fragments. This inference was further substantiated by the nuclear Overhauser effect (NOE) enhancement of the H(7) signal when the H(2) signal was irradiated, an observation which cannot be rationalized for a compound containing only one indenyl unit. The connectivity in **9**, initially ascertained on the basis of these data, was subsequently verified by a single-crystal X-ray diffraction study; the structure appears as Figure 1. Although the crystal structure is seriously disordered (preventing a satisfactory anisotropic refinement), all of the heavy atoms were found and the location of the trimethylsilyl groups at the C(3) positions of bis-(trimethylsilyl)dibenzo[*a,d*]fulvalene (**9**) is evident. The X-ray crystal structure of the corresponding hydrocarbon *trans*-1,1′-bis(indenylidene) has been reported and reveals an overall molecular structure which is qualitatively similar to that of the silylated complex **9**.[11]

Although the formation of the dibenzofulvalene **9** is surprising, precedent for the generation of dimeric indene species from isoindenes does exist. Warrener and co-workers report that, in addition to the well-known cycloaddition chemistry exhibited by molecules which contain the *o*-xylylene moiety, the dimerization of iso-indenes via ene-type mechanisms can occur if a hydrogen atom is present at the C(2) position.[12–14] It is also noteworthy that dimeric compounds closely related to **9** have received recent attention in the literature. Olmstead and co-workers[15] have discussed the unexpected isolation of **10** (Chart 2) in their attempt to

(8) (a) Andrews, M. N.; Rakita, P. E.; Taylor, G. A. *Tetrahedron Lett.* **1973**, *21*, 1851. (b) Andrews, M. N.; Rakita, P. E.; Taylor, G. A. *Inorg. Chim. Acta* **1975**, *13*, 191.

(9) (a) Rigby, S. S.; Gupta, H. K.; Werstiuk, N. H.; Bain, A. D.; McGlinchey, M. J. *Polyhedron* **1995**, *14*, 2787. (b) Rigby, S. S.; Gupta, H. K.; Werstiuk, N. H.; Bain, A. D.; McGlinchey, M. J. *Inorg. Chim. Acta* **1996**, *251*, 355.

(10) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935.

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(12) Warrener, R. N.; Harrison, P. A.; Russell, R. A. *J. Chem. Soc., Chem. Commun.* **1982**, 1134.

(13) Warrener, R. N.; Pitt, I. G.; Russell, R. A. *J. Chem. Soc., Chem. Commun.* **1982**, 1136.

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(15) Olmstead, M. M.; Hitchcock, S. R.; Nantz, M. H. *Acta Crystallogr.* **1996**, *C52*, 1523.

Scheme 2.   Proposed Synthetic Route to 1,1,3-Tris(trimethylsilyl)indene (7) and Its Isomerization to the Corresponding Isoindene 8
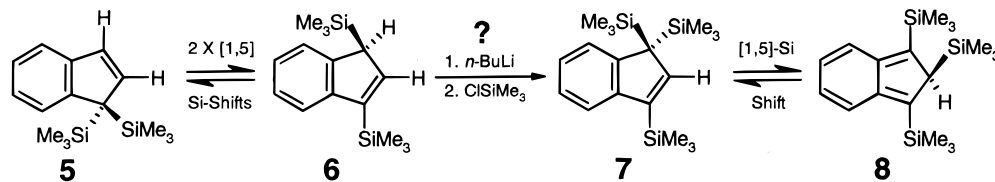
Scheme 3.   Unexpected Generation of 9 during the Attempted Preparation of 7[a]
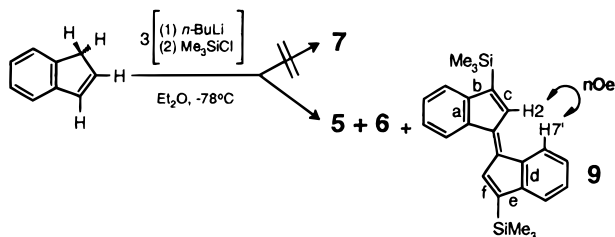
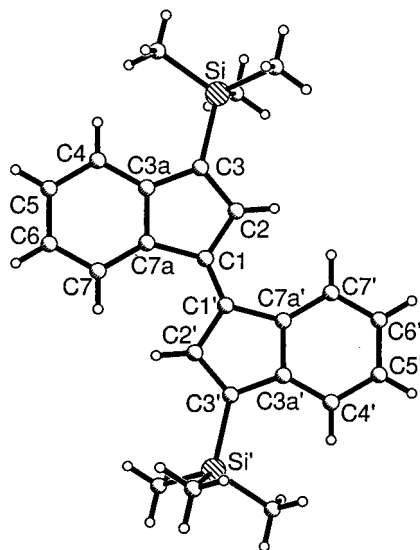[a] Dibenzofulvalenes are named according to the bonds that are benzannulated.

Figure 1. Structure of **9**, determined by X-ray crystallography.

generate an *ansa*-titanocene, while Youngs et al.[16,17] demonstrated that geometrically constrained bis(trimethylsilyl)dibenzo[*a,f*]fulvalenes, such as **11**, can be readily prepared via oxidative coupling using group 13 metal halides.

In the absence of conclusive experimental data, decisive commentary on the mechanistic pathway leading to the formation of **9** cannot be provided. Nevertheless, given the paucity of evidence for either **7** or **8**, and in consideration of the highly basic experimental conditions employed, it is possible to rationalize the generation of **9** on the basis of known synthetic methodologies.[18,19] In the presence of excess base, abstraction of either SiMe$_3^+$ (in **5**) or a proton (in **3** or **6**) would

Chart 2
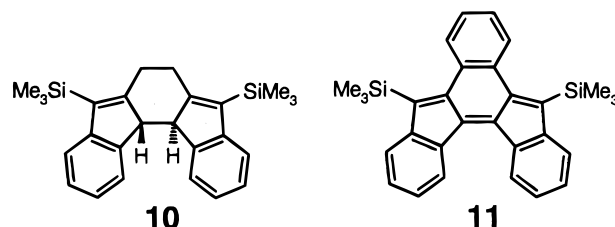
generate an indenide ion, as depicted in Scheme 4. Formation of the substituted 1,1′-biindene **12**, followed by attack by base, would lead to the generation of the dianion **13**. Subsequent oxidative coupling of the tethered anions in **13** produces the dibenzofulvalene **9**. Although the origin of the oxidant is not certain, such a process would be greatly facilitated by the eventual formation of the highly conjugated, 18-π-electron system in **9**. Indeed, molecular oxygen itself has proven effective[20] in the formation of related conjugated organic structures.[21]

Extended planar aromatic systems are of considerable interest, both as ligands in the preparation of organometallic complexes[22] and as precursors to materials with novel electronic, magnetic, and conductive properties.[23] Given the potential utility of compound **9**, its rational preparation was undertaken, using the approach summarized in Scheme 5. With 3,3′-biindene (**14**) and/or 1-(indanylidene)-1-indene (**15**) as starting materials, treatment with base followed by quenching with chlorotrimethylsilane yielded **16** as an inseparable mixture of *meso* and *d,l* isomers. Subsequent double deprotonation of **16** generated the previously invoked dianion **13**, which was efficiently oxidized, by use of iodine, to the dibenzofulvalene **9**.

To summarize, in an attempt to prepare the sterically protected isoindene **8**, the silicon-substituted dibenzofulvalene **9** was serendipitously generated; this latter compound was subsequently prepared in a rational manner from the dimer of 1-(trimethylsilyl)indene, **16**, via oxidation of the corresponding dianion **13**. Although the generation of **9** represents a chemically interesting result, the fact that the desired compound, **7**, could not be synthesized is perplexing. Given that the bis(trimethylsilyl)indenes **5** and **6** are readily prepared as a mixture (~1:1) of interconverting isomers, it is evident that the Si−C(1) indenyl bonds in **5** are sufficiently long

(16) Malaba, D.; Djebli, A.; Chen, L.; Zarate, E. A.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1993**, *12*, 1266.

(17) Malaba, D.; Tessier, C. A.; Youngs, W. J. *Organometallics* **1996**, *15*, 2918.

(18) Simmross, U.; Müllen, K. *Chem. Ber.* **1993**, *126*, 969.

(19) Rutsch, W.; Escher, A.; Neuenschwander, M. *Chimia* **1983**, *37*, 160.

(20) Escher, A.; Rutsch, W.; Neuenschwander, M. *Helv. Chim. Acta* **1986**, *69*, 1644.

(21) As noted by an astute reviewer, the formation of compound **9** via oxidative coupling of indenyl fragments followed by reductive elimination of hexamethyldisilane cannot be ruled out. We were unable to conclusively identify Me$_3$SiSiMe$_3$ in the product mixture by use of NMR spectroscopic techniques.

