bond lengths are equal at 2.494 Å. Since this is the first linear triiron complex no comparisons are possible; however, it is of interest that a predicted bond length of 2.708 Å has been published for a linear triiron cluster, albeit without bridging ligands.[24] The two almost planar α-diazo thioketone units complex on the same side of the linear triiron backbone, with a dihedral angle of 80°, forming a delightful butterfly configuration.

We are currently investigating the synthetic utility of the complexes discussed above, in particular the chemical properties of the various organic fragments liberated via decomplexation reactions.

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Supplementary Material Available: Observed and calculated structure factors for the iron carbonyl sulfur complex (8 pages). Ordering information is given on any current masthead page.

Methyl Effects on the Basicities of Cyclopentadienide and Indenide Ions and on the Chemistry of Their Transition-Metal Complexes

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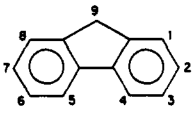
The replacement of cyclopentadiene ligands in transition-metal complexes by pentamethylcyclopentadiene ligands often leads to striking changes in their chemistry. In this paper we show that this is associated with a large increase in basicity of the pentamethylcyclopentadienide ion.

1,3-Cyclopentadiene (C_5H_5H) is the most acidic of the monocyclic hydrocarbons. Its conjugate base, cyclopentadienide ion ($C_5H_5^-$), is aromatic and forms strong multicentered bonds with most transition metals.[1] The cyclopentadienyl moieties in fluorene (**1**) and indene (**2**) exhibit similar properties, but fusion of benzene rings onto the cyclopentadiene C=C bonds causes a progressive decrease in acidity and modifies the ability of the conjugate bases to act as ligands.[2] Replacement of C_5H_5 ligands by $C_5(CH_3)_5$ ligands in metal complexes has been shown to give rise to compounds with significantly different chemistry.[1,3] The changes in properties of these complexes are believed to be due to increased electron density and donor strength of the permethylated ligand ring[4] and perhaps, in certain instances, to steric protection of the metal by the methyl groups.[1,3,5,6] For example, the shifts to lower frequencies of the carbonyl stretches of $Rh(\eta^5\text{-}C_5H_5)(CO)_2$ from 2051 and 1987 cm^{-1} to 2020 and 1965 cm^{-1} for $Rh[\eta^5\text{-}C_5(CH_3)_5](CO)_2$ indicate that Rh is more electron rich in the pentamethylcyclopentadienyl compound due to the increased electron-donor strength of the permethylated ligand.[6] A larger steric effect for the $C_5(CH_3)_5$ ligand is suggested by examples such as the formation of $U[\eta^5\text{-}C_5(CH_3)_5][N(C_2H_5)_2]_3$ from the reaction of $C_5(CH_3)_5H$ (**3**) with $U[N(C_2H_5)_4]$ under conditions where $U(\eta^5\text{-}C_5H_5)_2[N(C_2H_5)_2]_2$ was formed from C_5H_5H and $U[N(C_2H_5)_4]$.[5] We now wish to report results of a study of the acidities of some methyl-substituted cyclopentadienes, indenes, and fluorenes, which provide new insights into methyl effects in these hydrocarbons and their conjugate bases (Table I).



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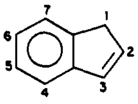

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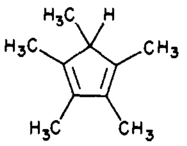

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Table I. Comparison of the Effect of Methyl Substitution on the Equilibrium Acidities of Cyclopentadiene, Indene, and Fluorene in Me_2SO Solution at 25 °C

hydrocarbon	pK_a[a]	ΔpK_a[g]
1,3-cyclopentadiene (C_5H_5H)	18.0[b]	(0.0)
1,2,3,4,5-pentamethylcyclopentadiene ($C_5(CH_3)_5H$)	26.1	7.8
indene	20.1[c]	(0.0)
2-methylindene	21.8	1.7[h]
3-methylindene	22.5	2.4[h]
1,2,3,4,5,6,7-heptamethylindene ($C_9(CH_3)_7H$)	27.4	7.0
fluorene	22.6[d]	(0.0)
9-methylfluorene	22.3[d]	−0.6
2-methylfluorene	23.1[e]	0.5
3-methylfluorene	23.4[f]	0.8

