Organometallics **1997,** *16,* 5563−5568

The Fluxional Character of (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_9H_7): Evidence for the [4 + 2] Cycloaddition of a Metal-Substituted Isoindene with Tetracyanoethylene

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Received August 5, 1997[⊗]

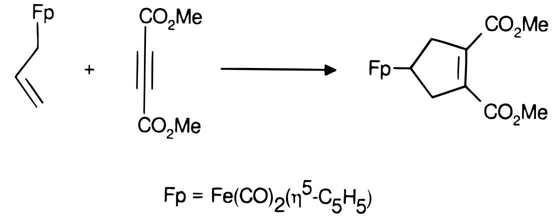
The variable-temperature NMR spectra of (η^5-cyclopentadienyl)Fe(CO)$_2$(η^1-indenyl), **1**, do not exhibit noticeable line-broadening below 70 °C, at which point decarbonylation to yield benzoferrocene, **8**, is rapid. Nevertheless, 2D-EXSY data show clearly that **1** is indeed fluxional; it undergoes successive [1,5] shifts with an activation energy of ~20 kcal mol^{-1}. Contrary to an earlier report, the intermediate isoindene, **2**, is sufficiently long-lived to yield a crystallographically-characterized [4 + 2] cycloadduct, **10**, with tetracyanoethylene.

Introduction

A recent claim[1] that dicarbonyl(η^5-cyclopentadienyl)(η^1-indenyl)iron, **1**, "lacks a diene unit and is incapable of participating in a Diels−Alder [4 + 2] reaction, so that only [3 + 2] cycloadditions should be found" merits re-examination. The [3 + 2] cycloaddition reaction, as typified by the allyliron complex shown in Scheme 1, has been comprehensively reviewed by Welker.[2]

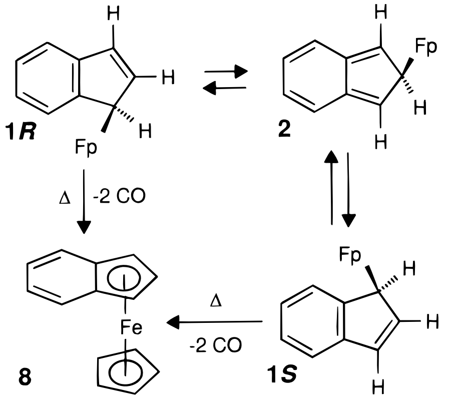
For the indenyl system **1**, the [3 + 2] process could, in principle, occur directly whereas the [4 + 2] cycloaddition would require prior isomerization to the isoindene, **2**, with its attendant diminution of aromatic character. It is, therefore, crucial to establish whether **1** is indeed a fluxional molecule, whereby the enantiomers **1*R*** and **1*S*** are interconverted *via* **2**, as shown in Scheme 2.

Scheme 1. The [3 + 2] Cycloaddition Reaction of (η^1-Allyl)Fe(CO)$_2$Cp with Dimethyl Acetylenedicarboxylate



Fp = Fe(CO)$_2$(η^5-C_5H_5)

Scheme 2. 1,5-Suprafacial Shifts in the (η^1-Indenyl)Fe(CO)$_2$Cp System, 1



Results and Discussion

Fluxionality in η^1-Indenyl Complexes. Any historical perspective on the origins of fluxionality in organometallic chemistry must cite the now classic 1966 paper on (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5), **3**, by Cotton, Davison, and colleagues.[3] In this pioneering investigation, the authors not only established the solid-state structure of **3** and correlated it with the low-temperature limiting ^{1}H NMR spectrum, but they also showed how careful line-shape analysis could elucidate the pathway to molecular rearrangement. In the particular case of **3**, the "ring-whizzing" of the metal around the cyclopentadienyl ring was shown to occur *via* sequential 1,2-shifts with a barrier of approximately 10.7 kcal mol^{-1};[4] this can be reformulated in orbital symmetry terms as a 1,5-suprafacial shift, but the essential correctness of the approach has been abundantly demonstrated over the intervening three decades.[5]

A cornerstone of the analysis of such molecules involved the nonfluxional character of the analogous indenyl complex (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_9H_7), **1**, for which a 1,5 shift would require the intermediacy of the isoindene **2**. It is evident that such a process would at least partially disrupt the aromatic character of the system and, presumably, raise the activation energy for the migration.[6] In contrast, if the ring-whizzing in (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5), **3**, were to occur *via* a series of

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1997.

