Electrophilic Discrimination of the Ambident Organometallic Nucleophile $(\eta^3\text{-}C_7H_7)Fe(CO)_3^-$ in Its Reaction with Group 14 Halides: Synthesis and Fluxional Behavior of $(\eta^3\text{-}C_7H_7)Fe(CO)_3EPh_3$ (E = Sn, Pb)

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The reaction of $(\eta^3\text{-}C_7H_7)Fe(CO)_3^-$ (1) with Ph_3ECl (E = Sn, Pb) leads to the formation of $(\eta^3\text{-}C_7H_7)Fe(CO)_3EPh_3$ (E = Sn, Pb) (3) complexes. This is in contrast to the reaction of 1 with Si- and Ge-based electrophiles, which has been shown previously to give ring-substituted derivatives, $[\eta^4\text{-}(R_3E)C_7H_7]Fe(CO)_3$ (2), thus establishing the subtle electrophilic discrimination of 1. The spectroscopic data on complexes 3 are consistent with the *fac-exo* disposition of the ligands around the formally six-coordinate iron center. In solution the molecules are fluxional and exhibit both metal migration and carbonyl group scrambling processes. It is shown that the metal migration consists of a series of 1,2-shifts and that this movement is independent of the carbonyl exchange process.

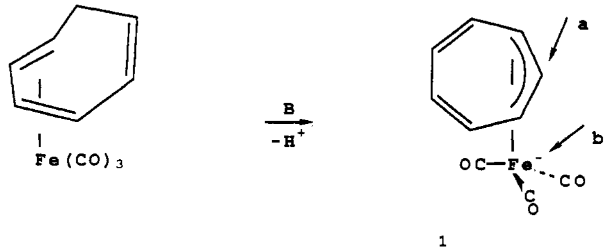
Introduction

The effective stabilization of neighboring carbanions by polyhapto organometallic groups is by now a well-recognized phenomenon.[2] The multiple nucleophilic sites made available by the delocalized nature of the negative charge in such molecules renders them potentially more useful and more versatile for the preparation of new organometallic species than the straightforward metal carbonyl anions.[3]

A particularly striking example of this behavior is provided by the organometallic anion obtained by proton abstraction from (η^4-cycloheptatriene)tricarbonyliron[4] (Scheme I). The deprotonation can be affected by a variety of strong bases and indicates an acidity enhancement of the coordinated cycloheptatriene by some 17 pK_a units over that of the free ligand.[2] The stabilization of the formal cycloheptatrienide anion, $C_7H_7^-$, is achieved by formation of the closed-shell allyl anion complex $(\eta^3\text{-}C_7H_7)Fe(CO)_3^-$ (1). The latter bonding mode of the coordinated cycloheptatrienyl ring was confirmed by single-crystal X-ray crystallography.[5]

The potential for ambident nucleophilic behavior by 1 is also indicated in Scheme I by showing the two obvious sites, ring carbon (path a) and iron center (path b), for electrophilic attack. Indeed there are reports in the literature already that establish the ambident nucleophilicity of 1. We[6] and others[7-9] have shown that carbon-, and silicon-, and germanium-based electrophiles react with 1 to give ring-substituted compounds, $(\eta^4\text{-}C_7H_7R)Fe(CO)_3$. The *exo* disposition of the ring substituent R is consistent with direct ring attack (path a) for the formation of these compounds. In contrast to this, the reaction of 1 with transition-metal carbonyl halides appears to proceed via iron attack (path b) and gives cycloheptatrienyl-bridged heterobimetallic complexes, $(\mu\text{-}C_7H_7)Fe(CO)_3MLL'$ (M = Rh, Ir; L, L′ = 2 CO, cyclooctadiene; L = CO, L′ = PR_3).[10,11]

Scheme I



B = LiBu, KO^{t}Bu, KH, NaN$(SiMe_3)_2$

Scheme II

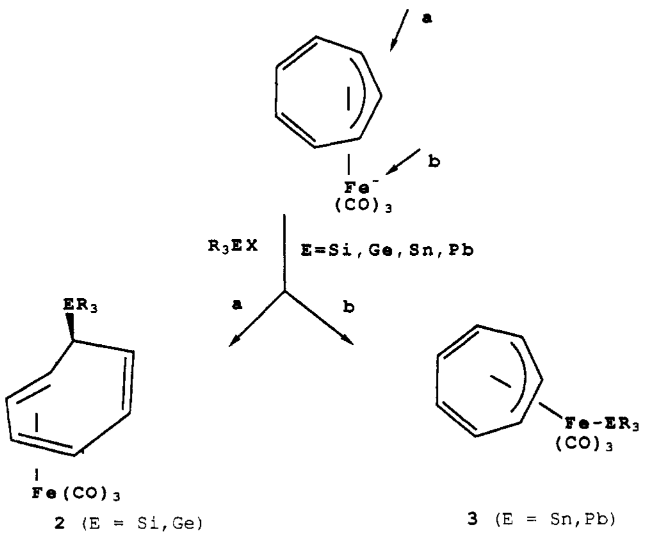


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Table I. ^{1}**H and** ^{13}**C NMR Data**[a] **for** $(\eta^3\text{-}C_7H_7)Fe(CO)_3EPh_3$ **(E = Sn (3a), Pb (3b))**

	assignt[b]					fast-exchange limit[e]
compd	H(1)	H(2)	H(3)	H(4)	temp, °C	C_7H_7
3a	3.36	4.36	6.40	5.71	−105	5.18
3b	3.46	4.59	6.32	5.68	−100	5.15

	assignt[c]						fast-exchange limit		
compd	C(1)	C(2)	C(3)	C(4)	CO	temp, °C	C_7H_7	CO	temp, °C
3a	58.5	67.4	135.2	121.9	208.5 (1) 213.5 (2)	−103	103.0	212.5	33
3b	60.7	68.4	*d*	122.2	208.9 (1) 213.2 (2)	−95	103.1	212.2	30

