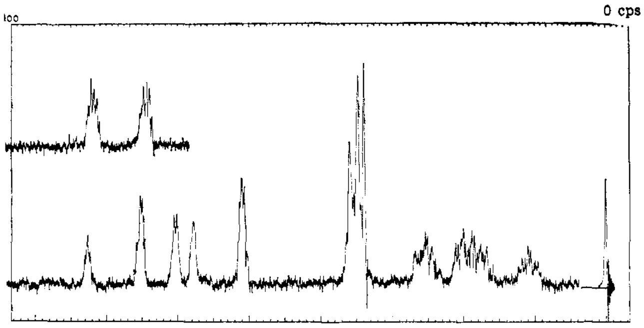

Figure 1. Nmr spectrum of II in carbon tetrachloride (*ca.* 10%) with tetramethylsilane as an internal reference using a Varian A-60 spectrometer. The two scans are 100-cps full scale: the lower is offset 240 cps; the upper, which shows the absorption due to H^1, is offset 900 cps.

H^6, H^7 (area 2) are complex multiplets. That the molecule contains a *trans* double bond with one bromine on it can be deduced from (a) the apparent doublet for H^1 [10] and (b) from the coupling constant J_{12}. The system which includes H^1, H^2, H^3 in II is that found in substituted butadienes. The characteristic range of values for J_{23} (across the formal single bond) in dienes that are in *s-trans* planar conformations is 10.3–12.5 cps.[11] On the other hand, the typical range for sp^2–sp^2 proton coupling across the formal single bond in *cis* dienes is 5–7 cps.[12] The observed value for J_{12} of 9.4 cps corresponds best to a *trans* arrangement for H^1 and H^2 in II.

The most striking feature of the nmr spectrum of II is the chemical shift of the one hydrogen assigned H^1. This hydrogen exhibits an absorption at τ *−6.4* (985 cps downfield from that of tetramethylsilane). Previously we predicted[1] that I was interconverting between two equivalent planar conformers and that the chemical shift of the inner hydrogen of I would be observed at *ca.* τ −6.4[13] for the frozen conformer. In the case of II no such conformational interconversion can occur, since the bromine atom is too large to fit through the ring and thus the nmr spectrum of II is that of a single conformer.

We conclude from these data that II is planar or nearly so and that the value of the chemical shift for H^1 is due to an induced paramagnetic ring current of a $4n$ π-electron cyclic system. It should also be pointed out that local anisotropic effects of the two triple bonds in close proximity to this inner hydrogen would, if operative, cause an upfield shift.

To our knowledge, no hydrogen bonded to carbon in hydrocarbons or simple derivatives has been observed at such a *low-field* value. The only other kind of shift of similar magnitude previously noted is in the $4n + 2$ π-electron annulenes. The largest *upfield* shift among these is found for the inner hydrogens of 1,8-bisdehydro[14]annulene at τ 15.5,[14] a shift of *ca.* 11 ppm compared to cyclic monoolefins, τ 4.4. The same comparison made with the value of the chemical shift for H^1 in II also gives a shift of *ca.* 11 ppm, but in the *opposite* direction, downfield (a difference of *ca. 22* ppm for the inner hydrogens of these two kinds of conjugated cyclic systems).[15]

Such dramatic changes in chemical shifts for corresponding inner hydrogens of $4n + 2$ π-electron systems are compelling. The argument that an induced diamagnetic ring current be a criterion for aromaticity now seems strengthened by this and other demonstrations[4] of induced paramagnetic ring currents in cyclic $4n$ π-electron systems.

Acknowledgment. The authors are grateful to Mr. R. E. Rhodes for obtaining the mass spectrometric measurements and to the National Science Foundation (Grant GP-6612) for partial support of this work.

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[10] If H^1 were flanked by two adjacent hydrogens, its absorption pattern would be more complex, ranging from perhaps a triplet to an ABC pattern with additional long-range couplings.