(22) McGovern, P. A.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun.* **1996**, 1593.
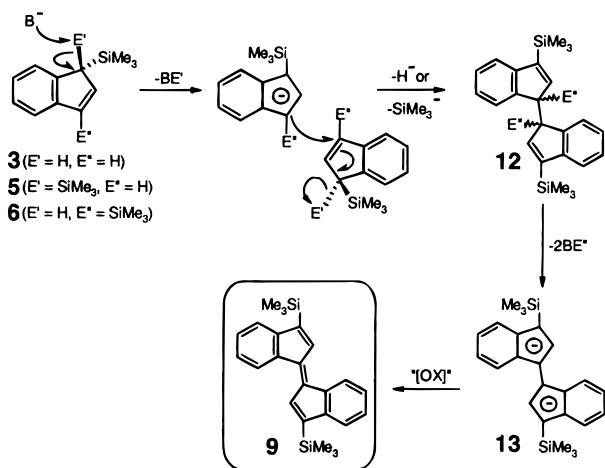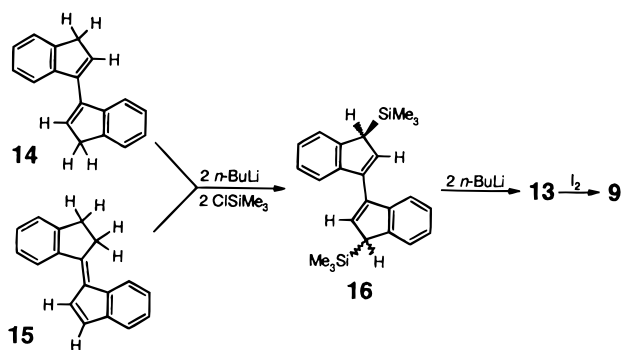
(23) Baumgarten, M.; Tyutyulkov, N. *Chem. Eur. J.* **1998**, *4*, 987.

Scheme 4. Generalized Mechanistic Rationale for the Formation of 9

3 (E' = H, E* = H)
5 (E' = SiMe₃, E* = H)
6 (E' = H, E* = SiMe₃)

Scheme 5. Rational Synthesis of 9 via 16, the Dimer of 3

so as to accommodate two *gem*-trimethylsilyl groups. Additional evidence in support of the viability of **7** comes from the existence of the corresponding quasi-fluxional tris(trimethylsilyl)cyclopentadiene series, which is readily prepared via deprotonation of the cyclopentadienyl analogue of **5**, followed by quenching with chlorotrimethylsilane.[24,25] As such, unfavorable steric requirements in **7** can be ruled out as a significant factor preventing the generation of this compound, and without a persuasive argument based on electronic effects, one is left to consider the experimental conditions employed. On the basis of the tentative mechanism depicted in Scheme 4, a critical step leading to the formation of **9** may involve the attack of an indenyl anion on a substituted indene, giving rise to **12**. Perhaps more dilute conditions would lead to the preferential addition of a third trimethylsilyl group to the anion derived from **5** and **6**. Efforts to prepare **7** via alternative synthetic routes are ongoing.

Synthesis and Dynamics of a Dimethylindenylsilane. In 1970, Davison and Rakita noted that the presence of methyl groups at the indenyl C(1) and C(3) positions in 1,3-dimethyl-1-(trimethylstannyl)indene (**17**) does little to lower the barrier to tin migrations, relative to the parent compound 1-(trimethylstannyl)-indene;[1c] a comparative study involving the corresponding 1-indenylsilane **18** proved impossible, since they

Scheme 6. Molecular Rearrangements Involving 18 and Diels−Alder Trapping of the Corresponding Isoindene 18-*iso* with Tetracyanoethylene
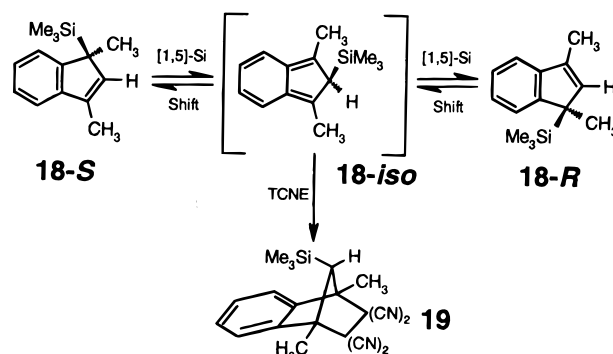
were unable to develop a suitable synthesis of this molecule. Data obtained from dynamic NMR studies involving **18** would, however, be instructive, given that the contracted metal−indene distance in this molecule, relative to **17**, would be expected to lead to an increased ground state energy for the indene structure and possibly to a reduced barrier to [1,5]-silicon shifts. In contrast to the 1-indenylsilane **4a**, which possesses C(4) and C(7) methyl substituents, any reduction in the barrier to silicon migrations in **18**, relative to **3**, is best rationalized not in terms of electronic stabilization but, rather, as arising from the alleviation of unfavorable steric interactions between the indene methyl groups and the methyl substituents on the silicon fragment. The considerable appeal of **18** prompted a reinvestigation of this compound.

In an effort to prepare 1,3-dimethyl-1-(trimethylsilyl)-indene (**18**), Davison and Rakita utilized a synthetic protocol that involved quenching of (dimethylindenyl)-lithium with chlorotrimethylsilane in hexane, followed by workup with deuterium oxide (D₂O). The formation of the isolated product, 1-deuterio-1,3-dimethylindene, can be rationalized both in terms of the quenching of the unreacted lithium indenide and as arising from the hydrolytic cleavage of the silicon−indene bond in the desired product **18**. Interestingly, these workers omitted this workup step in the successful synthesis of the indenylstannane **17**.

On the basis of the successful preparation of **17**, (1,3-dimethylindenyl)lithium was quenched with chlorotrimethylsilane in tetrahydrofuran, *without aqueous workup*. Following purification via flash chromatography on silica, 1,3-dimethyl-1-(trimethylsilyl)indene (**18**) was isolated as an analytically pure solid in 89% yield; indeed, during the preparation of this report, Rausch and co-workers reported the preparation of **18** under anhydrous conditions.[26]

Having successfully prepared the desired dimethyl-indenylsilane **18**, the dynamic behavior of this compound (Scheme 6) was examined by use of 2D-EXSY and single selective inversion NMR techniques.[27] The ¹H−¹H EXSY spectra obtained for **18** clearly indicate the

(24) Ustynyuk, Yu. A.; Luzikov, Yu. N.; Mstislavsky, U. J.; Azizov, A. A.; Pribytkova, J. M. *J. Organomet. Chem.* **1975**, *96*, 335.
(25) Jutzi, P.; Sauer, J. *J. Organomet. Chem.* **1973**, *50*, 29.

(26) Ready, T. E.; Chien, J. C. W.; Rausch, M. D. *J. Organomet. Chem.* **1999**, *583*, 11.
(27) (a) Bain, A. D.; Cramer, J. A. *J. Magn. Reson.* **1993**, *A103*, 217. (b) Bain, A. D.; Cramer, J. A. *J. Phys. Chem.* **1993**, *97*, 2884. (c) Muhandiram, D. R.; McClung, R. E. D. *J. Magn. Reson.* **1987**, *71*, 187.
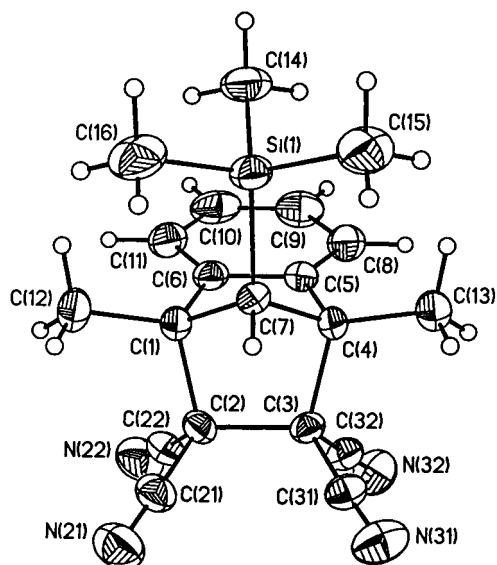
Figure 2. Crystallographically determined structure of **19** (shown with 30% thermal displacement ellipsoids).

operation of an exchange process which permutes the C(1)−CH_3 and C(3)−CH_3 chemical environments; the corresponding off-diagonal peaks linking the aromatic hydrogen atom resonances are much more difficult to discern, owing to the extensive overlap of these signals. Moreover, as the mixing time is increased, the off-diagonal peaks linking the C(1)−CH_3 and the C(3)−CH_3 sites in **18** grow in intensity and are consistently of the same phase as the diagonal signals; this serves to identify the origin of these off-diagonal signals as arising from chemical exchange, not NOE interactions. Data obtained from single selective inversion NMR experiments allowed the barrier to [1,5]-silicon shifts in **18** to be estimated ($\Delta G^{\ddagger} = 23 \pm 1$ kcal mol^{-1}). This value does not deviate significantly from those found for 1-(trimethylsilyl)indene (**3**; ~24 kcal mol^{-1}) and the C(4) and C(7) methylated 1-indenylsilane **4a** (~22 kcal mol^{-1}). As such, it is evident that methyl substitution at the C(1) and C(3) positions on indene does not contribute in any significant way to a reduction in the barrier to silicon migrations in **18**. It is apparent that if sterically promoted rearrangements of 1-indenylsilanes are to be realized, the introduction of even bulkier molecular fragments will be required in order to perturb the indene ground-state structure.