[a] Chemical shifts (δ) in ppm from Me_4Si by appropriate conversion from the internal reference solvent CD_2Cl_2. [b] Assignment based on homonuclear spin-decoupling experiments, which established the following coupling pattern: $J_{12} = 5.9$, $J_{23} = 6.9$, $J_{34} = 10.0$, and $J_{34'} = 2.4$ Hz. Ph resonances are at δ 7.3–7.7 ppm. [c] Assignment based on heteronuclear decoupling experiments; relative intensities of the CO signals are in parentheses. Ph resonances are as follows: **3a**, δ 128.2 (2), 128.7 (1, p), 136.1 (2), 138.6 (1, ipso) ppm; **3b**, δ 128.2 (1, p), 129.2 (2), 136.9 (2), 150.5 (1, ipso) ppm. [d] Resonance hidden by Ph signals. [e] 0 °C.

It may be argued that in view of the very different nature of the two classes of electrophiles the change in reactivity is not that unusual, nor should it be totally unexpected.

Here we wish to report on the reaction of **1** with Ph_3SnCl and Ph_3PbnCl, which reveals that the electrophilic discrimination of **1** is stronger and more subtle than hitherto anticipated.

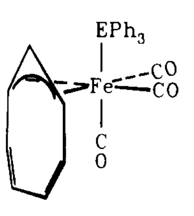
Results and Discussion

Due to its ambident nucleophilicity the reaction of **1** with group 14 halides can give rise to two distinct structural isomers with vastly different properties (Scheme II). These can be easily distinguished on the basis of spectroscopic data. As discussed above, direct ring attack (path a) leads to ring-substituted derivatives **2** and this is the exclusive reaction product that has been observed with carbon-, silicon-, and germanium-based halides, including Ph_3GeBr.[6] Compounds **2** show complex ^{1}H and ^{13}C NMR spectra due to the asymmetric nature of the η^4-bonded, substituted cycloheptatriene ring[6] and carry the typical IR signature of $(\eta^4\text{-diene})Fe(CO)_3$ type molecules, three strong terminal CO stretching bands, two of which are close together due to their doubly degenerate, E-mode, parentage under local C_{3v} symmetry.[12] On the other hand, attack on iron (path b) results in the formation of an Fe-to-element bond, maintains the η^3-bonded cycloheptatrienyl ring, and gives $(\eta^3\text{-}C_7H_7)Fe(CO)_3ER_3$ (**3**). Such species are typically fluxional[13] and exhibit a single time-averaged C_7H_7 signal in their NMR spectra at room temperature. The IR spectrum shows at least three well-separated terminal CO stretching bands due to the maximum C_s local symmetry;[12] extra bands may appear due to conformational effects.

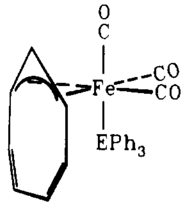
Synthetic and Spectral Studies. The reaction of Ph_3SnCl and Ph_3PbCl with **1** in THF at room temperature resulted in the formation of red, air-stable solids that, on the basis of elemental analysis and their mass spectra (see Experimental Section), are formulated as $Fe(CO)_3(C_7H_7)EPh_3$ (E = Sn (**3a**), Pb (**3b**)). The yields range from moderate (43%) for **3b** to good (72%) for **3a**.

The infrared spectra of complexes **3** display three, well-separated, strong absorption bands in the terminal carbonyl region (2039, 1987, and 1958 cm^{-1} (**3a**); 2034, 1984, and 1958 cm^{-1} (**3b**)). The ^{1}H and ^{13}C NMR spectra at room temperature show only a single time-averaged signal for the cycloheptatrienyl ring (Table I). The fluxional behavior of the molecules was proved by the temperature dependence of the NMR line shapes. The low-temperature limiting spectra exhibited four resonances for the seven-membered ring in a 2:2:2:1 ratio. As detailed above, these observations uniquely identify **3** as $(\eta^3\text{-}C_7H_7)Fe(CO)_3EPh_3$ type molecules.