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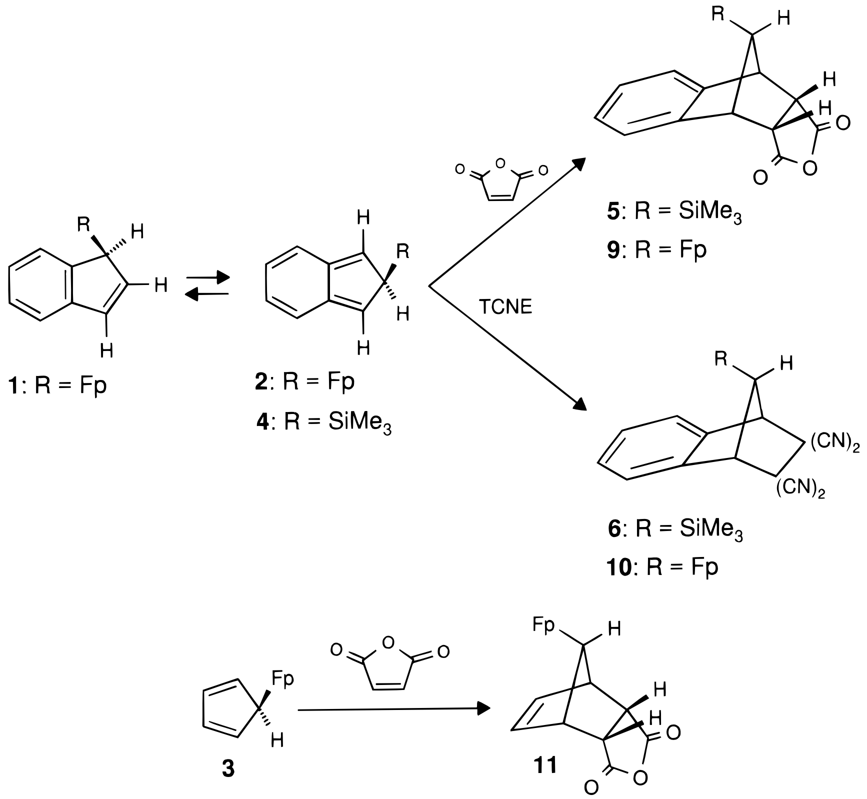
S0276-7333(97)00686-9 CCC: $14.00

Scheme 3. Diels–Alder Cycloadditions to Isoindene and Cyclopentadiene Complexes



1: R = Fp

2: R = Fp
4: R = $SiMe_3$

5: R = $SiMe_3$
9: R = Fp

6: R = $SiMe_3$
10: R = Fp

3

11

1,3-shifts, then the indenyl analogue, **1**, should exhibit fluxional behavior similar to **3**, since no disruption of the aromaticity in the 6-membered ring is required.

When bis(η^1-indenyl)mercury was shown to be fluxional, even at room temperature, it was suggested that a direct 1,3-shift involving the mercury 6p orbitals might be a viable explanation.[7] However, a subsequent ^{13}C study on (η^1-C_5H_5)HgCl indicated a 1,5-shift mechanism and yielded a migration barrier of 7.7 kcal mol^{-1}; this may be compared to the value of 13 kcal mol^{-1} in (η^1-C_9H_7)$_2$Hg. In contrast, in (η^1-C_5H_5)$_2$Hg, the activation energy was too small to permit the observation of the limiting spectrum, clearly showing that the migration is considerably retarded in the indenyl system.[8]

This markedly enhanced barrier to metal (or metalloid) migrations in indenyl complexes, relative to those found in their cyclopentadienyl analogues, is also observed in R_3Si- and R_3Ge-substituted molecules. These systems have been intensively studied,[9] and it is now generally agreed that these migrations proceed *via* successive 1,5-suprafacial shifts; indeed, 2-(trimethylsilyl)isoindene, **4**, has been trapped as the corresponding Diels–Alder adduct with maleic anhydride, **5**, and tetracyanoethylene (TCNE), **6**, as depicted in Scheme 3.

It is particularly crucial to note that the nonequivalent Me_3Si groups in 1,2-bis(trimethylsilyl)indene, **7**, are equilibrated on the NMR time scale with the same barrier (26 kcal mol^{-1}) as that for the exchange between H(1) and H(3).[9c] This observation provides compelling evidence for a 1,5-shift mechanism in which both trimethylsilyl moieties reside temporarily at C(2), as shown in Scheme 4.