Although the introduction of the indenyl methyl substituents in **18** does not lead to an increased rate of [1,5]-silicon shifts, the fact that these migrations continue to occur is important in and of itself. Indeed **18** serves as a model compound in the development of systems which have the capacity to undergo *intramolecular* Diels−Alder reactions. With the quasi-fluxional nature of this compound ascertained, the propensity of the corresponding isoindene **18-*iso*** for [4 + 2] cycloadditions was examined by stirring a solution of **18** with tetracyanoethylene (Scheme 6).

The expected Diels−Alder cycloaddition product **19** was isolated in 83% yield and fully characterized by use of standard spectroscopic techniques and also by single-crystal X-ray diffraction methods; the structure of **19** appears as Figure 2, while crystallographic data and selected metrical parameters are collected in Tables 1
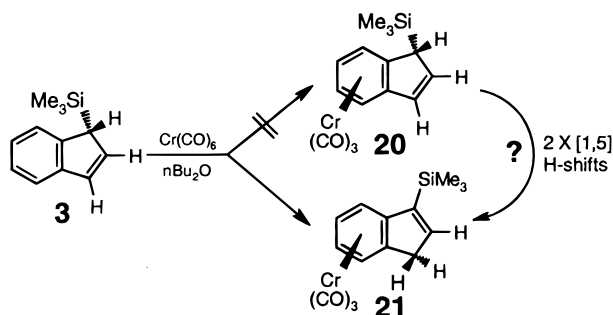
Table 1. Crystal Data and Structure Refinement Parameters for 19 and 22

	19	22
empirical formula	$C_{20}H_{20}N_4Si$	$C_{17}H_{20}O_3SiCr$
mol wt	344.49	352.42
description	colorless prism	yellow plate
temp, K	299(2)	299(2)
wavelength, Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	9.601(1)	9.691(11)
b, Å	14.782(2)	9.877(9)
c, Å	13.977(2)	10.395(12)
α, deg	90.000	67.98(3)
β, deg	105.040(3)	81.98(2)
γ, deg	90.000	82.94(2)
V, Å^3	1915.7(5)	910(2)
Z	4	2
calcd density, g/cm^3	1.194	1.285
scan mode	ω scans	ω scans
$F(000)$	728	368
θ range for collecn, deg	2.04−22.50	2.12−22.50
index ranges	$-10 \le h \le 10$	$-11 \le h \le 12$
	$-15 \le k \le 15$	$-12 \le k \le 12$
	$-14 \le l \le 15$	$-12 \le l \le 13$
no. of rflns collected	11384	5572
no. of indep rflns	2501	2376
no. of data/restraints/ params	2501/0/226	2353/0/200
goodness of fit on F^2	0.854	0.995
final R indices ($I > 2\sigma(I)$)	R1 = 0.0448	R1 = 0.0672
	wR2 = 0.0870	wR2 = 0.1507
R indices (all data)	R1 = 0.1104	R1 = 0.1317
	wR2 = 0.1016	wR2 = 0.1644
mean shift/error	<0.001	0.005
max shift/error	<0.001	<0.001
transmissn (max, min)	0.979, 0.690	0.901, 0.571
largest diff Peak, e/Å^3	0.152	0.31
largest diff Hole, e/Å^3	−0.195	−0.29

Table 2. Selected Bond Lengths (Å) and Angles (deg.) for 19 and 22

19		22	
Si(1)−C(15)	1.850(3)	Cr(1)−C(3A)	2.280(7)
Si(1)−C(14)	1.857(3)	Cr(1)−C(5)	2.172(8)
Si(1)−C(16)	1.859(3)	Cr(1)−C(6)	2.205(9)
Si(1)−C(7)	1.913(3)	Cr(1)−C(4)	2.217(6)
C(1)−C(6)	1.511(4)	Cr(1)−C(7)	2.237(8)
C(1)−C(12)	1.519(4)	Cr(1)−C(7A)	2.293(6)
C(1)−C(7)	1.547(4)	Si(1)−C(1)	1.938(7)
C(1)−C(2)	1.608(4)	Si(1)−C(8)	1.847(8)
C(2)−C(3)	1.591(4)	Si(1)−C(9)	1.853(9)
C(3)−C(4)	1.612(4)	Si(1)−C(10)	1.831(7)
C(4)−C(13)	1.505(4)	C(1)−C(2)	1.479(9)
C(4)−C(5)	1.509(4)	C(1)−C(7A)	1.496(8)
C(4)−C(7)	1.554(4)	C(1)−C(11)	1.540(8)
C(5)−C(6)	1.377(4)	C(2)−C(3)	1.34(1)
C(5)−C(11)	1.387(4)	C(3)−C(33)	1.51(1)
C(6)−C(8)	1.379(4)	C(3A)−C(7A)	1.413(8)
C(8)−C(9)	1.393(4)	C(3A)−C(4)	1.42(1)
C(9)−C(10)	1.368(5)	C(4)−C(5)	1.40(1)
C(10)−C(11)	1.388(5)	C(5)−C(6)	1.40(1)
		C(6)−C(7)	1.38(1)
		C(7A)−C(7)	1.403(9)
C(1)−C(7)−Si(1)	117.9(2)	C(2)−C(1)−C(7A)	100.9(5)
C(4)−C(7)−Si(1)	119.6(2)	C(2)−C(1)−C(11)	116.1(7)
C(1)−C(2)−C(3)	102.3(2)	C(2)−C(1)−Si(1)	106.3(4)
C(2)−C(3)−C(4)	102.7(2)	C(7A)-C(1)−C(11)	115.4(6)
C(2)−C(1)−C(6)	103.5(2)	C(7A)-C(1)−Si(1)	107.4(4)
C(3)−C(4)−C(5)	103.8(2)	C(11)−C(1)−Si(1)	109.8(5)
C(12)−C(1)−C(7)	120.7(3)		
C(13)−C(4)−C(7)	120.9(3)		

and 2, respectively. In the crystal **19** possesses an effective σ-plane defined by Si(1) and C(7) and bisecting the C(2)−C(3) bond, giving rise to identical bond lengths

Scheme 7. Attempted Preparation of the η⁶-Cr(CO)₃-Complexed Indenylsilane 20

Scheme 8. Molecular Rearrangements Involving 22 and the Attempted Diels−Alder Trapping of the Isoindene 22-*iso* with Tetracyanoethylene

and angles (within experimental error) for all fragments related by this mirror plane. Moreover, despite the presence of the methyl substituents at the bridgehead positions in **19**, the geometric characteristics of this molecule in the solid state parallel those found in other crystallographically characterized metalloisoindene cycloadducts of TCNE, including (a) *anti*-oriented trimethylsilyl and TCNE fragments, (b) elongated incipient Diels−Alder (C(1)−C(2) and C(3)−C(4)) and formerly olefinic (C(2)−C(3)) bonds, and (c) expanded Si(1)−C(7)−C(1) and Si(1)−C(7)−C(4) angles (average ∼119°).[6]

Assessing the Impact of π-Cr(CO)₃ Complexation. Both Kündig[28] and Butenschön[29] and have demonstrated that the ring opening of benzocyclobutenes to the corresponding *o*-xylylene is tolerant to the presence of a coordinated η⁶-tricarbonylchromium moiety. In light of the similarity between this ring-opening process and the isomerization of indenes to the corresponding isoindenes, the effect of chromium complexation on the rate of [1,5]-silicon shifts in 1-indenylsilanes was examined. The tricarbonylchromium complex of 1-(trimethylsilyl)indene (**20**) was initially identified as a candidate for such dynamic NMR studies, and its synthesis was undertaken. Using the method described by Fischer and Kriebitzsch for the preparation of (indene)tricarbonylchromium,[30] 1-(trimethylsilyl)indene (**3**) and excess Cr(CO)₆ were heated to reflux in a mixture of dibutyl ether and tetrahydrofuran for 72 h. However, the indenylchromium product isolated from this reaction, following chromatographic purification, was not the desired complex **20** but rather the corresponding 3-indenyl isomer **21**, for which [1,5]-silicon migrations are not possible; the ¹H and ¹³C NMR signals attributable to the methylene group and the single vinylic methine unit were diagnostic of the structure depicted in Scheme 7. The generation of **21** can be rationalized in terms of two consecutive [1,5]-hydrogen shifts that become possible at the high temperatures employed in the synthesis. It is not known whether these hydrogen migrations occur in the precursor **3**, in the complex **20**, or via some bimolecular chromium-mediated reaction pathway. The last possibility is
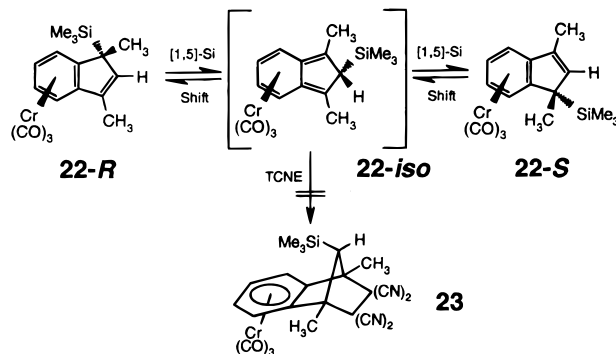
supported by a report from Ceccon and co-workers, who noted that the rearrangement of 1-phenylindene to 3-phenylindene is accelerated by the addition of (CH₃-CN)₃Cr(CO)₃ in tetrahydrofuran.[31]