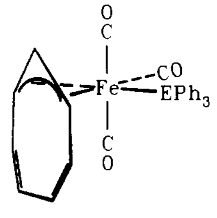
With the usual convention of counting the $\eta^3\text{-}C_7H_7$ moiety as occupying two coordination positions, these formally six-coordinate molecules can in principle exist as two geometrical isomers, *fac*-**3** and *mer*-**3**. The former isomer may also exhibit conformational mobility of the seven-membered ring and, as for the related $(\eta^3\text{-allyl})Fe(CO)_3X$ molecules,[14] present *endo* and *exo* orientations of the ring with respect to the EPh_3 moiety. The presence of isomers and/or conformers in solution can be easily diagnosed from IR and NMR spectroscopies. Faller and Adams[14] have shown that the $(\eta^3\text{-allyl})Fe(CO)_3X$ (X = halides and pseudohalides) compounds exist exclusively as the *fac* isomer with the *endo* conformer predominating, although a different type of geometry, perhaps best described as a distorted *mer*-coordination mode, has been discovered for $(\eta^3\text{-}C_3H_5)Fe(CO)_3AuPPh_3$. Conformational isomerism was also detected in $CpMo(CO)_2(\eta^3\text{-}C_7H_7)$.[16]



fac-exo



fac-endo



mer

In the present context the simple three-band IR spectra and the appearance of the low-temperature limiting ^{1}H and ^{13}C NMR spectra, exhibiting four signals for the $\eta^3\text{-}C_7H_7$ moiety in 2:2:2:1 ratio (see Figures 1 and 2), uniquely identify compounds **3** as existing in the single *fac* isomeric form. Spectroscopy does not allow a distinction to be made between the *exo* and *endo* conformers since both have C_s point group symmetry. But the strong steric crowding between the large EPh_3 moiety and the uncoordinated diene part of the seven-membered ring in the *fac-endo* conformer leads to the confident prediction that the alternate *fac-exo* orientation is the preferred situation for compounds **3**.[17]

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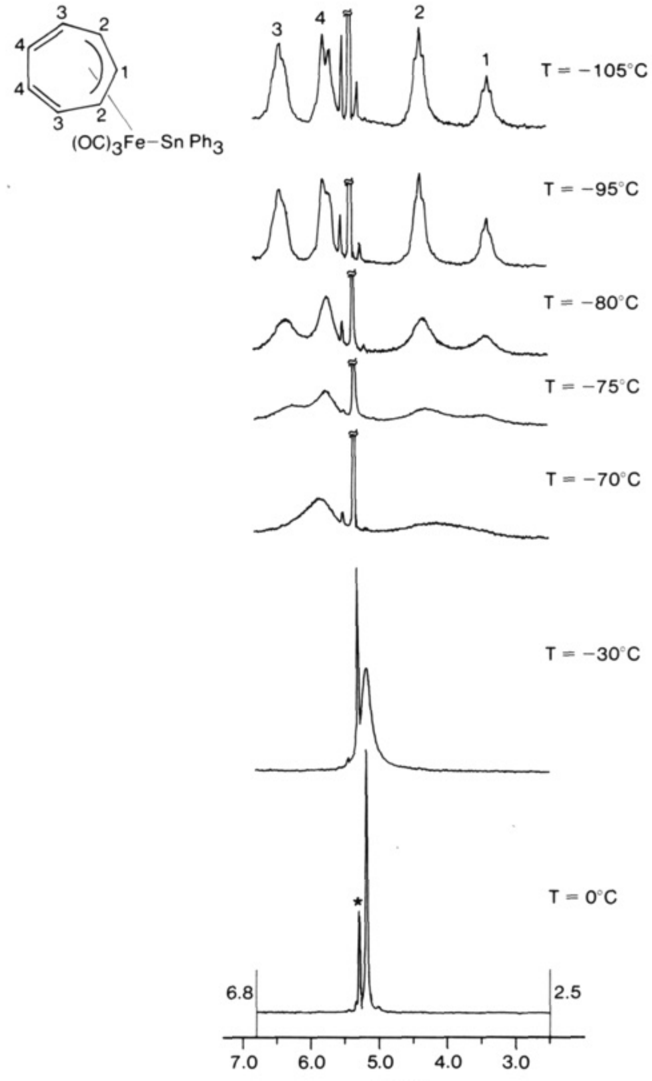


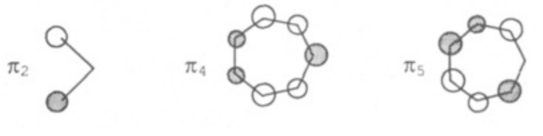
Figure 1. Variable-temperature ^{1}H NMR spectra of (η^3-C_7H_7)Fe(CO)$_3$SnPh$_3$ (**3a**) in CD_2Cl_2 (*).

Table II. ^{1}H NMR Data for η^3-C_7H_7 and Related η^3-C_3H_5 Compounds^a

compd^b	H(1)	H(2)	H(3)	H(4)	solvent	ref
3a	3.36	4.36	6.40	5.71	CD_2Cl_2	this work
3b	3.46	4.59	6.32	5.68	CD_2Cl_2	this work
4	3.5	4.95	6.5	5.8	CF_2Cl_2	18
5	3.08	4.75	6.10	5.15	CD_2Cl_2	19
6	2.32	4.59	6.50	5.40	$CHCl_2F$	16
7	2.26	4.99 4.63	6.65 6.48	5.40 5.35	acetone-d_6	20
8	4.91	3.66				21
9	3.08	2.60				22
10	4.73	2.89				23

^{a} Chemical shifts in ppm from TMS. ^{b} Legend: **4**, (η^3-C_7H_7)Co(CO)$_3$; **5**, (η^3-C_7H_7)Fe(η^5-C_5H_5)(CO); **6**, (η^3-C_7H_7)Mo(η^5-C_5H_5)(CO)$_2$; **7**, (η^3-C_7H_7)Mo(CO)$_2$(en)Cl; **8**, (η^3-C_3H_5)Co(CO)$_3$; **9**, (η^3-C_3H_5)Mo(η^5-C_5H_5)(CO)$_2$; **10**, (η^3-C_3H_5)Re(CO)$_4$.