[11] A. A. Bothner-By, *Advan. Magnetic Resonance*, **1**, 195 (1965): butadiene, J_{23} = 10.41 cps; 1,4-dichlorobutadienes, J_{23} = 10.84 ± 0.5 cps.

[12] *E.g.*, 1,3-cyclohexadiene, J_{23} = 5.14 cps; see footnote 8 in ref 7.

[13] This predicted value (τ −6.4) cited in ref 1 is in error. The corrected value is τ − 7.3. The arguments made remain unchanged.

[14] F. Sondheimer, Y. Gaoni, L. M. Jackman, N. A. Bailey, and R. Mason, *J. Am. Chem. Soc.*, **84**, 4595 (1962).

[15] Consistent with an induced paramagnetic ring current, the outer hydrogens of II are shifted upfield from the olefinic value to τ 4.6–5.7.

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Protonation of Norbornadienetricarbonyliron

Sir:

Norbornadienetricarbonyliron (**1**), in contrast to norbornadiene itself, can be recovered unchanged from sulfuric acid solution.[1] We have undertaken an nmr study of **1** in strongly acidic media and find that, unlike tricarbonyliron derivatives of conjugated dienes,[2] it undergoes protonation on iron.

The nmr spectrum of **1** in liquid sulfur dioxide is simple, reflecting its apparent C_{2v} symmetry. The hydrogens at C_7 appear as a triplet at τ 8.75 while the olefinic and bridgehead protons appear as an overlapping triplet (τ 6.85)[3] and multiplet (τ 6.65), respectively. Addition of fluorosulfonic acid to the deep red solution of **1** in sulfur dioxide at −70° changes the color to pale yellow-green and gives the nmr spectrum shown in Figure 1. A triplet (1 H, J = 13 Hz) has appeared at τ 17.3 while below TMS all signals have been shifted to lower fields, and the symmetry of the spectrum has been reduced considerably. The two triplets separated by 13 Hz are caused by two equivalent hydrogens coupled by 13 Hz to the high-field hydrogen. Experiments at 60 and 100 Mc show that this splitting (in hertz) is field independent and therefore caused by spin–spin coupling. The spectrum of **1** in D_2SO_4 is the same as that in FSO_3H–SO_2 except that the high-field proton is missing, and the two triplets have collapsed to a single multiplet. Compound **1** can be recovered unchanged from these strongly acidic solutions by pouring into ice water and subsequent ether extraction. Nmr integration of recovered **1** establishes that no incorporation of deuterium into the norbornadiene ligand occurred in the D_2SO_4 solution.

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[1] R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

[2] G. F. Emerson and R. Pettit, *ibid.*, **84**, 4591 (1962).

[3] Attachment of a transition metal to a double bond causes a large upfield shift of the olefinic hydrogens: M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).

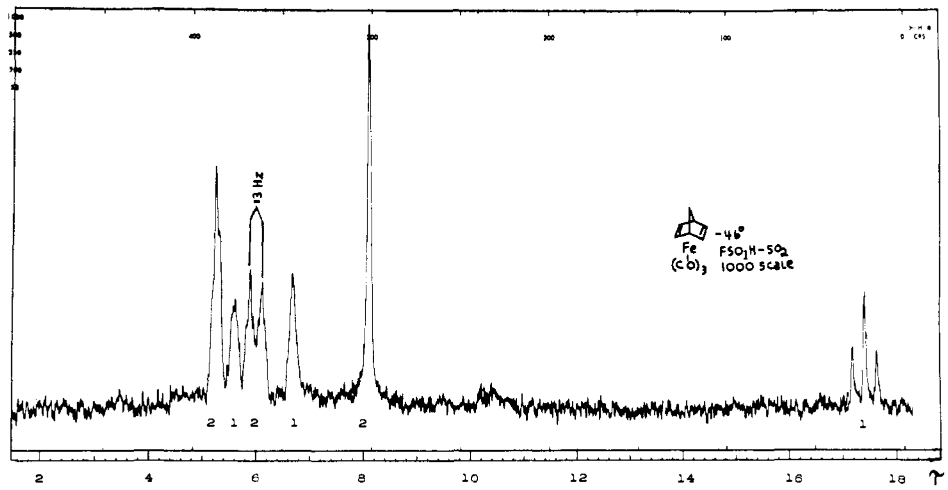
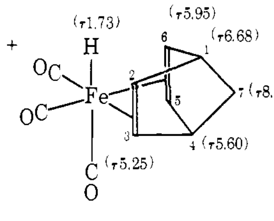
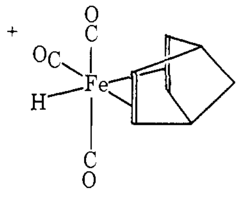