Moreover, in the molecules $Me_3E-C_5H_5$ and $Me_3E-C_9H_7$, where E = Si, Ge, Sn, the $\Delta G^{\ddagger}$ values for the group 14 element migrations in the indenyl systems are consistently ~8.5 kcal mol^{-1} higher than in the corresponding cyclopentadienes.[9h] The overall pattern which emerges is that of a common mechanistic pathway, *i.e.*, 1,5-suprafacial shifts, for both the cyclopentadienyl and indenyl frameworks. In the latter cases, the barriers are larger because of decreased aromatic character in the isoindene intermediates, which can also be trapped as Diels–Alder adducts by suitably reactive dienophiles.

In light of these data on a wide variety of indenyl organometallics, Sergeyev *et al.* hypothesized that in (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_9H_7), **1**, the barrier toward iron mi-

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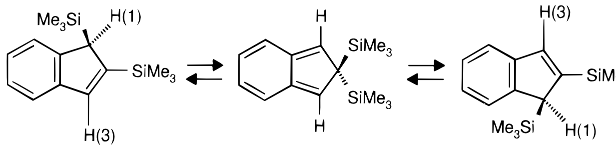
Scheme 4. Mechanism of Trimethylsilyl Scrambling in 7



7*R* **7*S***

gration should exceed 20 kcal mol^{-1}.[9h] Although the nonfluxional nature of **1** has almost been granted an imprimatur, one should perhaps recall that the original workers were more precise. Cotton and Marks noted that "in the case of (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_9H_7), the 2-indenyl structure is so unfavorable that it does not serve as a suitable transition state or intermediate for the interconversion ... of **1R** and **1S**... at a rate sufficient to cause broadening of the NMR spectrum even at +70 °C (above which temperature the compound undergoes rapid decomposition)".[7] These authors never stated that the interconversion of the enantiomers of **1** could not occur, they merely placed limits on the rate!

NMR Studies. With modern 2D-EXSY[10] and single selective inversion NMR techniques,[11] it is straightforward to demonstrate that **1** is indeed fluxional, even at temperatures where no line broadening is evident. Figure 1 shows the results of a phase-sensitive 2D-EXSY experiment acquired at 45 °C with a mixing time of 5 s; at this temperature, decarbonylation of **1** to yield benzoferrocene, **8**, is relatively slow.[12] One can clearly observe off-diagonal correlations between H(1) and H(3) and also between the aromatic protons H(4) and H(7), which are indicative of chemical exchange arising from an *overall* 1,3-migratory process.

From a given two-dimensional spectrum, one can readily extract a number of one-dimensional spectra in the form of perpendicular "slices". Figure 2 shows a stacked plot of such 1D slices comprised of rows containing the H(3) diagonal peak and its off-diagonal correlation peak with H(1); these spectra were extracted from a series of 2D-EXSY spectra that were acquired by using various mixing times. From the stacked plot of 1D spectra, it is evident that the magnitude of the off-diagonal cross peak relating the H(3) and H(1) sites, relative to the H(3) diagonal peak, grows with increasing mixing time. Moreover, since the diagonal and off-diagonal resonances have the same phase, one can be sure that these correlations arise as the result of chemical exchange not from NOE interactions.

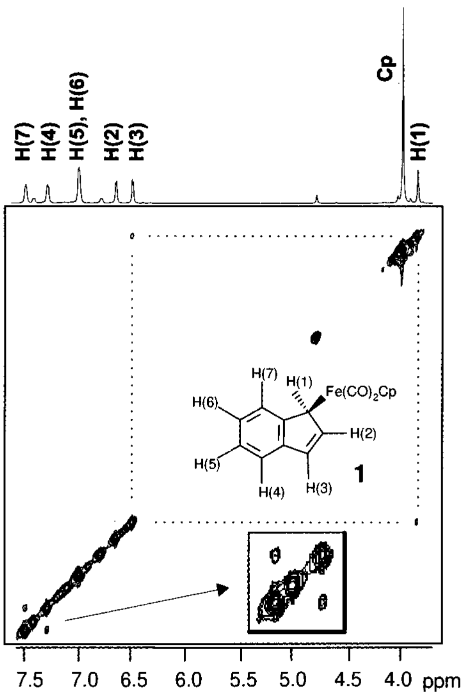


Figure 1. 2D-EXSY spectrum of **1** in C_6D_{12} at 45 °C, acquired with a mixing time of 5 s.