Chart I. Frontier MO's of C_3H_5 and C_7H_7 Fragments



Fluxional Behavior of Compounds 3a and 3b in Solution. The variable-temperature ^{1}H and ^{13}C NMR spectra of compound **3a** are shown in Figures 1 and 2, respectively. The temperature behavior of the analogous PbPh$_3$ derivative **3b** is very similar. The NMR data are collected in Table I.

Clearly the molecules are fluxional. As the temperature is lowered, the single, sharp, time-averaged signal of the η^3-C_7H_7 ring broadens, disappears, and finally reemerges as four distinct signals. The resolution of spin–spin coupling in the ^{1}H NMR spectrum suggests that we are indeed close to the low-temperature limiting spectrum. The temperature behavior of the line shapes is reversible and is independent of the concentration of **3** and of the solvent used, establishing that the rearrangement process is intramolecular.

As discussed before, the observation of four signals for the η^3-C_7H_7 moiety at low temperature in a 2:2:2:1 ratio is consistent with the *fac-exo* disposition of the ligands around the iron atom in compounds **3**. This conclusion is further corroborated by the appearance of two CO signals in a 2:1 ratio, representing the two equivalent equatorial CO groups and the unique axial CO ligand, respectively. The temperature-dependent line-shape changes of the CO ligands indicate that, in addition to the ring-whizzing motion, carbonyl group scrambling is also featured in these formally six-coordinate molecules.

In order to deduce the mechanism governing the rearrangement process, an unambiguous assignment of the resonances of the η^3-C_7H_7 ring is necessary. The high-field signal, with a relative intensity of 1, can be easily assigned to the H(1)/C(1) sites. With the aid of this assignment, homo- (^{1}H–^{1}H) and heteronuclear (^{1}H–^{13}C) decoupling experiments led uniquely to the assignments appearing in Figures 1 and 2 and Table I. The assignment is in agreement with previous studies on η^3-C_7H_7 compounds and confirms the unusual chemical shifts of the ring hydrogen atoms, namely the high-field position of H(1) and the deshielding of the outer protons of the η^3-enylic unit, H(2), which is the reverse of the order normally found in η^3-allyl complexes. The relevant data are summarized in Table II. From the present study it is clear that the ^{13}C chemical shifts follow the same trend.

It has been argued that the anomalous chemical shifts of the H(1) and H(2) protons are due to the anisotropy effects of the uncomplexed diene portion of the seven-membered ring.[18] The reciprocal effect of the bound η^3-allyl part is cited as responsible for the downfield position of H(3) relative to that of H(4) in the free diene portion.[19] No doubt these factors are important, but perhaps equally important is the different nature of the ligand molecular orbitals that are potentially involved in the interactions between the metal and the η^3-allyl and the η^3-cycloheptatrienyl moieties, respectively. The relevant frontier molecular orbitals of the allyl and cycloheptatrienyl ligands are shown in Chart I. Although the

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(17) An attempt was made to corroborate the solid-state structure of **3a** by X-ray crystallography. However, disorder problems prevented satisfactory refinement of the structure. The η^3-bonding mode of the C_7H_7 ring and the *exo-fac* disposition of the ligands were established in the related (η^3-C_7H_7)Fe(CO)$_3$SnPhCl$_2$ (obtained from the reaction of **3a** with HCl in diethyl ether: Gittawong, S. Unpublished results). Details about the X-ray results can be obtained from V. W. Day, Department of Chemistry, University of Nebraska.