Although the low-temperature metalation of **3** using (CH₃CN)₃Cr(CO)₃ represents a feasible route to **20**,[32] complexation of the dimethylindenylsilane **18** was selected as an alternative means of generating a chromium-containing 1-indenylsilane. Since the barrier to [1,5]-methyl shifts is considerably higher than that associated with hydrogen migrations, it was anticipated that the use of **18** as a precursor would circumvent the isomerization pathways which eventually lead to the formation of sp²-bonded silicon complexes. Using the aforementioned synthetic approach, **18** and excess Cr(CO)₆ were allowed to react in a refluxing mixture of dibutyl ether and tetrahydrofuran for 96 h. Gratifyingly, the single product isolated from this reaction yielded spectroscopic data consistent with the formation of a single complex containing the required C(1)-bonded trimethylsilyl unit. The *exo* geometry of the product, depicted in Scheme 8, was ascertained by use of X-ray crystallographic techniques; the structure of **22** appears as Figure 3, while crystallographic data and selected metrical parameters are collected in Tables 1 and 2.

Congestion at the quaternary C(1) center in **22** results in an elongated C(1)−silicon bond (C(1)−Si(1) = 1.938(7) Å) relative to tris(1-indenyl)silane[33] (C−Si(1) = 1.896(5), 1.889(4), and 1.895(5) Å), although statistically significant lengthening of the C(1)−Me bond in **22** (C(1)−C(11) = 1.540(8) Å), in comparison to the other carbon−methyl distance in this compound (C(3)−C(33) = 1.508(9) Å) and those found in the cycloadduct **19** (C−CH₃ = 1.519(4), 1.505(4) Å), is not observed. Moreover, while the C₅ and C₆ rings in **19** deviate only modestly from planarity (0.0217 and 0.0128 Å, respectively), the plane defined by the allylic unit (C(1)−C(2)=C(3)) intersects the C₆ plane (C(3a), C(4), C(5), C(6), C(7), and C(7a)) at an angle of approximately 3.2°, possibly due to unfavorable steric interactions between the C(1)−methyl group and the chromium fragment. Such a phenomenon may also be responsible for the asymmetric bonding that is observed between the chromium group and the arene

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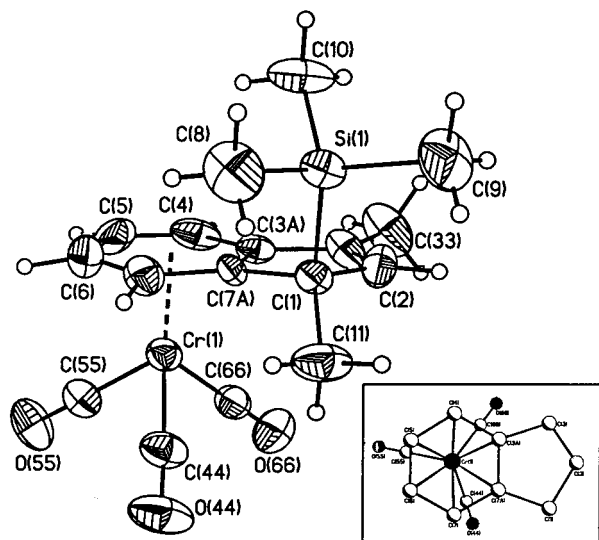
Figure 3. Crystallographically determined structure of **22** (shown with 30% thermal displacement ellipsoids).

ring. When the C_6 unit is traversed from the annulated edge (Cr(1)−C(3a) = 2.280(7) Å, Cr(1)−C(7a) = 2.293(6) Å), through the centroid of the ring (Cr(1)−C(4) = 2.217(6) Å, Cr(1)−C(7) = 2.237(8) Å), to the rear edge (Cr(1)−C(5) = 2.172(8) Å, Cr(1)−C(6) = 2.205(9) Å), the distances between the chromium unit and the arene ring gradually contract. While this differential bonding pattern seems to be slightly more pronounced than in related complexes reported by Kerber and Waldbaum[34] and Ustynyuk and co-workers,[35] such distortions in **22** are apparently less than those found in the crystal structure of the η^6-Cr(CO)$_3$ complex of naphthalene.[36] In the crystal, the tricarbonylchromium unit in **22** adopts an approximate staggered-*anti* orientation (Figure 3, inset); both staggered-*anti* and staggered-*syn* geometries have been observed in such annulated polycyclic chromium complexes.[36,37]

Having synthesized and fully characterized the required tricarbonylchromium complex **22**, we probed the resilience of the suprafacial [1,5]-silatropic shift process in 1-indenylsilanes. On the basis of the aforementioned findings by both Kündig and Butenschön, it is reasonable to suggest, a priori, that the presence of the chromium fragment in **22** could possibly facilitate the generation of isoindenes. However, it is also evident that the conversion of the 1-indenylsilane **22** into the isoindene **22-*iso*** gives rise to what can formally be considered a 16-electron chromium center in this intermediate species. If geometric constraints exist in the isoindene that are not present in the *o*-xylylene (perhaps arising as a result of the methylene unit in the former), then possible long-range coordination to the C_5 diene[38] fragment may be prohibited in the isoindene, leading
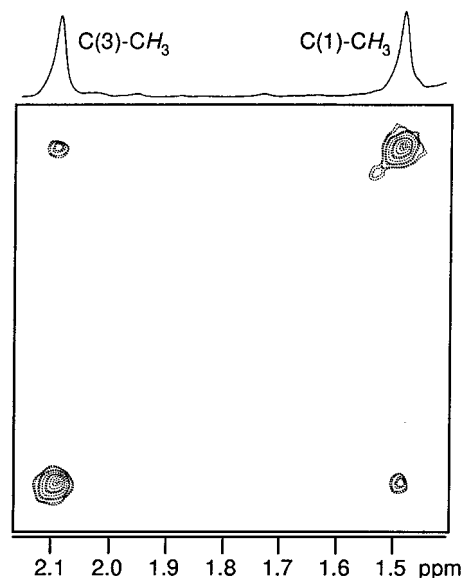
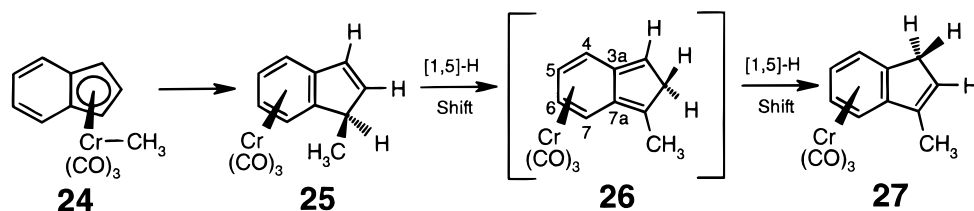(34) Kerber, R. C.; Waldbaum, B. *Organometallics* **1995**, *14*, 4742.

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Figure 4. Indene−CH$_3$ region of the ^{1}H−^{1}H EXSY spectrum of **22**, acquired in tetrachloroethane-d_2 at 105 °C with a mixing time of 1.0 s.

to a destabilization of the 16-electron metalloisoindene **22-*iso***. Such a scenario could, in principle, lead to a reduction in the rate of [1,5]-silicon shifts in **22**, relative to the uncomplexed compound **18**.

The molecular dynamics of **22** were qualitatively examined by use of 2D-EXSY NMR techniques; a portion of a ^{1}H−^{1}H EXSY spectrum acquired from a sample of this complex is presented as Figure 4. The off-diagonal peaks linking the C(1)−CH_3 and C(3)−CH_3 sites verify that [1,5]-silicon migrations continue to occur in **22**. The low-frequency shift[39] of the arene ^{1}H NMR resonances following complexation by a Cr(CO)$_3$ fragment is particularly fortuitous in the present case, as the heavily overlapped aromatic ^{1}H NMR resonances in **18** are converted into well-resolved multiplets in **22**, allowing for the observation of distinct 2D-EXSY off-diagonal signals that correlate the exchanging arene ring environments in **22**.

