is reduced because of the positive charge resulting from coordination of ferrous ion.

Previously direct alkylation of benzene, naphthalene, and phenanthrene by lithium reagents was reported to occur very slowly even at 165°.[10] In contrast, the critical C–C bond-forming step in our sequence occurs rapidly near room temperature despite an electron-rich ring with potential problems of steric hindrance and without competing hydrogen–metal exchange. Direct substitution of aryl or vinyl groups for hydrogen on benzene rings by aryllithium or vinyllithium compounds has not been described.

Although addition of RLi compounds to other transition-metal complexes such as cobalticinium ion has been reported, it is the bisarene 2+ cations that offer a unique opportunity for organic syntheses because of their desirable combination of 2+ charge, arene complexation, and symmetry.

A broad investigation of the extensions of this chemistry is in progress.

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(10) J. A. Dixon and D. H. Fishman, *J. Amer. Chem. Soc.*, **85**, 1356 (1963).

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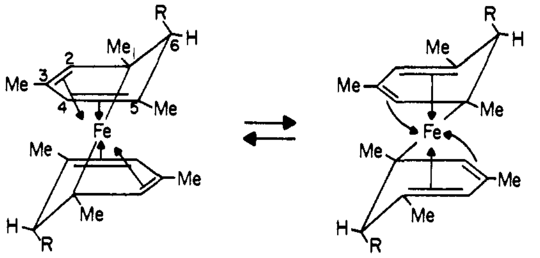
New Fluxional Organometallic Compounds. Pseudoferrocene Systems[1]

Sir:

In the preceding communication[2] we reported the synthesis of bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II) and bis(6-phenyl-1,3,5-trimethylcyclohexadienyl)iron(II) from the reactions of *tert*-butyllithium and phenyllithium with bismesityleneiron(II) hexafluorophosphate. We now wish to describe their properties in greater detail.

For each compound the nmr spectrum is temperature dependent. In the case of the diphenyl adduct the limiting high-temperature spectrum (Figure 1) in CS_2 is attained near +2° and consists of four sharp singlets and two aryl multiplets. The limiting low-temperature spectrum is reached near −75° and consists of six sharp singlets and two aryl multiplets. We believe these spectra are indicative of fluxional behavior[3] (eq 1).



(1)

Because of the simplicity of the spectra, peak assignments can be made easily (Table I). The peaks at τ 9.08 and 7.98 coalesce at about −42° to a peak which appears at τ 8.53 in the high-temperature spectrum and the peaks at τ 6.79 and 6.15 coalesce at about −48° to a peak which appears at τ 6.47 in the high-temperature spectrum.

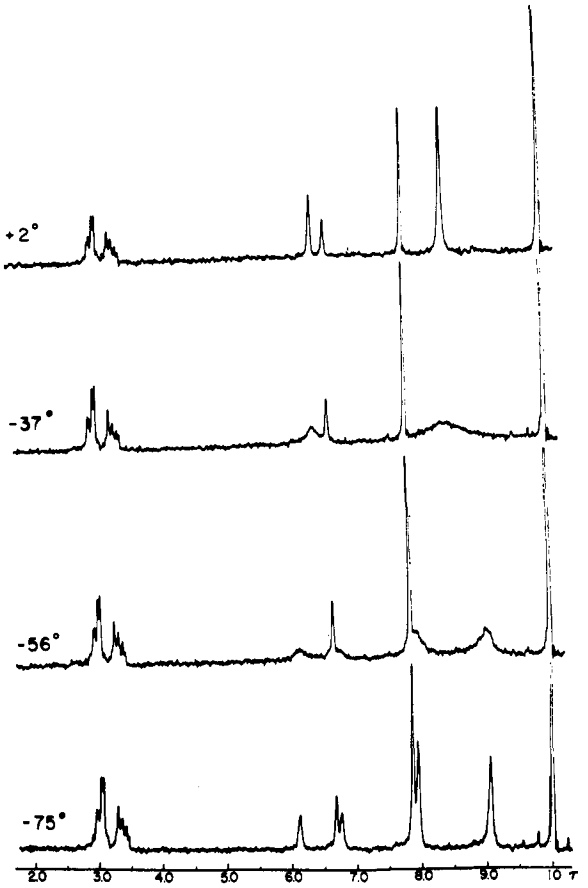


Figure 1. The 60-MHz ^1H nmr spectrum of bis(6-phenyl-1,3,5-trimethylcyclohexadienyl)iron(II) in CS_2 measured relative to TMS.

Table I. Nmr Spectrum of Bis(6-phenyl-1,3,5-trimethylcyclohexadienyl)iron(II) in Carbon Disulfide at −75°

Position (τ)	Rel area	Assignment
~3.05 (multiplet)	3	6-Phenyl (meta and para)
~3.35 (multiplet)	2	6-Phenyl (ortho)
6.15	1	4-H
6.71	1	Endo 6-H
6.79	1	2-H
7.88	3	3-Methyl
7.98	3	5-Methyl
9.08	3	1-Methyl

The limiting low-temperature spectrum of the di-*tert*-butyl adduct in CS_2 is attained near −38° and consists of seven sharp singlets. The peak assignments are given in Table II. The peaks at τ 6.35 and 6.95 coalesce at about 22° while those at τ 7.86 and 8.95 coalesce at about 37°.

The limiting high-temperature spectrum is attained near +100° (measured in deuteriotoluene) and consists of five sharp singlets.

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(1) Presented in part at the 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, Abstract ORGN-77.

(2) J. F. Helling and D. M. Braitsch, *J. Amer. Chem. Soc.*, **92**, 7207 (1970).