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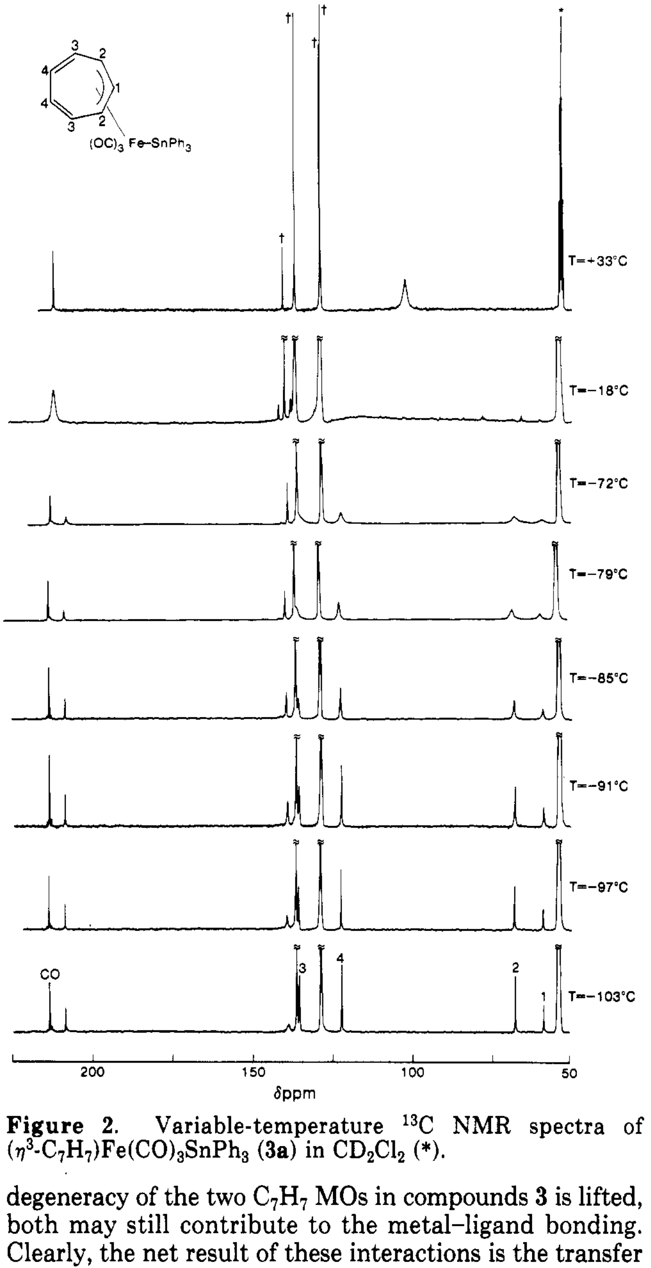

Figure 2. Variable-temperature ^{13}C NMR spectra of $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$ (**3a**) in CD_2Cl_2 (*).

degeneracy of the two C_7H_7 MOs in compounds **3** is lifted, both may still contribute to the metal–ligand bonding. Clearly, the net result of these interactions is the transfer of electron density to all three carbon atoms of the η^3-enyl portion, C(1) and C(2) of the seven-membered ring. On the other hand, the nodal properties of the unique π_2 MO of the allyl fragment is such that metal electrons are transferred to the end carbons C(2) only. In line with these arguments the ^{13}C chemical shifts of C(1) and C(2) in $(\eta^3\text{-}C_3H_5)Mn(CO)_4$, a molecule isoelectronic with **3**, are at 93.8 and 43.2 ppm, respectively,[24] some 35 ppm to the low-field side and 24 ppm to the high-field side of the corresponding resonances in **3a**.

With an unambiguous assignment of the NMR spectra at our disposal, the mechanism for the metal migration can now be elucidated. From Figures 1 and 2 it is evident that the resonances which are assigned to H(4) and C(4), the inner sites of the uncomplexed diene part of the seven-membered ring, collapse at a much slower rate than the remaining three signals. This immediately rules out a random shift of the $Fe(CO)_3SnPh_3$ fragment as a plausible mechanism. A delineation between the remaining distinct 1,2-, 1,3-, and 1,4-Fe shifts can be made by careful examination of the exchanges in environments produced by the

Scheme III

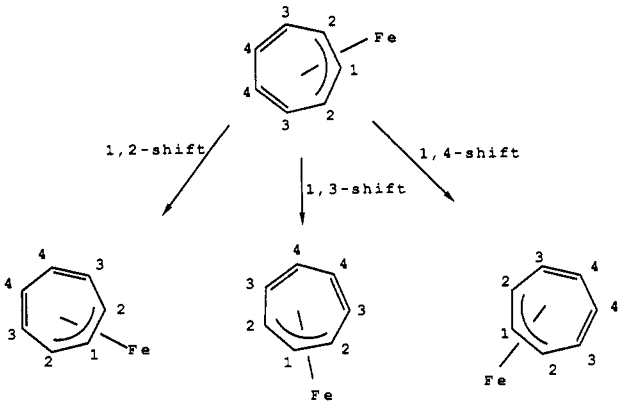

Table III. Rate Constants[a,b] for 1,2-Fe Migration (k_{12}) and for Carbonyl Scrambling (k_{CO}) in $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$ (3a)

T, °C	k_{12}, s^{-1}	k_{CO}, s^{-1}	T, °C	k_{12}, s^{-1}	k_{CO}, s^{-1}
−103	9.5		−72	305	27.0
−97	16.5		−60	1025	90.0
−91	33.0	3.5	−48		265
−85	67.5	6.5	−36		700
−79	150	13.5	−18		2650

[a] Rate constant is defined as the one-way rate by which the particular moiety (Fe or CO) leaves one site. [b] Activation parameters from Eyring plots are as follows (input uncertainties were ±10% for k and ±1.0 °C for T): $\Delta H^*_{12} = 31.8$ (1.0) kJ mol^{-1}, $\Delta S^*_{12} = -35$ (5) J mol^{-1} K^{-1}, $\Delta G^*_{12} = 40.6$ kJ mol^{-1} ($T_c = -20$ °C); $\Delta H^*_{CO} = 35.6$ (1.0) kJ mol^{-1}, $\Delta S^*_{CO} = -36$ (5) J mol^{-1} K^{-1}, $\Delta G^*_{CO} = 43.6$ kJ mol^{-1} ($T_c = -50$ °C).