Given that [1,5] silatropic shifts are operative in **22**, single selective inversion NMR experiments were conducted in order to quantify the effect of chromium complexation on the rate of [1,5]-silicon shifts. An analysis of the temperature-dependent rate data obtained during these dynamic NMR experiments revealed the barrier to silicon shifts in **22** ($\Delta G^{\ddagger} = 24 \pm 1$ kcal mol^{-1}) to be indistinguishable from the uncomplexed silane **18** ($\Delta G^{\ddagger} \approx 23$ kcal mol^{-1}). The fact that the presence of the chromium fragment served neither to increase nor to diminish the rate of [1,5]-silicon shifts was unexpected, and as such, the behavior of the Cr(CO)$_3$ unit throughout the migratory process was reexamined.

During the course of this investigation, a report was published by Ustynyuk and co-workers which is of considerable relevance to the molecular dynamics of **22**.[40] These workers noted that, upon warming, (σ-methyl)(η^5-indenyl)tricarbonylchromium (**24**) is quantitatively converted into (η^6-1-*endo*-methylindene)-

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Scheme 9. "Ricochet" Inter-ring Haptotropic Rearrangement of 24[a]

[a] The numbering in the isoindene **26** is carried over from **25**.

Table 3. Computationally and Experimentally Determined Bond Lengths (Å) for Indenylchromium Complexes

	26[a]	**28**[b]	**29**[b]	**30**[c]
Cr−C(3a)	2.440	2.375(4)	2.448(3)	2.434(7)
Cr−C(7a)	2.417	2.401(4)	2.448(3)	2.464(6)
Cr−C(4)	2.247	2.239(4)	2.258(3)	2.255(7)
Cr−C(7)	2.230	2.257(4)	2.271(3)	2.267(5)
Cr−C(5)	2.209	2.181(5)	2.208(4)	2.194(6)
Cr−C(6)	2.206	2.188(4)	2.197(5)	2.189(5)

[a] DFT calculations.[40] [b] X-ray diffraction data.[41] [c] X-ray diffraction data.[42]

tricarbonylchromium (**25**) and ultimately the thermodynamically favored C(3)−methyl isomer **27** (Scheme 9). Mechanistic aspects of these rearrangements were examined by use of density functional theory (DFT) calculations, which revealed that the conversion of **25** into **27** occurs via the isoindene intermediate **26**. Once the chromium-bonded methyl fragment in **24** is delivered to the indenyl C(1) position, the Cr(CO)$_3$ group migrates to the C$_6$ ring rapidly and irreversibly; thus, during the hydrogen migratory process which takes **25** via **26** into **27**, the Cr(CO)$_3$ fragment remains bonded to the C$_6$ ring of the indene skeleton. This hydrogen migratory process is qualitatively similar to the conversion of the metalated 1-indenylsilane **20** into the 3-indenylsilane **21** (Scheme 7). The energy-minimized structure provided by Ustynyuk and co-workers for **26** contains bond lengths (Table 3) that are indicative of an η^4-Cr(CO)$_3$ fragment, especially when compared to the metrical parameters associated with the crystallographically characterized η^6-bonded indenylsilane **22**; short distances are observed between the chromium center and C(4), C(5), C(6), and C(7) in **26**, while the bonds to C(3a) and C(7a) are considerably longer. Experimental support for the viability of complexes possessing such geometries has also been provided by Ceccon and various co-workers, who have crystallographically characterized a series of bimetallic indenyl complexes, including **28**−**30** (Scheme 10).[41,42] In these compounds, the chromium and rhodium moieties share the same face of the indenyl ligand, which forces these fragments toward the periphery of the C$_6$ and C$_5$ rings, respectively. In fact, the solid-state structures of these stable molecules exhibit approximate η^4−η^3 configurations, despite the fact that the chromium and rhodium fragments in these molecules preferentially coordinate to indene via η^6 and η^5 bonding modes, respectively, in

Scheme 10. Chromium−Rhodium Bimetallic Indenyl Complexes 28−30 (NBD = Norbornadiene; COD = 1,5-Cyclooctadiene) and a Pictorial Representation of the Electron Sharing in These Compounds

28: L$_n$ = (CO)$_2$
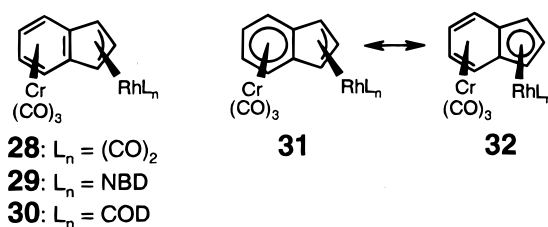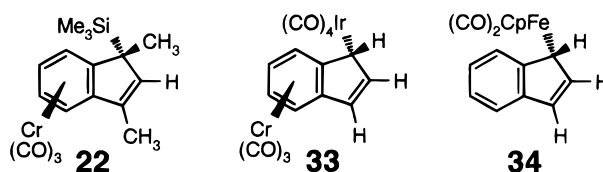**29**: L$_n$ = NBD
30: L$_n$ = COD

Chart 3

the absence of the second organometallic unit (**31** and **32** in Scheme 10).

In light of the computational and crystallographic results presented above, it appears that although a 16-electron chromium intermediate (**22-iso**) can formally be invoked during the interconversion of the 18-electron species **22-S** and **22-R**, the energy cost associated with this process is not sufficiently large as to lead to a statistically significant increase in the barrier to [1,5]-silicon shifts, relative to the unmetalated compound **18**. In effect, the chromium fragment in this system can be classified as a spectator group with respect to the operation of suprafacial [1,5]-silicon shifts. As a result, the dynamic behavior of the η^6-Cr(CO)$_3$-containing η^1-indenyl complex of iridium **33** (Chart 3) need not be rationalized in terms of symmetry-forbidden [1,3]-shifts, as originally suggested by Ceccon et al.[43] It is plausible that this mechanistic pathway was proposed by these workers so as to avoid invoking the intermediacy of a high-energy η^4-Cr(CO)$_3$-complexed metalloisoindene and because of the presumed static nature of $(\eta^5$-C$_5$H$_5)$Fe-(CO)$_2(\eta^1$-C$_9$H$_7)$ (**34**).[44] However, in light of the fact that [1,5]-iron shifts in **34** have recently been detected,[6c] it is possible to envision an analogous symmetry-allowed [1,5]-iridium shift process involving **33**.

The assertion that the Cr(CO)$_3$ unit remains fixed to the C$_6$ ring during the interconversion of **22-S** and **22-R**

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(41) Bonifaci, C.; Ceccon, A.; Gambaro, A.; Ganis, P.; Santi, S.; Valle, G.; Venzo, A. *Organometallics* **1993**, *12*, 4211.
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suggests that the C_5 diene unit in the purported intermediate, **22-*iso***, should be available to participate in cycloaddition reactions. In an attempt to intercept this intermediate, pale yellow solutions of **22** and tetracyanoethylene were combined, generating a dark blue mixture typically observed during these trapping reactions involving TCNE. However, in contrast to the successful Diels–Alder trapping of **18-*iso***, the reaction involving **22** yielded a dark solid, from which only a small amount (approximately 10%, based on **22**) of the uncomplexed cycloadduct **19** could be extracted. The deeply colored solution formed upon addition of TCNE to a solution containing a metalloindene is consistent with the formation of a charge-transfer (CT) complex; arene[45] and (arene)tricarbonylchromium[46,47] CT complexes with TCNE are well-documented. Although the significance of these CT complexes as precursors to the isolated isoindene cycloadducts is unclear, it is possible that, in the case of the chromium complexes **22** and **22-*iso***, CT makes available reaction pathways which result in decomposition. Kündig and co-workers have recently reported that the addition of an olefinic compound capable of η^4-coordination, such as methyl acrylate, to (benzene)tricarbonylchromium leads to rapid cleavage of the arene–metal linkage under mild conditions.[48] Since (arene)tricarbonylchromium compounds are known to react with nitriles,[49,50] it is feasible that TCNE may also serve to promote demetalation of the indenyl ligand in **22-*iso***, via addition to what can be described as a coordinatively and electronically unsaturated chromium center in this molecule. The isolation of **19** as a side product in reactions involving **22** is in keeping with the occurrence of a decomplexation event. Finally, it is also possible to argue that the formation of **23** is disfavored on steric grounds, since the generation of such a cycloadduct possessing *anti*-disposed silyl and dienophilic fragments would require that TCNE add to the isoindene **22-*iso*** on the face occupied by the bulky $Cr(CO)_3$ unit. Although chromium complexes similar to the desired adduct **23** have been prepared[51,52] and crystallographically characterized,[53] the generation of these species typically involves the introduction of a chromium fragment to a preformed benzonorbornene.

