

A further analysis, including spectra taken at 35 GHz, seems to be needed before a complete model could be given of the anion radicals fixed to the resin by the carboxylic group.

Further investigations are in progress with ion exchangers with different exchange groups and with other nitroxide radicals in addition to that so far used.

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Intermediacy of Metal-Olefin Complexes in Cycloaddition and Insertion Reactions at Transition Metal- η^1 -Allyl Bonds

Sir:

Synthetic aspects of cycloaddition and insertion reactions of transition metal- η^1 -allyl complexes have been the subject of a number of investigations.^{1,2} More recently, interest has developed in the mechanism of these processes.²⁻⁴ Although it is generally accepted²⁻⁴ that they proceed through a dipolar metal-olefin intermediate, no direct evidence has been presented in support of this hypothesis.⁵ Herein we wish to report spectroscopic detection and isolation as the cationic η^2 -(allyl sulfone) complexes of such zwitterionic intermediates.

Reactions of η^5 -C₅H₅Fe(CO)₂(η^1 -allyl) (**1a-d**) with SO₂ are known to afford S-bonded sulfinato complexes (**2a-d**, respectively).⁷⁻⁹ We now find that freshly prepared (5-10-min old) solutions of **1a-d** ($\sim 7 \times 10^{-3}$ M) in neat SO₂ at -35 to -18° show two intense $\nu_{C=O}$ ir bands at 2085-2078 and 2050-2040 cm⁻¹.¹⁰ These frequencies are much too high to be attributed to the parent η^1 -allyl complex (2018-2005, 1962-1945 cm⁻¹)^{6,7}

(1) (a) F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta*, **2**, 289 (1968); (b) Y. Yamamoto and A. Wojcicki, *Inorg. Chem.*, **12**, 1779 (1973).

(2) (a) W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, **93**, 5299 (1971); (b) W. P. Giering, S. Raghu, M. Rosenblum, A. Cutler, D. Ehntholt, and R. W. Fish, *ibid.*, **94**, 8251 (1972); (c) A. Rosan, M. Rosenblum, and J. Tancrede, *ibid.*, **95**, 3062 (1973); (d) M. Rosenblum, *Accounts Chem. Res.*, **7**, 122 (1974).

(3) A. Wojcicki, *Advan. Organometal. Chem.*, **12**, 31 (1974).

(4) C. V. Magatti and W. P. Giering, *J. Organometal. Chem.*, **73**, 85 (1974).

(5) However, protonation of iron- η^1 -allyl complexes to the corresponding iron- η^2 -olefin cations has been known for some time.⁸

(6) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

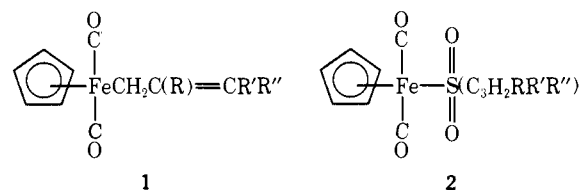
(7) (a) R. L. Downs and A. Wojcicki, *Inorg. Chim. Acta*, to be submitted for publication; (b) R. L. Downs, Ph.D. Thesis, The Ohio State University, 1968.

(8) J.-Y. Merour, *C. R. Acad. Sci.*, **271**, 1397 (1970).

(9) A. Cutler, R. W. Fish, W. P. Giering, and M. Rosenblum, *J. Amer. Chem. Soc.*, **94**, 4354 (1972). These authors reported the formation of **2a** from **1a** but did not furnish any spectroscopic properties.