different metal-shift processes. This is shown in Scheme III. It is clear from the scheme that the 1,2-Fe shift leaves one of the H(4)/C(4) sites unchanged, whereas the 1,3-Fe and 1,4-Fe shifts do not change the environment of one of the H(2)/C(2) and H(3)/C(3) sites, respectively. Since the resonances from which the nuclei leave faster will also broaden faster, the analysis shows that a sharper H(4)/C(4) resonance during the initial stages of line broadening is indicative of 1,2-Fe shift mechanism. It is evident that the experimental observations are thus compatible with a 1,2-Fe shift as the major rearrangement process in **3a**. The similar line broadening observed in the analogous lead complex indicates a 1,2-Fe shift in **3b** as well. These results are not surprising, since in all $\eta^3\text{-}C_7H_7$ complexes studied so far it has been established that 1,2-metal shifts are responsible for the dynamic behavior.[13]

The energetics of the rearrangement have been determined by visually matching computer-simulated NMR spectra, based on the 1,2-Fe shift mechanism, with those obtained experimentally. The rate data and the associated activation energies for compound **3a**, obtained from the variable-temperature ^{13}C NMR study (Figure 2), are listed in Table III. In general, the larger chemical shift differences and especially the absence of coupling between resonances in the ^{13}C NMR spectra render these spectra much more amenable to line-shape analysis and the determination of accurate activation parameters than the ^1H NMR spectra.[25,26]

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[25] For compound **3b** only the ^1H NMR spectra were simulated. Although the parameters so derived are expected to be less accurate, since no explicit account was taken of spin–spin coupling, the relative ordering of the ΔG^* values should be reliable. On this basis it can be concluded that **3b** ($\Delta G^*_{T_c} \approx 46$ kJ mol^{-1}, $T_c \approx -70$ °C) is somewhat less fluxional than **3a** ($\Delta G^*_{T_c} \approx 41$ kJ mol^{-1}, $T_c \approx -60$ °C). Note that for **3a** ΔG^* from the ^1H NMR data is in acceptable agreement with the value in Table III.

[26] Modern pulse methods have been supplanting classical line-shape analysis both as a mechanistic probe and for rate analysis.[27] The use of the ^{13}C nucleus is not of prime concern with these newer methods.

The low value of the activation energy for Fe migration in **3a** and **3b** is in line with the high fluxionality observed previously in related mononuclear complexes containing the η^3-C_7H_7 moiety.[13] Some relevant data are as follows: ($\Delta G^\ddagger$ kJ mol^{-1}): $(\eta^3\text{-}C_7H_7)Fe(\eta^5\text{-}C_5H_5)(CO)$ (**5**), ~55 < $(\eta^3\text{-}C_7H_7)Mo(\eta^5\text{-}C_5H_5)(CO)_2$ (**6**), ~40 = $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$ (**3a**), 41 < $(\eta^3\text{-}C_7H_7)Co(CO)_3$ (**4**), ~30. The breakdown of conjugation between the allyl and uncomplexed diene portions of the seven-membered ring, as reflected by the C–C distances and the dihedral angle between the two planes, was cited as a most important electronic factor modulating $\Delta G^\ddagger$ for metal migration.[28] In the absence of structural data, except for **6**, it is difficult to argue about the respective positions of the compounds in the above series. The very small $\Delta G^\ddagger$ value for **4** perhaps reflects its five-coordinate structure and absence of steric congestion. The importance of electronic and steric factors on fluxionality in compounds **3** is evidenced by a lowering of the coalescence temperature upon stepwise substitution of the Ph group by Cl in **3a**; in $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnCl_3$ the coalescence temperature is below −100 °C.[29]

Also shown in Table III are the rate data and activation energies for carbonyl scrambling in **3a**. Such processes are well documented in compounds containing the $M(CO)_3$ unit, and values of 35–50 kJ mol^{-1} for the free energy of activation are common.[30] The magnitude of $\Delta G^\ddagger$ varies with the nature of the metal and its coordination number. Typically, as the "six-coordinate" nature of the complex increases, so does $\Delta G^\ddagger$. For instance, in the related $(\eta^3\text{-allyl})Fe(CO)_3X$ complexes,[31] slow-exchange spectra are already observed at +10 °C. The carbonyl-exchange process in **3a** is therefore more facile than anticipated, and a possible reason for this could be sought in the metal migration, also featured in the molecule. Reference to Table III shows that, although the energetics for the two processes are similar, the differences in rates at specific temperatures are large, the carbonyl scrambling being some 10 times slower than metal migration. This leaves little doubt that the carbonyl exchange in **3a** is not coupled to the 1,2-Fe shifts around the ring. We shall comment fully on the implication of this concerning the intimate motion associated with metal migration in cycloheptatrienyl complexes in a future report on the fluxionality of the analogous osmium complex[32] $(\eta^3\text{-}C_7H_7)Os(CO)_3SnPh_3$.

Experimental Section

General Considerations. All manipulations were carried out under a static atmosphere of rigorously purified nitrogen or argon,[10a] with use of standard Schlenk techniques. All solvents were dried by refluxing under nitrogen with the appropriate drying agent and distilled just prior to use.