Conclusions

In comparison to complexes comprising group 13 or group 15 elements, the role of substituents in determining the rate of [1,5]-metalloid shifts in group 14 cyclopentadienyls is considerably less important;[7b] a similar scenario has emerged for the indenylsilane series. Indeed, the suprafacial [1,5]-silicon shift process in these compounds has demonstrated remarkable tolerance to organic and organometallic derivatization, both on the

indenyl skeleton and at the migrating silicon center.[1,6] In the present study, the robustness of this silatropic shift phenomenon in indenylsilanes was revealed by 2D-EXSY experiments, which exposed the quasi-fluxional character of both the methylated indenylsilane **18** and the chromium complex **22**. Moreover, kinetic data obtained from 1D-selective inversion NMR experiments revealed migratory barriers for **18** and **22** which do not deviate significantly from the parent species, 1-(trimethylsilyl)indene (**3**). In the case of **18**, Diels–Alder trapping with tetracyanoethylene yielded experimental evidence in support of the intermediacy of isoindenes in these rearrangements; crystallographic data were obtained for the cycloadduct **19**.

During the pursuit of a sterically loaded indene, **7**, the conjugated dimeric compound **9** was unexpectedly generated; while a mechanism has been proposed in an attempt to rationalize the formation of this compound, conclusive experimental evidence is still lacking. The processes leading to **9** and the ensuing chemistry of this compound are of considerable interest and will be the focus of future study.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of dry nitrogen in oven-dried glassware, using freshly distilled solvents that were purified according to standard procedures. Unless otherwise stated, reagents were obtained from Aldrich Chemical Co. and used as received; hexacarbonylchromium was purchased from Strem Chemical and deuterated NMR solvents were obtained from Cambridge Isotope Laboratories and used as received. Mass spectrometric data were obtained using a Finnigan 4500 spectrometer by direct electron impact (DEI) or by chemical ionization (CI) with NH_3. Infrared spectra were obtained on a Bio-Rad FTS-40 FT-IR spectrometer. Melting points were measured in open glass capillaries using a Thomas-Hoover Unimelt capillary melting point apparatus. Microanalyses were performed by Guelph Chemical Laboratories (Guelph, Ontario, Canada). One-dimensional NMR spectroscopic data were recorded using a Bruker AC-200, Bruker AC-300, or Bruker Avance DRX-500 spectrometer. In all cases, NMR spectra were obtained from samples dissolved in deuterated solvents, with NMR signals referenced internally to tetramethylsilane. Two-dimensional NMR experiments were conducted on the DRX-500 instrument, equipped with an 11.74 T superconducting magnet, a Bruker B-VT 2000 temperature controller, and a 5 mm multinuclear inverse probe possessing three-axis gradient capabilities. These consisted of $^1H-^1H$ COSY, $^1H-^{13}C$ HSQC, $^1H-^{13}C$ HMBC, $^1H-^1H$ EXSY, and $^1H-^{29}Si$ HMBC experiments. Sample temperatures were set and maintained throughout the course of these studies by use of the temperature controller and externally calibrated by placing a copper–constantan thermocouple, contained within an NMR tube, into the probe. Using this procedure, absolute temperatures were measured and maintained within ±0.5 °C.

$^1H-^1H$ EXSY (Exchange Spectroscopy) Experiments. Two-dimensional $^1H-^1H$ EXSY[10] spectra were recorded in the phase-sensitive mode, using the gradient implementation of the NOESY ($90°-t_1-90°-t_m-90°-$ACQ) pulse sequence. In a typical experiment, 512 FID's were recorded in the f_2 dimension, with each FID acquired in 16 scans. These FID data were subsequently Fourier-transformed using Gaussian window functions in both f_1 and f_2, with line broadening set to 3.0 Hz. For both **18** and **22**, tetrachloroethane-d_2 was employed as the solvent, and experiments were conducted at 105 °C, with mixing times ranging from 0.3 to 1.5 s; the relaxation delay and the initial value for the 2D evolution were set to 1.0 s and 10 μs, respectively.

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Single Selective Inversion NMR Experiments. All kinetic data were obtained in the slow-exchange regime by use of ¹H selective inversion NMR experiments,[27] in which the low-frequency methyl resonance was perturbed using a $90°-\tau-90°$ pulse sequence ($\tau = \frac{1}{2}\Delta\nu$), and then the return to equilibrium of this and the other methyl signal involved in the chemical exchange process was monitored as a function of time, as in an inversion-recovery T_1 experiment. These experiments were conducted on a Bruker AC-300 spectrometer, equipped with a 7.65 T superconducting magnet, a Bruker B-VT 2000 temperature controller, and a 5 mm QNP probe; spectral data were obtained between 95 and 110 °C. Nonlinear least-squares fitting of the experimental data was performed using a C programming language version of the SIFIT program provided by McClung,[27c] which permitted the extraction of rate data. Analysis of these temperature-dependent rates using Eyring theory allowed for an estimate of the free energy of activation associated with the dynamic process; in both cases $\Delta G^{\ddagger}$ is reported at 303 K.

X-ray Crystallography. X-ray crystallographic data for **19** and **22** were collected from single-crystal samples, which were mounted on a glass fiber. Single-crystal diffraction experiments were carried out using a P4 Siemens diffractometer, equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector (using the program SMART) and a rotating anode using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The crystal-to-detector distance was 3.991 cm, and the data collection was carried out in 512 × 512 pixel mode, utilizing 2 × 2 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular settings of the strong reflections, collected by a 4.5° scan in 15 frames over three different parts of reciprocal space (45 frames total). One complete hemisphere of data was collected, to better than 0.8 Å resolution. Upon completion of the data collection, the first 50 frames were re-collected in order to improve the decay corrections analysis. Processing was carried out by use of the program SAINT, which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. Structures were solved by using the direct methods procedure in the Siemens SHELXTL program library, and refinement was carried out by using full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added at calculated positions and refined using a riding model with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the attached carbon.[54]

1,1- and 1,3-Bis(trimethylsilyl)indene (5 and 6). These compounds, which exist as a set of interconverting isomers, were prepared using previously reported methods.[1c] Data for **5**: ¹H NMR (CDCl₃, 500 MHz) δ 7.12 (d, $^3J = 5.2$ Hz, 1H, H(2)), 6.81 (d, $^3J = 5.2$ Hz, 1H, H(3)), 0.04 (s, 18H, Si(CH₃)₃); ¹³C NMR (CDCl₃, 125 MHz) δ 47.1 (C(1)), −0.8 (CH₃); ²⁹Si NMR (CDCl₃, 99.35 MHz) δ 0.5. Data for **6**: ¹H NMR (CDCl₃, 500 MHz) δ 6.97 (d, $^3J = 1.7$ Hz, 1H, H(2)), 3.68 (d, $^3J = 5.2$ Hz, 1H, H(1)), 0.44 (s, 9H, Si(CH₃)₃ at C(3)), 0.03 (s, 9H, Si(CH₃)₃ at C(1)); ¹³C NMR (CDCl₃, 125 MHz) δ 49.2 (C(1)), −0.5 (Si(CH₃)₃ at C(1)), −2.3 (Si(CH₃)₃ at C(3)); ²⁹Si NMR (CDCl₃, 99.35 MHz) δ 1.6, −9.7. Data for **5** and **6**: ¹H NMR (CDCl₃, 500 MHz) δ 7.67−7.24 (m, 8H, aromatic); ¹³C NMR (CDCl₃, 125 MHz) δ 147.9, 146.9, 146.1, 145.8, 145.1, 141.8, 138.5,

136.3, 128.6, 125.0, 123.8, 123.6, 123.3, 122.5, 121.5, 121.3 (vinyl and aromatic); mass spectra (DEI, m/z (%)) 260 (21, [M]⁺), 245 (38, [M − CH₃]⁺), 73 (100, [Si(CH₃)₃]⁺); mass spectra (high resolution, DEI) calculated mass for ¹²C₁₅H₂₄Si₂ (M)⁺ 260.1417 amu, observed mass 260.1430 amu.

Bis(trimethylsilyl)dibenzo[a,d]fulvalene (9). Method a. In an effort to synthesize 1,1,3-tris(trimethylsilyl)indene (**7**), n-butyllithium (43.1 mL of a 1.6 M hexane solution, 68 mmol) was added dropwise over a 1 h period to a solution of indene (4.0 g, 34 mmol) in freshly distilled diethyl ether (100 mL) at −78 °C. After the addition of chlorotrimethylsilane (7.5 g, 68 mmol), the solution was stirred for 1 h and additional n-butyllithium (21.5 mL, 34 mmol) and chlorotrimethylsilane (3.8 g, 34 mmol) were added. The mixture was then warmed to room temperature and stirred for an additional 18 h. Extraction of the resulting opaque milky solution with water (3 × 100 mL) gave rise to a clear, bright red organic phase, which was dried over anhydrous MgSO₄; alternatively, the lithium salts can be removed directly from the crude reaction mixture by filtration. After removal of the solvent, the organic residue was subjected to flash chromatography on silica gel. Elution with hexanes gave 1,1- and 1,3-bis(trimethylsilyl)-indene (identified by comparison to an authentic sample; see **5** and **6**) as a yellow oil (4.12 g, 15.9 mmol, 46%, *based on indene*). Subsequent elution with hexanes/dichloromethane (5:1) yielded **9** as a bright red powder, mp 129−130 °C (0.38 g, 1.0 mmol, approximately 6% *isolated yield based on indene*; in analogous experiments, yields of **9** ranged between 5 and 10%).