Figure 1. Nmr spectrum of 1 in FSO_3H-SO_2 at −46°. Peak positions were measured relative to internal tetramethylsilane, and integrated peak areas are given below the signals themselves.

The signal at τ 17.3 suggests strongly that **1** is protonated on iron.[4-6] The low-field spectrum is consistent with an ion of C_s symmetry in which the mirror plane contains C_1, C_7, and C_4, *e.g.*, **2**. In **2** each of the two bridgehead hydrogens is structurally unique. The alternative C_s structure **3**, in which each of the two hydrogens at C_7 is structurally unique, is not consistent with the observed chemical shifts of the unique hydrogens, τ 5.60 and 6.68. Furthermore, the singlet at τ 8.10 (2 H) seems to be consistent only with two equivalent hydrogens at C_7.

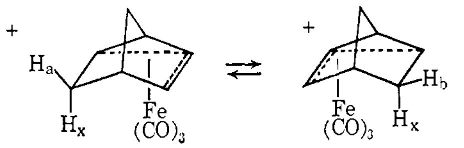


2



3

Protonation on carbon can be ruled out by our nmr data. C-protonation of **1** would give the homoallyltricarbonyliron cation **4a**. The correct apparent symmetry would be observed if **4a** and **4b** were rapidly interconverted by a 6,2-hydride shift similar to that which occurs in the 2-norbornyl cation.[7] This structure requires three unlikely assumptions: that H_x give a signal at τ 17.3, that J_{ax} and J_{bx} be about −26 Hz,[8,9] and that H_x be coupled to no other norbornenyl protons.[10] The nmr spectrum is temperature independent down to −75°. Therefore, we have no evidence for any dynamic process such as a 6,2-hydride shift.



4a **4b**

Our data are consistent only with the octahedral iron-protonated structure **2**. Assignments of nmr signals are indicated on the structural formula above. A model suggests that the carbonyl group *trans* to hydrogen in **2** approaches H_3 and H_5 closely and should deshield these hydrogens. The signal at lowest field has been assigned to these hydrogens. Assignment of the singlet at τ 8.10 to the hydrogens at C_7 leaves the pair of triplets centered at τ 5.95 for H_2 and H_6. Assignment of the bridgehead hydrogens has not been made on a firm basis and may be reversed. The large stereospecific coupling of the proton on iron with H_2 and H_6 is unusual. Typically the observed values of this type of coupling in protonated organotransition metal compounds are small or zero.[5,6,11]

Formation of the cation **2** in preference to cation **3** can be understood in terms of steric effects. Examination of a model shows that the carbonyl group *trans* to hydrogen in **2** interacts sterically with the norbornadiene ligand while the other two carbonyl groups experience little steric crowding. Structure **3** which places two carbonyl groups at sterically crowded sites should be destabilized relative to **2**. The tetracarbonyl chromium and molybdenum derivatives of norbornadiene

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[4] M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960).

[5] T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5249 (1960).