(1-4-η-Cycloheptatriene)tricarbonyliron, $(\eta^4\text{-}C_7H_8)Fe(CO)_3$, and potassium (1-3-$\eta$-cycloheptatrienyl)tricarbonylferrate(1−), K-$(\eta^3\text{-}C_7H_7)Fe(CO)_3$, were prepared by literature procedures.[6] Triphenyltin chloride from Alfa/Ventron Corp. and triphenyllead chloride from Strem Chemicals were used without further purification.

Infrared spectra were obtained with a Perkin-Elmer Model 337 grating spectrometer and recorded in expanded form on a Hewlet-Packard 7127A recorder. The spectra were measured in matched NaCl or KBr cells and were calibrated with gaseous carbon monoxide. NMR spectra were obtained on Varian HA-100 (^{1}H) and Bruker HFX-90 and WP-400 (^{13}C) spectrometers. Chemical shifts are reported in units of parts per million (ppm), δ, from tetramethylsilane (TMS) by application of the accepted shifts of the internal solvent resonances. Mass spectra were taken with an AEI MS-12 spectrometer operating at 70 or 16 eV. The samples were introduced into the ion source by using the direct inlet technique at a temperature just sufficient to record the data. Field ionization mass spectra were obtained on an AEI MS-9 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of this department or by the Analytische Laboratorien, Engelskirchen, West Germany.

Synthesis of $(\eta^3\text{-}C_7H_7)Fe(CO)_3SnPh_3$ (3a). A solution of $K(C_7H_7)Fe(CO)_3$ ([K]1) (35.00 mmol) in 130 mL of THF was added dropwise, at room temperature, over 3 h to a magnetically stirred solution of Ph_3SnCl (13.46 g, 35.00 mmol) in 100 mL of THF. After the addition was completed, the red reaction mixture was stirred for an additional 2 h and inverse-filtered. Solvent was removed from the dark red solution in vacuo, and the resulting sticky residue was dried in vacuo overnight. Trituration with pentane (2 × 25 mL) and removal of the supernatant liquid via inverse filtration gave **3a** as a fine orange-red powder (14.56 g, 72%). The material so obtained is sufficiently pure for further reactions. Crystallization from saturated pentane solution at −20 °C gave analytically pure, red crystals of **3a** melting at 122–123 °C. Anal. Calcd for $C_{28}H_{22}O_3SnFe$: C, 57.93; H, 3.79; O, 8.28. Found: C, 57.96; H, 3.84; O, 8.20. Mass spectrum (70 eV, 130 °C; *m/e* (relative intensity)): 582 (M^+, 0.1), 554 ($M^+ - CO$, 0.5), 526 ($M^+ - 2CO$, 4.1), 498 ($M^+ - 3CO$, 33.4), 351 ($SnPh_3^+$, 15.6), 330 ($FeSnPh_2^+$, 12.6) 224 ($C_7H_7FePh^+$, 100.0). The parent peak was confirmed by field-desorption mass spectrometry. Infrared spectrum (pentane, room temperature, cm^{-1}): ν_{CO} 2039 vs, 1987 s, 1958 vs.

Various amounts of $Ph_3SnOSnPh_3$ were obtained in this reaction. The purpose of the trituration with pentane is to remove this byproduct. If this is not sufficient, **3a** can be easily freed from this impurity by fractional crystallization. Attempts to purify **3a** by chromatography on Florisil (hexane) or alumina II (hexane or benzene) led to decomposition. **3a** could be chromatographed on a short column of silica gel with benzene as eluant, but with no improvement of purity over fractional crystallization.

Synthesis of $(\eta^3\text{-}C_7H_7)Fe(CO)_3PbPh_3$ (3b). The reaction was carried out as described for **3a** with use of 7.41 mmol of [K]1 in 40 mL of THF and 3.20 g (6.78 mmol) of triphenyllead chloride in 80 mL of THF. At the completion of the reaction the solvent was removed in vacuo, the residue extracted with 50 mL of toluene, and the red solution inverse-filtered. The volume of the solution was reduced to ca. 20 mL in vacuo, 50 mL of hexane added, and the mixture filtered over Celite. Cooling the solution to −15 °C gave **3b** as dark red crystals (1.94 g, 43%). Analytical samples were obtained by recrystallization from a toluene–hexane (1:2) solvent mixture. Anal. Calcd for $C_{28}H_{22}O_3PbFe$: C, 50.22; H, 3.29; O, 7.17. Found: C, 49.94; H, 3.35; O, 7.40. Mass spectrum (70 eV, 125 °C; *m/e* (relative intensity)): 439 ($PbPh_3^+$, 4.3), 224 ($C_7H_7FePh^+$, 28.2), 208 (Pb^+, 1.7). Infrared spectrum (hexane, room temperature, cm^{-1}); ν_{CO} 2034 vs, 1984 s, 1958 vs.