Method b. To a mixture of **5** and **6** (4.51 g, 17.3 mmol) in freshly distilled diethyl ether (120 mL) at −78 °C was added n-butyllithium (10.8 mL of a 1.6 M hexane solution, 17.3 mmol) dropwise over a 1 h period, followed by the addition of chlorotrimethylsilane (1.88 g, 17.3 mmol). The mixture was then warmed to room temperature and was stirred for an additional 18 h. Following extraction with water (3 × 100 mL) the organic phase was dried over anhydrous MgSO₄, the solvent was removed, and the organic residue was subjected to flash chromatography on silica gel. Compound **9** was isolated by elution with hexanes/dichloromethane (5:1) and isolated in yields ranging from 5 to 10%. Data for **9**: ¹H NMR (CDCl₃, 500 MHz) δ 7.93 (d, $^3J = 7.4$ Hz, 2H, H(4)), 7.54 (s, 2H, H(2)), 7.36 (d, $^3J = 7.3$ Hz, 2H, H(7)), 7.24 (m, 2H, H(6)), 7.19 (m, 2H, H(5)), 0.36 (s, 18H, Si(CH₃)₃); ¹³C NMR (CDCl₃, 125 MHz) δ 150.7 (C(1)), 147.2 (C(7a)), 141.1 (C(3)), 136.1 (C(2)), 138.0 (C(3a)), 128.3 (C(6)), 125.4 (C(5)), 125.2 (C(4)), 122.7 (C(7)), −1.1 (Si(CH₃)₃); ²⁹Si NMR (CDCl₃, 99.35 MHz) δ −9.0; IR (CDCl₃, cm⁻¹) 3155.7 s, 1469.7 m, 1382.3 m; mass spectra (DEI, m/z (%)) 372 (35, [M]⁺), 357 (17, [M − CH₃]⁺), 299 (14, [M − Si(CH₃)₃]⁺), 73 (100, [Si(CH₃)₃]⁺); mass spectra (high resolution, DEI) calculated mass for ¹²C₂₄H₂₈Si₂ (M)⁺ 372.1729 amu, observed mass 372.1736 amu. Anal. Calcd for C₂₄H₂₈Si₂: C, 77.38; H, 7.58. Found: C, 77.42; H, 7.55. A crystalline sample of this material, produced by slow growth from a mixture of dichloromethane and acetone (1:1), was mounted on a glass fiber and studied by single-crystal X-ray diffraction. The following unit cell parameters were determined: $a = 7.080(1)$ Å, $b = 17.678(4)$ Å, $c = 8.955(2)$ Å, $\alpha = 90.000°$, $\beta = 90.090(3)°$ and $\gamma = 90.000°$. Subsequent refinement in a monoclinic space group ($P2_1/c$) revealed the existence of two independent half-molecules per asymmetric unit. However, in the latter stages of refinement, a disorder problem prevented the structure from being refined to an acceptable level (R1 > 35%). As a result, a discussion of the metrical parameters associated with **9** is not presented. Some of the difficulties in refining the structure (including the appearance of nonpositive-definite atoms) may be a consequence of a pseudo-orthorhombic twinning process; attempts to solve and refine the structure of **9** based on an orthorhombic unit cell were also unsuccessful. Such a disorder does appear plausible,

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in that a decrease in the β angle of only 0.1° would give rise to an orthorhombic cell of higher crystallographic symmetry.

3,3′-Bis(1-trimethylsilylindene) (16). A solution of 3,3′-biindene (**14**)[55] and/or 1-(indanylidene)-1-indene (**15**)[56] (0.300 g, 1.3 mmol) in freshly distilled tetrahydrofuran (30 mL) was cooled to −78 °C, and *n*-butyllithium (2.2 mL of a 1.3 M hexane solution, 2.9 mmol) was added dropwise over a 1 h period. After the mixture was stirred for an additional 3 h at ambient temperature, chlorotrimethylsilane (0.45 g, 4 mmol) was added at −78 °C, and the mixture was stirred while being slowly warmed to ambient temperature over 18 h. The residue obtained after removal of the solvent was extracted with hexanes, and the insoluble lithium salts were separated by filtration. The filtrate was then concentrated and the residue subjected to flash chromatography on silica gel using hexanes, yielding **16** (a *meso* and *d,l* mixture) as a viscous yellow oil (0.200 g, 0.53 mmol, 41%). On the basis of the intensities of the observed NMR signals, it is evident that one isomer (either *meso* or *d,l*) predominates (∼1:1.3). Major isomer: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.62 (d, *J* = 7.5 Hz, 2H, H(4)), 7.51 (d, *J* = 7.5 Hz, 2H, H(7)), 7.30−7.22 (m, 4H, H(5) and H(6)), 6.85 (d, *J* = 1.8 Hz, 2H, H(2)), 3.69 (d, *J* = 1.8 Hz, 2H, H(1)), 0.02 (s, 18H, Si(CH$_3$)$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 146.0 (C(7a)), 143.3 (C(3a)), 136.3 (C(3)), 132.7 (C(2)), 124.7 (C(6)), 123.9 (C(5)), 122.9 (C(7)), 120.5 (C(4)), 45.9 (C(1)), −2.4 (Si(CH$_3$)$_3$); ^{29}Si NMR (CDCl$_3$, 99.35 MHz) δ 4.7. Minor isomer: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.54 (d, *J* = 7.1 Hz, 2H, H(4)), 7.49−7.26 (m, 6H, H(5), H(6), and H(7)), 6.80 (d, *J* = 1.8 Hz, 2H, H(2)), 3.66 (d, *J* = 1.8 Hz, 2H, H(1)), 0.03 (s, 18H, Si(CH$_3$)$_3$); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 146.1 (C(7a)), 143.6 (C(3a)), 136.8 (C(3)), 132.8 (C(2)), 124.7 (C(6)), 123.9 (C(5)), 122.8 (C(7)), 120.7 (C(4)), 45.8 (C(1)), −2.3 (Si(CH$_3$)$_3$); ^{29}Si NMR (CDCl$_3$, 99.35 MHz) δ 4.5. Mass spectra (DEI, *m/z* (%)): 374 (12, [M]$^+$), 359 (16, [M − Si(CH$_3$)$_3$]$^+$), 73 (100, [Si(CH$_3$)$_3$]$^+$). Mass spectra (high resolution, DEI): calculated mass for ^{12}C$_{24}$H$_{30}$Si$_2$ (M)$^+$ 374.1886 amu, observed mass 374.1884 amu.

Oxidation of 16. On the basis of methods previously described in the literature,[18,19] a solution of 3,3′-bis(1-trimethylsilyl)indene (**16**; 0.082 g, 0.22 mmol) in freshly distilled tetrahydrofuran (30 mL) was cooled to −78 °C, and *n*-butyllithium (0.4 mL of a 1.3 M hexane solution, 0.5 mmol) was added dropwise over a 1 h period. After the mixture was stirred for an additional 3 h at ambient temperature, iodine (0.110 g, 0.4 mmol) was added at −78 °C, and this mixture was stirred while being slowly warmed to ambient temperature over 18 h. After removal of the tetrahydrofuran solvent, the residue was subjected to flash chromatography on silica gel using pentane, yielding **9** (0.055 g, 0.51 mmol, 68%).

1,3-Dimethyl-1-(trimethylsilyl)indene (18). The synthesis of this compound has recently been reported in the literature.[26] 1,3-Dimethylindene (3.3 g, 22.9 mmol) in freshly distilled tetrahydrofuran (150 mL) was cooled to −78 °C, and *n*-butyllithium (15 mL of a 1.6 M hexane solution, 24 mmol) was added dropwise over 1 h, after which the mixture was stirred and warmed to ambient temperature over 2 h. Chlorotrimethylsilane (3.8 g, 35.2 mmol) was then added dropwise at −78 °C over 2 h, and the mixture was warmed to room temperature over 18 h followed by refluxing for an additional 6 h. The solvent was then removed and the residue extracted using diethyl ether (3 × 75 mL). Subsequent purification of the extracted material by flash chromatography on silica gel using hexanes yielded **18** as a viscous yellow oil (4.4 g, 20.3 mmol, 89%). Anal. Calcd for C$_{14}$H$_{20}$Si: C, 77.73; H, 9.33. Found: C, 77.68; H, 9.03. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.44−7.27 (m, 4H, H(4), H(5), H(6), and H(7)), 6.26 (s, 1H, H(2)), 2.28 (s, 3H, C(3)−CH$_3$), 1.53 (s, 3H, C(1)−CH$_3$), −0.06 (s, 9H,

Si(CH$_3$)$_3$). ^{1}H NMR (Cl$_2$DCCDCl$_2$, 500 MHz): δ 7.33−7.21 (m, 4H, H(4), H(5), H(6), and H(7)), 6.13 (s, 1H, H(2)), 2.16 (s, 3H, C(3)−CH$_3$), 1.41 (s, 3H, C(1)−CH$_3$), −0.19 (s, 9H, Si(CH$_3$)$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 151.0 (C(3a) or C(7a)), 144.6 (C(7a) or C(3a)), 137.7 (C(2)), 135.8 (C(3)), 124.7, 123.7, 121.7, 118.9 (C(4), C(5), C(6), and C(7)), 46.5 (C(1)), 16.0 (C(1)−CH$_3$), 12.7 (C(3)−CH$_3$), −3.56 (Si(CH$_3$)$_3$). ^{29}Si NMR (CDCl$_3$, 99.35 MHz): δ −0.1. MS (DEI, *m/z* (%)): 216 (61, [M]$^+$), 201 (48, [M − CH$_3$]$^+$), 143 (32, [M − Si(CH$_3$)$_3$]$^+$), 73 (100, [Si(CH$_3$)$_3$]$^+$). MS (CI, NH$_3$, *m/z* (%)): 217 (100, [M + H]$^+$).