(10) Recorded using a modified VLT-2 variable low-temperature cell unit from Research and Industrial Instruments Co., London, England. For details see S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, **95**, 6962 (1973).

but are virtually identical with those of several cationic complexes containing η^5 -C₅H₅Fe(CO)₂(η^2 -olefin)⁺ or



1 a, R = R' = R'' = H

b, R = R' = H; R'' = CH₃

c, R = H; R' = R'' = CH₃

d, R = CH₃; R' = R'' = H

η^5 -C₅H₅Fe(CO)₂(η^2 -allene)⁺.^{6,11} Storage of these solutions leads to the appearance and growth of the $\nu_{C=O}$ absorptions of **2a-d**^{7,8} at 2066-2065 and 2022-2020 cm⁻¹, as the intensities of the original bands decrease. The two sets of the $\nu_{C=O}$ absorptions attain comparable intensities as a function of the allyl fragment in the order: **1c** (100 min, -35°) \sim **1d** (110 min, -35°) $>$ **1b** (120 min, -18°) $>$ **1a** (\sim 200 min, -18°). In the spectra of **1a** in SO₂ there also appear, and increase in intensity, a broad band at 1967-1960 cm⁻¹ and a shoulder at \sim 2005 cm⁻¹; corresponding absorptions are not discernible for SO₂ solutions of **1b-d**.

Low-temperature nmr spectra of freshly prepared SO₂ solutions of **1a-d** in the C₅H₅ proton region (τ 4.0-5.5) show a strong resonance at τ 4.30-4.40 which is assigned to the reaction intermediate. The position of this signal is compatible with the positive charge on the iron as, e.g., in η^5 -C₅H₅Fe(CO)₂(η^2 -olefin)⁺.⁶ Upon storage of the solutions of **1b-d** at -40 to -22°, the resonance at τ 4.30-4.40 decreases and another resonance, due to **2b-d**,^{7,8} respectively, appears and grows at τ 4.75-4.78. The nmr spectrum of the SO₂ solution of **1a** undergoes the following changes with time at -22°.¹² The signal at τ 4.36 decreases in intensity and resonances appear at τ 4.78 (due to **2a**) and 5.00. This is followed by a gradual appearance of yet another signal, at τ 5.03, and diminution of intensity of the peak at τ 5.00. After the signal at τ 4.36 has virtually disappeared, the combined intensity of the resonances at τ 5.00 and 5.03 remains constant, with the latter increasing and the former decreasing. The limiting spectrum (\sim 5 days) shows only the peaks at τ 4.78 and 5.03.

On the basis of the above spectroscopic data and virtual lack of conductivity of a freshly prepared SO₂ solution of **1a**,¹³ the observed reaction intermediates are assigned zwitterionic structures **3a-d**. This assignment is strengthened by the preparation and characterization of **4a** via reaction of **3a** (from 1.0 g, 4.7 mmol, of **1a**) in neat SO₂ (5 ml) with (CH₃)₃O⁺BF₄⁻ (\sim 6

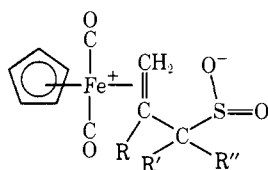
(11) $\nu_{C=O}$ absorptions occur at 2090-2080 and 2060-2040 cm⁻¹: (a) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963); (b) J. Benaim, J.-Y. Merour, and J.-L. Roustan, *C. R. Acad. Sci.*, **272**, 789 (1971); (c) D. W. Lichtenberg, Ph.D. Thesis, The Ohio State University, 1973.

(12) Only a qualitative description of changes in the τ 4.0-5.5 region is given herein. Details of the nmr spectra will be provided in our full paper.

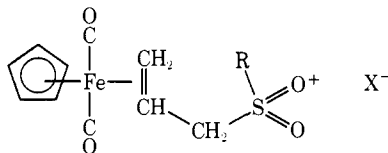
(13) A freshly prepared 1.2×10^{-2} M solution of **1a** in SO₂ at -70° exhibits $\Delta_M = 2.24$ ohm⁻¹cm². By comparison, $\Delta_M = 84$ ohm⁻¹cm² for [η^5 -C₅H₅Fe(CO)₂P(C₆H₅)₃]⁺PF₆⁻,¹⁴ which is in the region expected for 1:1 electrolytes.