[a] pK_a values were determined by the method previously described.[7] [b] Reference 8. [c] Reference 9. [d] Reference 7. [e] Reference 10. [f] Branca, J. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1977. [g] Statistically corrected for the number of protons at the acidic site. [h] Measurements in Me_2SO/H_2O give ΔpK_a values for 2- and 3-methylindenes of 1.0 and 1.3, respectively.[11]

Rapid perusal of Table I shows that methyl substitution at the 9-position of fluorene (**1**) is uniquely acid strengthening. This effect is believed to be caused by hyperconjugative stabilization in the delocalized anion accompanying the change in hybridization at the acidic site from sp^3 to sp^2 upon deprotonation.[10] A similar acid-strengthening hyperconjugative effect is expected in the indenide and cyclopentadienide ions if a methyl substituent is present at the acidic site in their conjugate acids. Further examination of Table I shows that 2-methyl- and 3-methylindene are 1.7 and 2.4 pK_a units less acidic than indene, respectively, and that 2-methyl- and 3-methylfluorene are 0.5 and 0.8 pK_a units less acidic than fluorene, respectively. These acid-weakening effects, which result from methyl substitution for hydrogen at an sp^2 carbon atom, are believed to be due in part to a greater hyperconjugative methyl stabilizing effect in the undissociated acid than in its conjugate base and in part to steric inhibition of solvation in the ion.[10] Variable Electronegativity SCF calculations predict a larger concentration of charge at the 3- than at the 2-position in both the indenide and fluorenide ions.[12] Therefore, the change in solvation due to the steric effect of methyl should be of greater magnitude and result in a greater acid-weakening effect when methyl is substituted for hydrogen at the 3-position of fluorene (**1**) and indene (**2**), rather than at the 2 position, as observed.

The acid-weakening effect of the five methyl groups in 1,2,3,4,5-pentamethylcyclopentadiene is 7.8 pK_a units (Table I). For each of the four methyl groups attached to the C=C bonds in the diene, the effect amounts to about 2 pK_a units per methyl group. (The methyl group attached to the acidic site is expected to have an *acid-strengthening* effect of about 0.6 pK_a unit by analogy with that found in 9-methylfluorene.) The seven methyl

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(1) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287–297. Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 119–133.

(2) King, R. B.; Efraty, A. *J. Organomet. Chem.* **1970**, *23*, 527–533.

(3) (a) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219–1238. (b) Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1–5.

(4) Calabro, D. C.; Hubbard, J. L.; Blevins, C. H.; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839–6846.

(5) Fagan, P. J.; Manriquez, J. M.; Mantu, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.

(6) Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372–376.

(7) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006–7014.

(8) Bordwell, F. G.; Drucker, G. E.; Fried, H. E. *J. Org. Chem.* **1981**, *46*, 632–635.

(9) Bordwell, F. G.; Drucker, G. E. *J. Org. Chem.* **1980**, *45*, 3325–3328.

(10) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3095–3101.

(11) Goutines, G.; Mathieu, A. *Analusis* **1973**, *2*, 584–589.

(12) Vos, H. W.; MacLean, C.; Velthorst, N. H. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72* (1), 63–75.

0002-7863/83/1505-6188$01.50/0

groups in 1,2,3,4,5,6,7-heptamethylindene, $C_9(CH_3)_7H$, also have a large cumulative acid-weakening effect (7.0 pK_a units). In both $C_5(CH_3)_5H$ and $C_9(CH_3)_7H$ the major acid-weakening effects are believed to be due to methyl hyperconjugative stabilization in the undissociated acids and methyl steric inhibition of solvation in the anions.