[6] A. Davidson, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

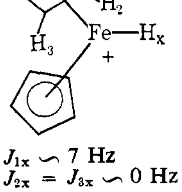
[7] P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. C. Olah, *J. Am. Chem. Soc.*, **86**, 5679 (1964); M. Saunders, P. von R. Schleyer, and G. C. Olah, *ibid.*, **86**, 5680 (1964).

[8] The lowest geminal coupling constant recorded is −22.3 Hz: R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron Suppl.*, 7, 355 (1966).

[9] Signals exhibited by a proton undergoing rapid intramolecular exchange have been discussed and documented. See, for example, C. MacLean and E. L. Makor, *Discussions Faraday Soc.*, **34**, 165 (1962), and E. W. Garbish, Jr., *J. Am. Chem. Soc.*, **85**, 1696 (1963).

[10] This is inconsistent with coupling constants observed in norbornenes. See P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1166 (1964).

[11] For example, the proton on iron in protonated ferrocene is coupled to the ten equivalent ring protons by an average J of 1.3 Hz.[6] This is not inconsistent with a larger stereospecific coupling, *e.g.*



$J_{1x} \backsim 7$ Hz
$J_{2x} = J_{3x} \backsim 0$ Hz

also appear to be protonated in FSO_3H-SO_2 at −45°. However, no high-field signals are observed in these cases. Experiments aimed at deduction of the structures of these compounds in strong acid media are in progress.

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Rates of Electron Exchange between Manganese(I) and -(II) Isonitrile Complexes

Sir:

Manganese–isonitrile complex ions $(R-NC)_6Mn^+$ and $(R-NC)_6Mn^{+2}$ exchange an electron at rates measurable by ^{55}Mn nmr line broadening. We have found that when the group R is saturated alkyl and therefore an electrical insulator, the mechanism of exchange is simple electron transfer, and the rate is slowed by bulky R groups. When R is unsaturated or aromatic, more complicated phenomena are observed, but these are consistent with the idea that the unsaturated group acts as an electron conductor.

Previously studied simple electron exchange systems, such as manganate–permanganate[1] and cuprous–cupric[2] ions, offered no opportunity for variation of the ligands. Taube and coworkers[3] and Gould[4] have found acceleration of reduction of cobalt(III) by chromium(II) when electron conduction through a ligand is possible, but these reactions involve a transfer of a ligand as well as an electron.

We prepared the diamagnetic, "krypton-configuration" manganese(I) complexes $(R-NC)_6Mn^+$ from the isocyanide and manganese(II) iodide in ethyl or *t*-butyl alcohol[5] and made the nitrate salts by ion exchange. These were obtained with R = ethyl, *t*-butyl, vinyl,[6] and phenyl.[7] Oxidation with nitric acid[8] yielded the corresponding $(R-NC)_6Mn^{+2}$ complexes, isolated as the hexafluorophosphates when R was alkyl and the tetrabromocadmiates when R was vinyl or phenyl.[7]

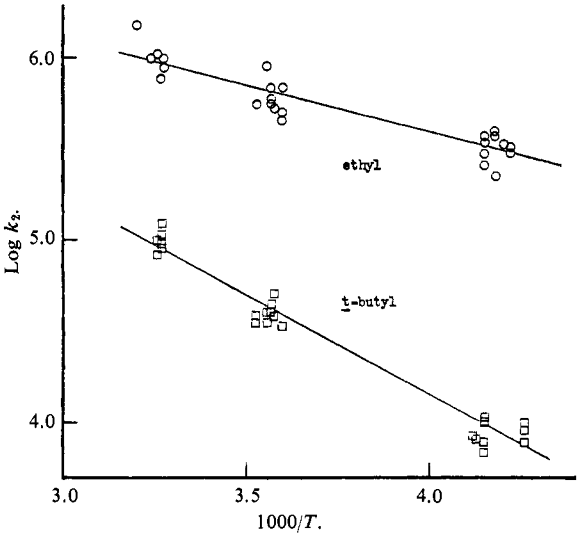

Figure 1. Plot of log k_2 *vs.* 1000/*T* for Mn(I)–Mn(II) electron exchange: ○, ethyl isocyanide complex; □, *t*-butyl isocyanide complex.