(14) S. E. Jacobson, P. Reich-Rohrwig, and A. Wojcicki, *Inorg. Chem.*, **12**, 717 (1973).

mmol).¹⁵ **4a**¹⁶ was isolated in 70% yield as a yellow solid, mp 130° dec. Similarly prepared, by treatment of **3a** with (C₆H₅)₃CCl and addition of NH₄PF₆, was **5a**,¹⁸ mp 135–136° dec. In contrast, treatment of **3a**



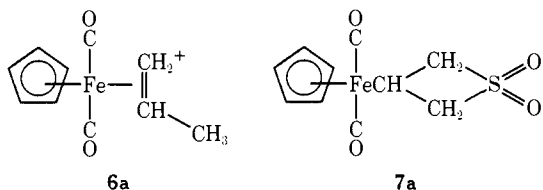
- 3a**, R = R' = R'' = H
b, R = R' = H; R'' = CH₃
c, R = H; R' = R'' = CH₃
d, R = CH₃; R' = R'' = H



- 4a**, R = CH₃; X = BF₄
5a, R = (C₆H₅)₃C; X = PF₆

with CH₃OSO₂F (or HCl gas) unexpectedly affords known⁶ **6a**.

Whereas rapid removal of the SO₂ from freshly prepared (or aged) solutions of **1b–d** yields only **2b–d**, respectively, similar treatment of the SO₂ solution of **1a** affords some (5%) **2a** and another 1:1 adduct of **1a** and SO₂, **7a**. **7a**, a yellow solid, mp 62–65°, is



monomeric¹⁹ and the suggested structure receives support from the ir and nmr data.²⁰ Surprisingly, **7a** polymerizes on storage in SO₂, CHCl₃, or CH₂Cl₂. Initially, soluble dimeric and/or trimeric species can be isolated,²¹ mp 150–160° dec. They show a new C₅H₅ ¹H nmr signal,²² a richer ν_{SO} ir region,²³ but vir-

(15) The same synthesis of **4a** was mentioned in a recent review.^{2d}

(16) *Anal.* Calcd for C₁₁H₁₃FeO₄SBF₄: C, 34.42; H, 3.41; S, 8.34. Found: C, 34.17; H, 3.31; S, 8.22. Δ_M = 111 ohm⁻¹ cm² (~5 × 10⁻⁴ M, acetone),¹⁷ ir ν_{C=O} 2072, 2041, ν_{SO} 1302, 1139 cm⁻¹ (Nujol); ¹H nmr (PF₆⁻ derivative of **4a**) C₅H₅ τ 4.00 s, CH₃ 6.95 s (deuterioacetone).

(17) Molar conductivities of ~1 × 10⁻³ M solutions of 1:1 electrolytes in acetone fall in the range of 100–150 ohm⁻¹ cm²; see M. B. Reynolds and C. A. Kraus, *J. Amer. Chem. Soc.*, **70**, 1709 (1948).

(18) *Anal.* Calcd for C₂₉H₂₈FeO₄SPF₆: C, 51.96; H, 3.76; S, 4.77. Found: C, 51.80; H, 3.76; S, 4.57. Δ_M = 134 ohm⁻¹ cm² (~5 × 10⁻⁴ M, acetone), ir ν_{C=O} 2081, 2039, ν_{SO} 1296, 1127 cm⁻¹ (Nujol); ¹H nmr C₅H₅ τ 4.10 s (deuterioacetone).

(19) Calcd molecular weight for C₁₀H₁₀FeO₄S: 282. Found: 285–288 (CHCl₃, osmometric). The compound is hygroscopic and was handled accordingly in a drybox for this and other measurements.

(20) Ir ν_{C=O} 2012, 1957, ν_{SO} 1302, 1109 cm⁻¹ (KBr), ¹H nmr τ 5.03 s (5 H), 6.5 complex (4 H), 7.8 complex (~1 H) (CDCl₃), τ 5.00 s (5 H) (SO₂).

(21) *Anal.* Calcd for (C₁₀H₁₀FeO₄S)₂ or ₃: C, 42.58; H, 3.57; O, 22.69; mol wt, 564 (dimer), 846 (trimer). Found: C, 42.33, 42.41; H, 3.63, 3.76; O, 22.65; mol wt, 571–577, 604–660 (CHCl₃, osmometric). The closely agreeing oxygen analysis is particularly important as it mitigates the possibility of a sulfonate formulation, (C₁₀H₁₀FeO₄S)_n (calcd O for C₁₀H₁₀FeO₄S: 26.85).