The acidity data revealing a large hyperconjugative methyl effect in $C_5(CH_3)_5^-$ ions are consistent with the chemistry found in the cyclopentadienyl- and pentamethylcyclopentadienylmetal complexes. The large, additive methyl hyperconjugative effect found in $C_5(CH_3)_5H$ must also be present in $C_5(CH_3)_5$ metal complexes. This hyperconjugative effect is the source of the increased electron-donor strength of $C_5(CH_3)_5$ ligands, relative to C_5H_5 ligands. The increased donor strength of $C_5(CH_3)_5$ ligands causes an increase in the electron density in $C_5(CH_3)_5$ metal complexes, relative to C_5H_5 metal complexes. For example, as the number of CH_3 groups in polymethylated ferrocenes increases, the electron density on the metal and the tendency to undergo spontaneous oxidation in air increases.[13] In another study, when $Rh[\eta^5\text{-}X](CO)_2$ was allowed to react with $n\text{-}Bu_3P$, the rate was about 100 times slower for $X = C_5(CH_3)_5$, compared to $X = C_5H_5$. This rate retardation was ascribed in part to the increased electron density on Rh in the pentamethylcyclopentadienylmetal complex. However, part of this retardation is believed to have a steric origin since $(n\text{-}BuO)_3P$ reacts more rapidly than $n\text{-}Bu_3P$ despite its lower basicity.[6] In contrast, in a somewhat related study, we have found that in S_N2 reactions of $C_5(CH_3)_5^-$ and $C_5H_5^-$ ions with several alkyl halides in Me_2SO solution, the methyl groups cause little or no steric hindrance to the approach of the electrophile.[14] With the aid of a linear Brønsted plot,[15] rate comparisons can be made at the same anion basicity, effectively eliminating any electron-density differences in $C_5H_5^-$ and $C_5(CH_3)_5^-$ ions.

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(13) Nesmeyanov, A. N.; Materikova, R. B.; Lyatifov, I. R.; Kurbanov, T. Kh.; Kochetkova, N. S. *J. Organomet. Chem.* **1978**, *145*, 241-243.

(14) Bausch, M. J., unpublished results.

(15) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1980**, *45*, 3314-3320.

Long-Range Proton-Nitrogen Spin Coupling Constants via Polarization-Enhanced Two-Dimensional ^{15}N NMR

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Most values of spin-spin coupling constants between ^{15}N and ^1H nuclei separated by two or more intervening bonds have been obtained from ^1H NMR spectra of ^{15}N-enriched compounds.[2] Such a strategy for determining long-range J_{NH} values is costly and may be synthetically impractical. Moreover there is no guarantee that ^1H NMR of enriched compounds will provide access to J_{NH} since the line widths of the pertinent proton multiplets and homonuclear couplings to other protons may obscure the coupling to ^{15}N. On the other hand, the direct evaluation and assignment of long-range J_{NH} from proton-coupled ^{15}N spectra is usually impractical because of the complexity of the spectra. In this paper we demonstrate a new two-dimensional Fourier-transform NMR method for observing and assigning $^{15}N-^1H$ coupling constants selectively. The technique substantially reduces the requirement for ^{15}N enrichment and at the same time eliminates the obfuscation created by line broadening and/or extraneous scalar couplings.