(3) A review of fluxional behavior is given by F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

Table II. Nmr Spectrum of Bis(6-*tert*-butyl-1,3,5-trimethylcyclohexadienyl)iron(II) in Carbon Disulfide at −38°

Position (τ)	Rel area	Assignment
6.35	1	2-H
6.95	1	4-H
7.86	3	5-Methyl
7.98	1	Endo 6-H
8.02	3	3-Methyl
8.95	3	1-Methyl
9.56	9	*exo*-6-*tert*-Butyl

The representations given in eq 1 differ from resonance structures in that they are intended to imply a rocking of the rings with respect to the iron atom so that changes in the relative positions of nuclei occur. At high temperatures delocalized structures would better represent the molecules. The failure of the peaks assigned to the 3-methyl protons to shift as the temperature is changed suggests that an alternative limiting structure with σ bonding from position 3 to iron is insignificant.

The spectra allow either free rotation with respect to the ring–Fe–ring axis at the temperature of measurement or lack of rotation, but they do not permit interpretation on the basis of partially restricted rotation. If that were the case, the peaks assigned to the 3-methyl protons and the 6 proton would also be expected to separate to two peaks each. Furthermore, the rotamers would be unequal in energy, the populations would be unequal, and the areas of the divided peaks should be unequal.

The elemental analyses and molecular weights (mass spectra) are consistent with the assigned structures. *Anal.* Calcd for the di-*tert*-butyl adduct, $C_{26}H_{42}Fe$: C, 76.08; H, 10.31; Fe, 13.61; mol wt, 410. Found: C, 75.52; H, 10.10; Fe, 13.6; mol wt, 410. *Anal.* Calcd for the diphenyl adduct, $C_{30}H_{34}Fe$: C, 79.99; H, 7.61; Fe, 12.40; mol wt, 450. Found: C, 79.86; H, 7.75, Fe, 11.29; mol wt, 450. Both complexes are soluble in hydrocarbons and may be chromatographed on alumina. The di-*tert*-butyl adduct, mp 203–204°, may be sublimed *in vacuo* and is thermally stable to about 250°. The diphenyl adduct undergoes thermal decomposition just above its melting range, 102–105°. Both are stable to air and water although the diphenyl compound deteriorates during long storage. The absence of infrared absorption in the region 2700–2800 cm^{-1} of the kind which has been attributed to exo C–H stretching in certain related complexes[4] supports the assignment of exo positions to the *tert*-butyl and phenyl groups.

In view of the marked spectral changes which have been observed for these compounds it is somewhat surprising that neither of the corresponding monoadduct hexafluorophosphates described in the preceding paper exhibits any temperature dependence of the nmr spectrum in deuterioacetone. To the best of our knowledge such temperature dependence has not been described for other cyclohexadienyl complexes of transition metals either.

At and above the temperature at which the limiting high-temperature spectrum is found, one may speculate as to the possibility of cyclic delocalization of π-electron density, a situation which would allow the interpretation that these are complexes of homocyclopentadienide anions, that they might be described as pseudoferrocene systems, and that they may exhibit some chemical properties like those of ferrocene.

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[4] P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967).

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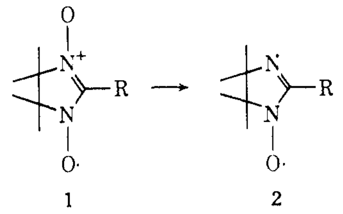
Stable Free Radicals. IX.[1] Use of Halogen Nuclear Quadrupole Coupling in Electron Spin Resonance Spectra of Imino Nitroxides for Determination of Solvent Effects on Rotational Correlation Times

Sir:

Hyperfine coupling to bromine and iodine in the esr spectra of organic radicals is rarely observed. The only previous examples include some iminoxyl σ radicals[2] and the bromo nitronyl nitroxide **1** (R = Br).[3] The difficulty in observing coupling is due to the large nuclear quadrupole moments of these elements. Fluctuations in the electric-field gradients at the halogen nuclei due to molecular tumbling produce nuclear spin relaxation that is fast relative to the hyperfine splitting and leads to averaging of the magnetic field contributions of the nuclear spin states. Where coupling is observed the line widths are predicted to be proportional to the rotational correlation time τ_c.[4] We describe here an empirical correlation of the effect of solvent on rotational correlation times employing esr spectra of new halo radicals.

The bromo and iodo nitronyl nitroxides **1**, R = Br and I, react with sodium nitrite in dimethylformamide to give the imino nitroxides, 2-bromo- and 2-iodo-4,4,5,5-tetramethylimidazoline-1-oxyl (**2**, R = Br and I). These products are stable orange radicals, the chemistry and characterization of which will be described elsewhere.[1] They display coupling to both nitrogens which has a small solvent dependence:[1] **2**, R = Br (C_6H_{14}), $a_{N(1)}$ 8.65 G, $a_{N(2)}$ 4.25 G; **2**, R = I (C_6H_{14}), $a_{N(1)}$ 8.60 G, $a_{N(2)}$ 4.20 G. In addition, coupling to bromine in **2**, R = Br, gives rise to four lines, a_{Br} 1.9 G (solvent independent), expected of nuclei with $I = {}^3/_2$. Resolution of separate lines due to ^{79}Br and ^{81}Br which have similar gyromagnetic moments was



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[1] For paper VIII see E. F. Ullman, L. Call, and J. Osiecki, *J. Org. Chem.*, **35**, 3623 (1970).

[2] (a) W. M. Fox and W. A. Waters, *J. Chem. Soc.*, 4628 (1965); (b) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967); (c) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc. B*, 981 (1967); *ibid.*, 123 (1968).

[3] D. G. B. Boocock and E. F. Ullman, *J. Amer. Chem. Soc.*, **90**, 6873 (1968).

[4] J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).