(22) At τ 5.03 (SO₂) or 5.08 (CDCl₃). The rest of the nmr spectrum is ill resolved but qualitatively similar to that of the monomer.

(23) 1324, 1298, 1126, 1109 cm⁻¹ (KBr).

tually unchanged in ν_{C=O} band positions. The mass spectra (70 eV, 100°) of these associated species contain peaks at *m/e* 190 (C₅H₅Fe(CO)₂CH⁺ and/or C₅H₅-Fe(CO)C₃H₅⁺, intensity 11.7), 162 (C₅H₅Fe(CO)CH⁺ and/or C₅H₅FeC₃H₅⁺, intensity 30.2), and 134 (C₅H₅-FeCH⁺, intensity 10.8),²⁴ thus suggesting the presence of an Fe–C σ-bond therein. However, the structure of the (C₅H₅SO₂)₂ or ₃ sulfone moiety is not evident from these data.²⁵ Prolonged storage of **7a** in solution yields insoluble, presumably more highly associated species. It is not obvious to us why **7a** should undergo this unusual behavior.²⁶

Two important conclusions emerge from this work. (1) It has been demonstrated unequivocally for the first time that reactions of η⁵-C₅H₅Fe(CO)₂(η¹-allyl) with SO₂, and very likely also with other electrophilic molecules such as (CN)₂C=C(CN)₂, ClSO₂NCO, and CF₃-COCF₃, *inter alia*,⁵ proceed *via* zwitterionic iron-olefin intermediates. Our observation that η⁵-C₅H₅Mo(CO)₃-CH₂CH=CH₂ interacts similarly to **1a** with SO₂ suggests that such behavior is general of transition metal-η¹-allyl complexes. (2) It is noteworthy that the rates of the rearrangement of the iron-olefin intermediates (**3a–d**) to the *S*-sulfinato products (**2a–d**, respectively) tend to increase with the increasing extent of alkyl substitution in the olefin fragment. This trend is consistent with transition metal-olefin bonding being destabilized by such alkyl substitution,²⁷ thus rendering the olefin more labile toward SN1 or SN2 displacement. Significantly, the least alkyl-substituted zwitterionic iron-olefin intermediate, **3a**, is the slowest to dissociate to yield **2a**. It is also the only intermediate which rearranges *via* cycloaddition, very likely because the iron binds this olefin most strongly and hence activates it best toward nucleophilic attack by the sulfinate oxygen or sulfur.

Acknowledgments. The financial support of this research by the National Science Foundation is gratefully acknowledged. We thank Professors Giering and Rosenblum for helpful comments.

(24) Intensity of C₅H₅Fe⁺ = 100. The *m/e* 134 peak may alternatively be assigned to C₆H₆Fe⁺, as suggested by a referee. However, we consider the presence of such an ion very improbable, especially since C₆H₆⁺ is not observed in the spectrum.

(25) Attempts are now being made to elucidate the structures of **7a** and its dimer by X-ray crystallography.

(26) η⁵-C₅H₅Fe(CO)₂CHCH₂CH₂S(O)₂CH₂, a homolog of **7a**, does not exhibit this behavior; instead it is converted to η⁵-C₅H₅Fe(CO)₂S(O)₂-CH₂CH₂CH=CH₂ on heating.^{2a} We find that the dimer or trimer of **7a** yields only a trace amount of **2a** on heating at 110–125° for 48 hr.

(27) For example, M. L. H. Green, "Organometallic Compounds," Vol. II, Methuen, London, 1968, p 21, and M. Herberhold, "Metal π-Complexes," Vol. II, Elsevier, New York, N. Y., 1974, pp 130–134.

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On the Problem of Assigning Values to Energy Changes of Electrode Reactions

Sir:

Unlike ionization potential or electron affinity measurements, the energy change during an electrode reaction is never assigned a real value but rather it is always necessary to refer the potential to that of a reference