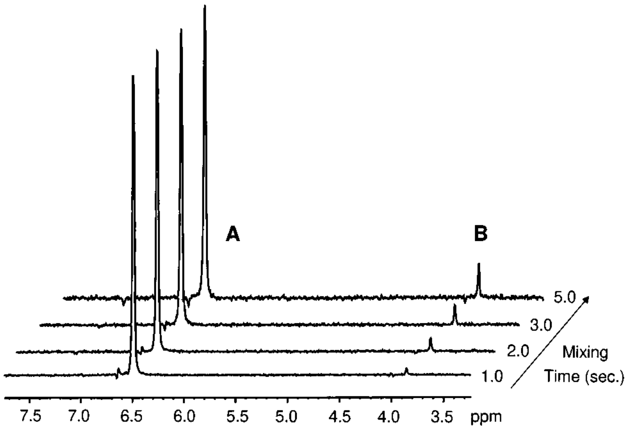


Figure 2. Cross-sections from 2D-EXSY spectra acquired with different mixing times. In each case, signal A is the diagonal peak attributable to H(3); signal B is the off-diagonal peak arising from chemical exchange with H(1).

Although 2D-EXSY experiments conveniently map out exchanging sites, for quantitative exchange measurements, one-dimensional NMR methods are often more efficient. In the present case, the problem of rapid sample decomposition at the elevated temperatures required to observe chemical exchange necessitates that the NMR measurements be carried out as rapidly as possible. For a given temperature, selective inversion experiments[11] utilizing single-scan acquisitions provided acceptable kinetic data in under 15 min. Analysis of such data collected over a range of temperatures yielded a $\Delta G^{\ddagger}$ value of 20 ± 2 kcal mol^{-1} for this **1*R*** ⇔ **1*S*** enantiomerization process.

Trapping of Isoindenes. This result has considerable relevance to the purported [3 + 2] reactions of **1**. It has been reported that **1** reacted slowly with maleic anhydride and more rapidly with TCNE to yield the adducts **9** and **10**, respectively, whose structures were assigned on the basis of their NMR spectra.[1] Since such products could have arisen *via* Diels–Alder [4 + 2] additions to the isoindene **2**, it was deemed necessary to unequivocally establish the stereochemistry of the products.

The X-ray crystal structure of the TCNE adduct, **10**, is presented in Figure 3; the important crystallographic parameters and selected geometrical data are listed in Tables 1 and 2, respectively. In the crystalline lattice, the adduct, **10**, packs with two crystallographically-independent, pseudoenantiomorphic rotamers per asymmetric unit, between which no unusually close inter-

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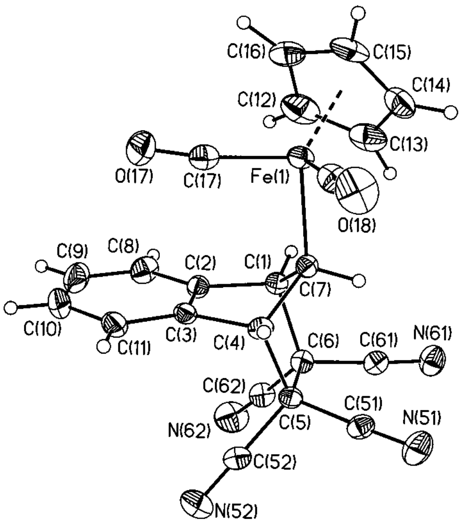

Figure 3. X-ray structure of **10**, showing the atomic-numbering scheme. Thermal ellipsoids are shown at the 30% probability level.