5,6-Benzo-2,2,3,3-tetracyano-1,4-dimethyl-7-(trimethylsilyl)bicyclo(2.2.1)hept-5-ene (19). The addition of tetracyanoethylene (0.64 g, 5.0 mmol) to a solution of **18** (1.0 g, 4.6 mmol) in acetonitrile (50 mL) produced a dark blue solution; the dark coloration subsided after 72 h. The residue obtained after removal of the solvent was washed with hexane (1 × 25 mL) and diethyl ether (3 × 15 mL) and then dried to give **19** as a beige powder (1.32 g, 3.8 mmol, 83%); mp 214−215 °C (with decomposition). Anal. Calcd for C$_{20}$H$_{20}$N$_4$Si: C, 69.74; H, 5.86; N 16.28. Found: C, 69.56; H, 5.91; N, 16.31. ^{1}H NMR (CD$_3$CN, 500 MHz): δ 7.51−7.48 (m, 2H, H(8), H(11)), 7.47−7.44 (m, 2H, H(9), H(10)), 2.01 (s, 1H, H(7)), 1.96 (s, 6H, C−CH$_3$), −0.23 (s, 9H, Si(CH$_3$)$_3$). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.50−7.44 (m, 2H, H(8), H(11)), 7.41−7.35 (m, 2H, H(9), H(10)), 1.90 (s, 1H, H(7)), 1.96 (s, 6H, C−CH$_3$), −0.20 (s, 9H, Si(CH$_3$)$_3$). ^{13}C NMR (CD$_3$CN, 125 MHz): δ 143.2 (C(5), C(6)), 130.5 (C(9), C(10)), 123.6 (C(8), C(11)), 113.3 (pseudoequatorial nitriles), 111.9 (pseudoaxial nitriles), 65.9 (C(1), C(4)), 57.6 (C(2), C(3), and C(7)), 15.5 (C-CH$_3$), −0.93 (Si(CH$_3$)$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 141.6 (C(5), C(6)), 130.2 (C(9), C(10)), 122.5 (C(8), C(11)), 111.9 (pseudoequatorial nitriles), 110.3 (pseudoaxial nitriles), 65.3 (C(1), C(4)), 57.0 (C(2) and C(3) or C(7)), 55.5 (C(7) or C(2) and C(3)), 15.2 (C−CH$_3$), −0.87 (Si(CH$_3$)$_3$). ^{29}Si NMR (CH$_2$Cl$_2$, 99.36 MHz): δ 2.4. Mass spectrum (DEI, *m/z* (%)): 343 (6, [M − H]$^+$), 329 (3, [M − CH$_3$]$^+$), 270 (11, [M − Si(CH$_3$)$_3$]$^+$), 216 (23, [M − C$_6$N$_4$]$^+$), 128 (17, C$_6$N$_4$]$^+$), 73 (100, [Si(CH$_3$)$_3$]$^+$). MS (CI, NH$_3$, *m/z* (%)): 362 (16, [M + NH$_4$]$^+$), 90 (42, [Si(CH$_3$)$_3$ + NH$_4$]$^+$). A sample suitable for structural determination (0.38 × 0.25 × 0.20 mm^3) by single-crystal X-ray diffraction was obtained by recrystallization from acetonitrile.

(η^6-3-(Trimethylsilyl)indene)tricarbonylchromium (21). To a solution of 1-(trimethylsilyl)indene (**3**; 1.5 g, 7.98 mmol) in *n*-butyl ether (200 mL) was added freshly distilled tetrahydrofuran (20 mL) and hexacarbonylchromium (3.51 g, 15.95 mmol) under nitrogen. The mixture was then heated at reflux for 72 h and the solvents removed under vacuum. The residue obtained was subjected to flash chromatography on silica gel using hexanes, yielding **21** as a bright yellow solid (1.71 g, 5.28 mmol, 66%); mp 94−95 °C. Anal. Calcd for C$_{15}$H$_{16}$SiCrO$_3$: C, 55.55; H, 4.98. Found: C, 55.63; H, 4.83. IR (KBr, cm^{-1}): ν_{CO} 1959.1, 1876.1. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 6.66 (m, 1H, H(2)), 5.29−5.13 (m, 2H, H(4), H(7)), 5.80−5.71 (m, 2H, H(5), H(6)), 3.49 (m, 2H, CH$_2$), 0.19 (s, 9H, Si(CH$_3$)$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 228.4 (CO), 146.5 (C(2)), 137.4 (C(3)), 91.0, 90.1, 89.5, 88.4 (C(4), C(5), C(6), and C(7)), 42.4 (C(1)), −1.6 (Si(CH$_3$)$_3$). ^{29}Si NMR (CH$_2$Cl$_2$, 99.35 MHz): δ −8.34. MS (DEI, *m/z* (%)): 324 (22, [M]$^+$), 268 (17, [M − 2(CO)]$^+$), 240 (82, [M − 3(CO)]$^+$), 73 (100, [Si(CH$_3$)$_3$]$^+$). HRMS (DEI): calcd for mass ^{12}C$_{15}$H$_{16}$SiCrO$_3$ ([M]$^+$) 324.0274 amu, found 324.0279 amu.

(η^6-1,3-Dimethyl-1-*exo*-(trimethylsilyl)indene)tricarbonylchromium (22). To a solution of **18** (1.3 g, 6.0 mmol) in *n*-butyl ether (100 mL) was added freshly distilled tetrahydrofuran (10 mL) and hexacarbonylchromium (2.5 g, 11.4). The mixture was heated at reflux for 96 h, the solvent removed under vacuum, and the residue subjected to flash chromatography on silica gel. Elution using a mixture of hexanes and dichloromethane (5:1) yielded **22** as a bright yellow solid (0.66 g, 1.9 mmol, 32%); mp 128−130 °C. Anal. Calcd for C$_{17}$H$_{20}$SiCrO$_3$: C, 57.94; H, 5.73. Found: C, 58.02; H, 5.61. IR (KBr,

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cm^{-1}): ν_{CO} 1956.6, 1879.3. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 6.23 (s, 1H, H(2)), 5.78 (d, J = 6.0 Hz, 1H, H(4) or H(7)), 5.48 (d, J = 5.8 Hz, 1H, H(7) or H(4)), 5.42 (m, 1H, H(5) or H(6)), 5.01 (m, 1H, H(6) or H(5)), 2.06 (s, 3H, C(3)−CH_3), 1.43 (s, 3H, C(1)−CH_3), −0.11 (s, 9H, Si(CH_3)$_3$). ^{1}H NMR (Cl$_2$DCCDCl$_2$, 500 MHz): δ 6.24 (s, 1H, H(2)), 5.76 (d, J = 6.0 Hz, 1H, H(4) or H(7)), 5.51 (d, J = 5.8 Hz, 1H, H(7) or H(4)), 5.38 (m, 1H, H(5) or H(6)), 5.03 (m, 1H, H(6) or H(5)), 2.08 (s, 3H, C(3)−CH_3), 1.47 (s, 3H, C(1)−CH_3), −0.07 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 238.1 (CO), 143.2 (C(2)), 135.0 (C(3)), 122.6 (C(3a) or C(7a)), 117.6 (C(7a) or C(3a)), 93.8, 90.2, 86.5, 83.2 (C(4), C(5), C(6) and C(7)), 46.3 (C(1)), 18.7 (C(1)−CH$_3$), 12.1 (C(3)−CH$_3$), −3.68 Si(CH_3)$_3$). ^{29}Si NMR (CDCl$_3$, 99.36 MHz): δ 9.7. MS (DEI, m/z (%)): 352 (7, [M]$^+$), 296 (11, [M − 2CO]$^+$), 268 (19, [M − 3CO]$^+$), 73 (100, [Si(CH$_3$)$_3$]$^+$). A sample suitable for structural determination (0.20 × 0.15 × 0.05 mm^3) by single-crystal X-ray diffraction was obtained by recrystallization from dichloromethane.

Supporting Information Available: Tables of atomic positions, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **19** and **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990650F