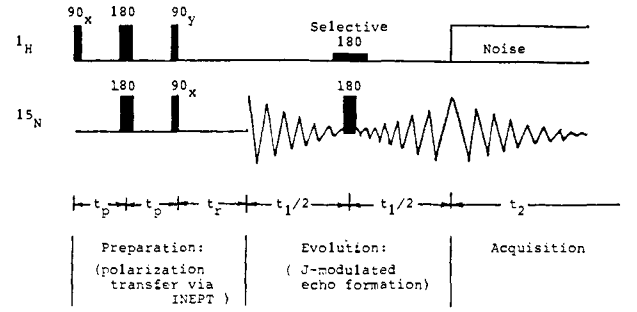

Figure 1. INEPT-enhanced, selective 2D-*J* pulse sequence. The pulses and delays in the preparative stage are standard for the refocused INEPT experiment[4b] with $t_p = (4J_{NH})^{-1}$ and $t_r = (2J_{NH})^{-1}$ for NH or $t_r = (4J_{NH})^{-1}$ for NH_2 and NH_3 spin systems. Here J_{NH} is the coupling between ^{15}N and the proton(s) used to effect the polarization transfer. In the evolution period, $t_1/2$ is incremented in 32 regular steps, each typically of 40-ms duration to give a spectral width of 12.5 Hz in the F_1 dimension. The selective 180° (^1H) pulse is 25 ms ($\gamma_H B_2 = 20$ Hz) and is applied at the center of the proton line of interest. If the proton of interest is coupled to nonequivalent ^{15}N spins, nonselective 180° (^1H and ^{15}N) pulses should be applied at the midpoint of the refocusing delay, t_r, to eliminate phase shifts introduced by the chemically shifted ^{15}N resonances.

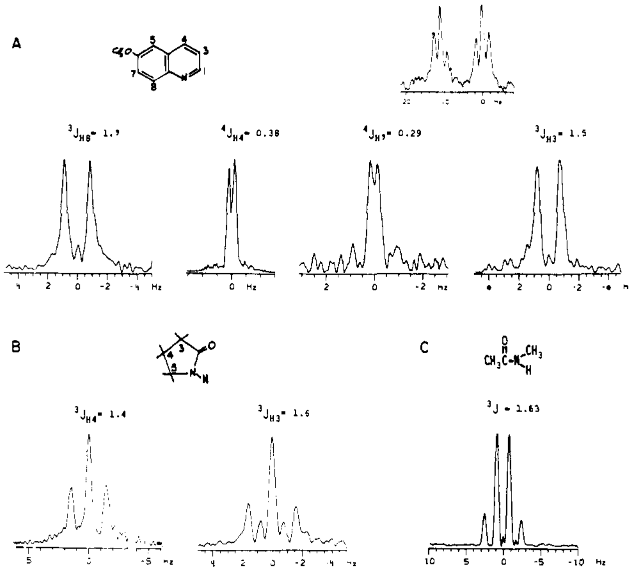

Figure 2. Long-range, natural-abundance $^{15}N-^1H$ coupling constants via INEPT-enhanced, selective 2D-*J* spectroscopy. (A) 6-Methoxyquinoline (2 M in chloroform-d_1), the chemical shifts of the selectively flipped protons were from left to right at 6.79, 7.42, 6.97, and 7.70 ppm from Me_4Si. (B) 2-Pyrrolidinone (2 M in H_2O), the chemical shifts of the $C(3)H_2$ and $C(4)H_2$ groups were at 2.92 and 2.71 ppm, respectively. (C) *N*-Methylacetamide (2 M in H_2O), the chemical shift of the acetyl CH_3 was at 2.55 ppm. (insert) 1-D, ^1H-coupled INEPT spectrum of (A). The coupling constants are accurate to ±0.05 Hz. The experiments were performed at 30.4 MHz by using a Nicolet-300 (wide bore) spectrometer equipped with a 293B pulse programer. Temperature was 25 °C.

The experiment is similar to the one performed in selective 2D-heteronuclear *J* spectroscopy[3] but with a important modification introduced in the preparative stage of the experiment (Figure 1). Namely, a *polarization-transfer* pulse sequence such as INEPT[4] is used to generate transverse ^{15}N magnetization, which is enhanced by a factor of $\gamma_{^1H}/\gamma_{^{15}N} = 10$ compared with that

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(1) (a) The Rockefeller University. (b) Adelphi University.

(2) See: (a) Webb, G. A. *Annu. Rep. NMR Spectrosc.* **1981**, *11b*, 1. (b) Martin, G. J., Martin, M. L.; Gouesnard, J. P. *NMR: Basic Princ. Prog.* **1981**, *18*, 1, for a recent review and tabulations of $^{15}N-^1H$ coupling constants.

(3) Bax, A.; Freeman, R. *J. Am. Chem. Soc.* **1982**, *104*, 1099-1100.

(4) (a) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760-762. (b) Morris, G. A. *Ibid.* **1980**, *102*, 428-429.