Table 1. Crystal Data and Structure Refinement Parameters for 10

empirical formula	$C_{22}H_{12}Fe_1N_4O_2$
mol wt	420.21
description	yellow plate
cryst size, mm	0.02 × 0.1 × 0.12
temperature, K	300(2)
wavelength, Å	(Mo Kα) 0.710 73
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.079(4)
b, Å	14.888(9)
c, Å	15.018(9)
α, deg	72.56(5)
β, deg	85.96(4)
γ, deg	88.63(4)
volume, $Å^3$	1932(1)
Z	4
calcd density, g/cm^3	1.445
scan mode	ω-scans
$F(000)$	856
θ-range for collection, deg	1.42−26.40
index ranges	$-11 \le h \le 11, -18 \le k \le 18, -18 \le l \le 18$
no. of reflns collected	13298
no. of unique reflns	5974
R(int)	0.0411
weighting scheme	$w = 1/[\sigma^2F_o{}^2 + (0.0194P^2) + 5.2743P]$
data/restraints/params	5974/0/524
goodness-of-fit on F^2	0.861
final R indices ($I > 2\sigma(I)$)^a	R1 = 0.0471; wR2 = 0.0954
R indices (all data)^a	R1 = 0.0744; wR2 = 0.1109
mean shift/error	<0.002
max shift/error	<0.002
effect trans (max, min)	0.9423, 0.8466
largest diff peak, e/$Å^3$	0.62
largest diff hole, e/$Å^3$	−0.34

^{a} $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]]^{0.5}$; $P = (F_o{}^2 + 2F_c{}^2)/3)$.

molecular contacts exist. Given the similarity between these two rotamers, commentary on specific geometric parameters in the following discussion is limited to only one of the independent molecules.

Perhaps the most striking structural feature is the *anti* orientation of the Fp and TCNE moieties in **10**, which parallels structural data previously reported for **6**, the Diels−Alder adduct of 2-(trimethylsilyl)isoindene, **4**, with TCNE,[13] and also for **11**, the cycloaddition product of **3** with maleic anhydride.[14] It is noteworthy that mechanistic studies carried out by both Glass and McConnell[15] and by Kerber *et al.*[1] strongly support a concerted [4 + 2] mechanistic pathway, rather than a [3 + 2] route, in the reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$, **3**, with electrophilic alkenes.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Both Molecules of 10

bond lengths		bond angles	
Fe(1)−C(7)	2.053(4)	Fe(1)−C(7)−C(1)	117.0(2)
Fe(2)−C(27)	2.042(4)	Fe(2)−C(27)−C(21)	120.5(3)
C(1)−C(6)	1.594(5)	Fe(1)−C(7)−C(4)	120.9(3)
C(21)−C(26)	1.593(7)	Fe(2)−C(27)−C(24)	118.8(3)
C(4)−C(5)	1.607(7)	Fe(1)−C(17)−O(17)	172.1(4)
C(24)−C(25)	1.606(5)	Fe(2)−C(37)−O(37)	178.1(6)
C(5)−C(6)	1.613(5)	Fe(1)−C(18)−O(18)	177.3(4)
C(25)−C(26)	1.604(6)	Fe(2)−C(38)−O(38)	175.0(6)

The steric demands of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ unit in **10** are evident in the expansion of the Fe(1)−C(7)−C(1) and Fe(1)−C(7)−C(4) angles from ideal tetrahedral geometry, an effect which has been observed for other related main-group[13] and transition-metal[14,16] complexes. Overall, however, the geometric features of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ fragment in **10** are generally quite similar to those previously reported for other $(\eta^5\text{-}C_5H_5)$-$Fe(CO)_2(\eta^1\text{-alkyl})$ complexes.[14,17] With the exception of observed lengthening in both the incipient Diels−Alder bonds, C(1)−C(6) and C(4)−C(5) and the formerly olefinic TCNE bond, C(5)−C(6), the carbocyclic framework in **10** exhibits no unusual features. Such an increase in the $C(sp^3)-C(sp^3)$ distance has been observed previously in the structure of **6**[13] and has been rationalized in other cyclic structures as resulting from the electron-withdrawing character of the cyano substituents.[17]

Additional evidence for isoindene intermediates arises from a recent report by Jordan and co-workers who described the synthesis and X-ray structure of a novel C_1-symmetric *ansa*-hafnocene $\{Me_2Si(\eta^5\text{-1-indenyl})(\eta^3\text{-2-indenyl})\}Hf(NMe_2)_2$, **14**, in which one of the indenyl moieties is bridged through the 2-position (Scheme 5).[18] Jordan rationalized the formation of **14** as resulting from intramolecular elimination of dimethylamine from the isoindene **13**, which is formed as a result of a single 1,5-silatropic shift of a $Me_2Si(\eta^5\text{-1-indenyl})Hf(NMe_2)_3$ fragment over the surface of the uncoordinated indenyl ring in **12**. The intramolecular "trapping" of the isoindenyl fragment in **13** strongly supports the viability of intermolecular [4 + 2] cycloadditions involving thermally-generated isoindenes and electron-deficient dienophiles.