The ^{55}Mn nmr signal of a solution of 0.3 *M* hexa(ethyl isocyanide)manganese(I) nitrate in Spectro Grade acetonitrile was broadened in direct proportion to increments of hexa(ethyl isocyanide)manganese(II) hexafluorophosphate added, up to a concentration of about 10^{-3} *M*. The rate constant for electron exchange calculated from the broadening[9] is 6.4×10^5 at 7°. The proper Arrhenius temperature dependence was observed, as illustrated in Figure 1; ΔH^* is 1.74×0.2 kcal/mole and ΔS^* is −25 eu. The rate constant for electron exchange between the *t*-butyl isocyanide complexes of Mn(I) and Mn(II) is significantly lower, 4.0×10^4 at 7°, ΔH^* is higher, 4.56 kcal, and ΔS^* is about the same, −21 eu. Solvent effects are slight, the rate for the ethyl isocyanide complexes being unchanged in ethanol and about doubled in dimethyl sulfoxide.

In contrast to the alkyl compounds, the vinyl and phenyl isocyanide manganese(II) complexes are not "well behaved." Magnetic susceptibilities were measured in acetonitrile solution by the proton nmr shift method.[10] The magnetic moments of the ethyl and *t*-butyl compounds are 1.95–2.1 BM, as expected for the strong-field d^5 Mn^{+2} ion with one unpaired electron. However, the magnetic moments of the vinyl and phenyl isocyanide complexes were found to be zero. The expected epr signal, six lines due to ^{55}Mn splitting, was found for both alkyl compounds, but no epr signal could be detected in freshly prepared acetonitrile solutions of $(C_6H_5NC)_6Mn^{+2}$. The alkyl compounds are pale pink solids and yield pale yellow solutions, in accord with the forbidden character of the Mn(II) t_{2g} to e_g transition, but the vinyl compound is a deep orange-red (λ_{max} 450 mμ) and the phenyl is purple-red (λ_{max} 490 mμ), comparable to previously reported $(Ar-NC)_6Mn^{+2}$ ions.[8]

Thus, the phenyl and vinyl isocyanide–manganese(II) complexes must exist as diamagnetic dimers. We postulate that these are π complexes involving face-to-face interaction of one or two of the phenyl (or vinyl) groups from each unit, as illustrated below. These resemble donor–acceptor π complexes of the usual variety in structure, but owe their stability to electron exchange and spin pairing.

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(1) O. E. Meyers and J. C. Sheppard, *J. Am. Chem. Soc.*, **83**, 4739 (1961).

(2) H. M. McConnell and H. E. Weaver, Jr., *J. Chem. Phys.*, **25**, 307 (1956).

(3) F. R. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **88**, 4295 (1966); R. T. M. Fraser and H. Taube, *ibid.*, **83**, 2239 (1961); R. T. M. Fraser, D. K. Sebera, and H. Taube, *ibid.*, **81**, 2906 (1959).

(4) E. S. Gould, *ibid.*, **88**, 2983 (1966).

(5) A. Sacco, *Gazz. Chim. Ital.*, **86**, 201 (1956); *Ann. Chim.*, **48**, 225 (1958); *Chem. Abstr.*, **53**, 204*g* (1959).

(6) Vinyl isocyanide: D. S. Matteson and R. A. Bailey, *Chem. Ind.* (London), 191 (1967).

(7) Satisfactory analyses for all elements (except oxygen) in each compound were obtained, except that the tetrabromocadmiate salts contained some cadmium bromide.

(8) L. Naldini, *Gazz. Chim. Ital.*, **90**, 971 (1960).

(9) M. W. Dietrich and A. C. Wahl, *J. Chem. Phys.*, **38**, 1591 (1963).

(10) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).