Solution Dynamics of Compounds 3a and 3b. Samples for variable-temperature NMR studies were sealed under vacuum following repeated freeze–pump–thaw cycles. Several spectra (see Table III) at 6–12 °C intervals were obtained in the exchange region. Temperature measurements were made with either a copper/constantan thermocouple (^{1}H NMR spectroscopy) or a Bruker temperature control unit, Model B-5T 100/700, and are believed to be accurate to ±1 °C. Exchange rates were determined by visual comparison of the observed and computer-simulated (DNMR4) by G. Binsch, QCPE, Bloomington, IN) spectra.[34] Rate

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constants with an estimated 10% error and temperatures (±1 °C) could be correlated at a confidence level greater than 99% with use of the Eyring and Arrhenius equations.

For the carbonyl group scrambling process, the free energy of activation at the coalescence temperature, $\Delta G^{\ddagger}_{T_c}$, was also calculated by using the approximate expressions applicable to the two-site exchange problem.[35]

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Registry No. [K]1, 75663-01-3; **3a**, 124266-09-7; **3b**, 124243-10-3; Ph$_3$SnCl, 639-58-7; Ph$_3$PbCl, 1153-06-6.

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η^1- and η^2-Alkaneimidoyl Complexes of Nickel: Synthesis and Properties

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The insertion of CNBu^t into the Ni–C bond of the alkyls *trans*-Ni(R)Cl(PMe$_3$)$_2$ gives the η^1-alkaneimidoyls Ni[η^1-C(NBu^t)R]Cl(PMe$_3$)$_2$ (R = CH$_3$ (**1**), CH$_2$CMe$_2$Ph (**2**)), but for R = CH$_2$SiMe$_3$ and CH$_2$CMe$_3$, both η^1 and η^2 species can be isolated, Ni[η^1-C(NBu^t)R]Cl(PMe$_3$)$_2$ (R = CH$_2$SiMe$_3$ (**3**), CH$_2$CMe$_3$ (**4**)), Ni[η^2-C(NBu^t)R]Cl(PMe$_3$) (R = CH$_2$SiMe$_3$ (**5**), CH$_2$CMe$_3$ (**6**)). Facile η^1–η^2 interconversions can be achieved; addition of PMe$_3$ to solutions of **5** or **6** produces **3** or **4**, respectively, while PMe$_3$ removal from the η^1 compounds affords the corresponding η^2-alkaneimidoyls. The analogous insertion of CNBu^t into the Ni–C bond of the alkyl-pyrrolyls Ni(R)(NC$_4$H$_2$X$_2$)(PMe$_3$)$_2$ affords only η^2-alkaneimidoyl structures, Ni[η^2-C(NBu^t)R](NC$_4$H$_2$X$_2$)(PMe$_3$) (X = H, R = Me (**7**); X = Me, R = Me (**8**), CH$_2$SiMe$_3$ (**9**), CH$_2$CMe$_3$ (**10**)). On the other hand, the 18-electron η^1-alkaneimidoyls CpNi[η^1-C(NBu^t)R]PMe$_3$ (R = Me (**11**), CH$_2$CMe$_2$Ph (**12**)) can be obtained by the reaction of NaCp with **1** and **2** respectively, while the interaction of **1** with NaS$_2$CNMe$_2$ yields Ni[η^1-C(NBu^t)Me](S$_2$CNMe$_2$)PMe$_3$ (**13**). The η^1-alkaneimidoyls also undergo facile protonation to the corresponding cationic aminocarbene complexes, e.g., [Ni(C(NHBu^t)Me)Cl(PMe$_3$)$_2$]Cl (**14a**). All the η^1-alkaneimidoyls display ν(C=N) in the range 1630–1590 cm^{-1}, while for the η^2-alkaneimidoyls a shorter and higher frequency range is observed (1730–1710 cm^{-1}). In the η^1-alkaneimidoyls, the nickel-bound carbon atom resonates at ca. 190–185 ppm (with the exception of the 18-electron complexes **11** and **12**, for which δ(Ni–*C*) $\simeq$ 177 ppm), while in the η^2-alkaneimidoyls this resonance appears at ca. 170 ppm.

The migratory insertion of isocyanides, CNR, into transition metal–carbon bonds is a commonly observed reaction that has received considerable attention in recent years, due in part to its similarity to the analogous, and technically more important, carbon monoxide insertion. Both η^1- and η^2-alkaneimidoyl functionalities[1] can in principle be obtained. The lanthanides, actinides, and the early transition metals (groups 3d to 5d) frequently yield η^2 structures,[2-4] possibly as a reflection of the high affinity that these elements exhibit toward nitrogen. Conversely, the softer later transition metals (groups 8d to 10d) provide mainly η^1 structures, and in fact there seems to be no fully characterized η^2-alkaneimidoyl (or acyl) complexes of the elements to the right of the iron triad.[1a] η^2-Alkaneimidoyl complexes of Fe and Ru and Co have been reported,[5] and bridging η^2-alkaneimidoyl structures have recently been ascertained,[6] but to our knowledge no mononuclear η^2-alkaneimidoyl complexes are presently known for the elements of the nickel triad. Furthermore, while the single and the multiple insertions of isocyanides into Pd–C and Pt–C bonds have been intensively studied,[7,8] information on the analogous nickel systems is more restricted.[9,10]

With the above considerations in mind and as a natural extension of our earlier work on the insertion of CO into nickel–carbon bonds,[11] we have undertaken an investiga-

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