Concluding Remarks. The possible intermediacy of 2-(trimethylsilyl)isoindene, **4**, in the formation of **6** was initially investigated by Ashe in 1970.[19] He used a dilatometric method to measure the temperature dependence of the rate of formation of **6** from 1-(trimethylsilyl)indene and TCNE and obtained an activation energy of ~22.5 kcal mol^{-1}. The striking similarity of this value to that found for silatropic shifts leads one

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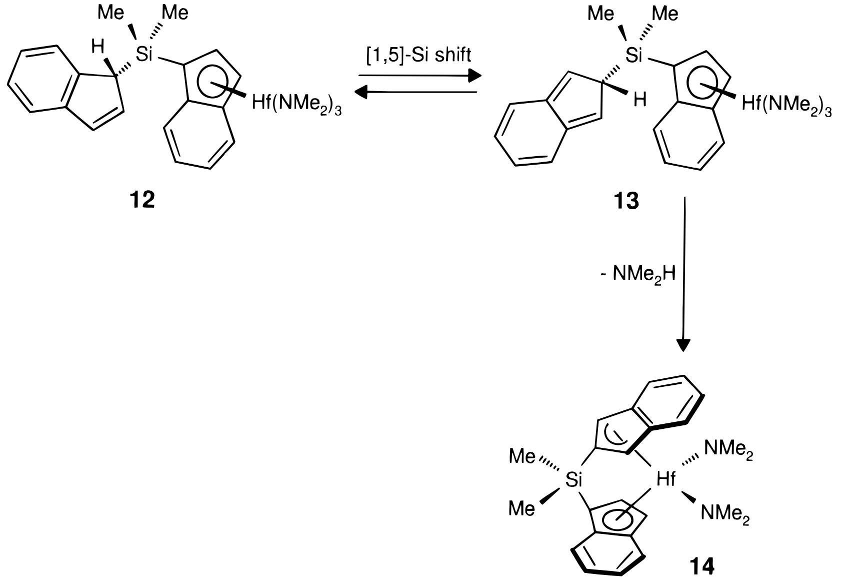
Scheme 5. Intramolecular Trapping of an Isoindene at a Hafnium Center (from Ref 18)



to conclude that these migrations occurred *via* successive 1,5-shifts and that Ashe had trapped the short-lived isoindene intermediate. The present work establishes clearly that (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_9H_7), **1**, is fluxional, and since sigmatropic shifts in metal−cyclopentadienyl or −indenyl complexes have been shown to proceed *via* 1,5-shifts, it is not necessary to invoke [3 + 2] cycloadditions to account for the formation of Diels−Alder adducts such as **5**, **6**, **9**, and **10**.

Finally, we note that there are a number of other reports of fluxional indenyl−transition-metal complexes, e.g., (η^1-indenyl)Re(CO)$_3$(PMe$_3$)$_2$ and (η^1-indenyl)ReO$_3$;[20,21] however, these were assumed to involve 1,3-shifts, and no attempts were made to intercept isoindene intermediates. Clearly, these systems merit further investigation.

Experimental Section

NMR spectra were acquired on a Bruker Avance DRX-500 spectrometer, equipped with an 11.74 T superconducting magnet. These experiments consisted of 1-D ^{1}H and ^{13}C NMR spectra as well as 2-D ^{1}H -^{1}H COSY, ^{1}H−^{1}H EXSY, ^{1}H−^{13}C shift-correlated, and long range ^{1}H−^{13}C shift-correlated spectra. Proton spectra were acquired at 500.13 MHz using a 5 mm broad-band inverse probe with triple axis gradient capability. Carbon-13 NMR spectra were recorded at 125.76 MHz using the aforementioned probe. All NMR spectra were recorded on spinning samples (except during the acquisition of 2-D spectra), locked to a solvent signal. Peaks were referenced to a residual proton signal of the solvent or to a ^{13}C solvent signal.

Selective Inversion Measurements. ^{1}H selective inversion NMR spectra were recorded on a Bruker AC 300 spectrometer with a 7.65 T superconducting magnet, equipped with a Bruker B-VT 2000 temperature controller, and a 5 mm QNP probe. The exchange rates were measured by selective inversion relaxation experiments.[22] The H-1 signal in the spectrum was perturbed using a 90−τ−90 pulse sequence,[23] and then the return to equilibrium was monitored as a function of time, as in an inversion-recovery T_1 experiment. Each temperature (318, 323, 328, 333, and 338 K) was measured by placing a copper-constantan thermocouple, contained in an NMR tube, into the probe. Spectra were processed on an Aspect 3000 computer, using the DISNMR program. A C programming language version of McClung's program SIFIT[23c] was used to do a nonlinear least-squares fit to the experimental results and to extract values for the rates. Typical errors in the rates are ±10%.

^{1}H−^{1}H EXSY Spectra. Two-dimensional ^{1}H−^{1}H EXSY spectra[10] were acquired on a Bruker Avance DRX-500 spectrometer in the phase-sensitive mode, using the pulse sequence 90°−t_1−90°−t_m−90°−ACQ. In a typical ^{1}H EXSY experiment, 512 FIDs were recorded in the F2 dimension, with each FID acquired in 16 scans over a 2.315 KHz spectral width. The FIDs were Fourier transformed with Gaussian window functions in both F1 and F2, with a line broadening of 3.0 Hz. At 318 K, mixing times of 1.0, 2.0, 3.0, and 5.0 s were employed. The relaxation delay was set to 1.0 s, and the initial value for the 2D evolution was set to 10 ms.

(η^5-C_5H_5)Fe(CO)$_2$(η^1-C_9H_7), 1. The title compound was prepared following a revised approach[1] to the preparation initially described by Cotton and co-workers.[6] A complete and unequivocal assignment of high-field ^{1}H and ^{13}C NMR data for **1** had not been published prior to this report. ^{1}H NMR (C_6D_{12}, 500 MHz): δ 7.49 (m, 1H, H-7), 7.28 (m, 1H, H-4), 6.98 (m, 1H, H-6), 6.97 (m, 1H, H-5), 6.64 (m, 1H, H-2), 6.49 (m, 1H, H-3), 3.98 (s, 5H, Cp), 3.85 (m, 1H, H-1). ^{13}C NMR (C_6D_{12}, 125 MHz): δ 217.4 (C≡O), 216.6 (C≡O), 157.6 (C-3a), 148.2 (C-2), 141.8 (C-7a), 124.1 (C-7), 123.9 (C-6), 123.6 (C-5), 121.7 (C-4), 120.8 (C-3), 87.1 (Cp), 26.8 (C-1).

Cycloadduct of (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_9H_7) and Tetracyanoethylene, 10. This compound was prepared using methods described by Kerber and co-workers.[1] A complete assignment of the high-field ^{13}C NMR spectrum of **10** had not been published prior to this report. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.54−7.49 (m, 2H, H-8,11), 7.48−7.43 (m, 2H, H-9,10), 4.82 (s, 5H, Cp), 4.05 (s, 2H, H-1,4), 3.15 (s, 1H, H-7). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 215.4 (C≡O), 139.7 (C-2,3), 130.2 (C-9,10), 125.6 (C-8,11), 113.3 (C≡N, pseudoequatorial), 110.6 (C≡N, pseudo axial), 86.0 (Cp), 68.3 (C-1,4), 48.7 (C-5,6), 39.6 (C-7). A sample suitable for structural determination by single-crystal X-ray diffraction was obtained by recrystallization from dichloromethane.

X-ray Crystallography. X-ray crystallographic data for **10** were collected from a single-crystal sample, which was mounted on a glass fiber. Data were collected using a P4

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Siemens diffractometer, equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector (using the program SMART[24]) 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, better than 0.8 Å resolution. Upon completion of the data collection, the first 50 frames were recollected in order to improve the decay corrections analysis. Processing was carried out by use of the program SAINT,[25] which applied Lorentz and polarization corrections to three-dimensionally integrated diffraction spots. The program SADABS[26] was utilized for the scaling of the diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The structure was solved by using the direct-methods procedure in the Siemens SHELXTL program library.[27] Refinement was carried out by using full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms. All 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 their attached carbon.

Acknowledgment. Financial support from NSERC Canada and from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. M.S. thanks NSERC for a postgraduate scholarship.

Supporting Information Available: Tables giving positional and thermal parameters and bond distances and angles for **10** (7 pages). Ordering information is given on any current masthead page.

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