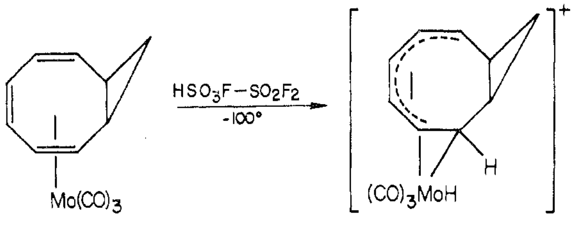
Correspondence

π to σ Rearrangements upon Metal Protonation of Polyolefin-Transition Metal Complexes

AIC30836*

Sir:

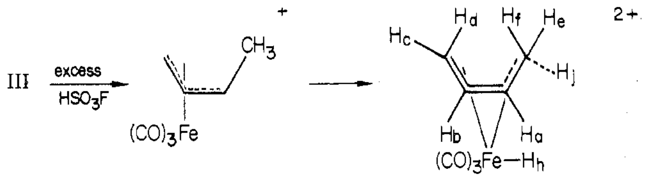
Recently we reported that bicyclo[6.1.0]nonatriene-molybdenum tricarbonyl, I, when dissolved in HSO_3F-SO_2F_2 at low temperatures undergoes protonation at molybdenum and a unique π to σ change in the metal-ligand bonding to yield the σ,π complex II.[1] We feel this π to σ isomerization may represent a more general class of rearrangements which can occur upon metal protonation of polyolefinic transition metal complexes and is one which must now be considered when analyzing the results of such protonation reactions.



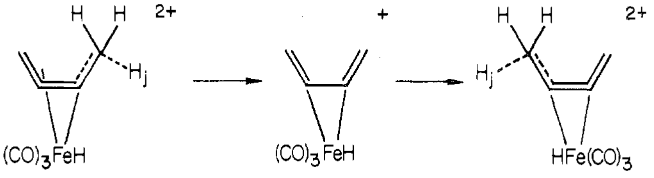
I II

In this correspondence we wish to site several previous literature reports where this π to σ rearrangement mechanism provides an alternative explanation of the reported data or suggests a more detailed explanation of observed phenomena.

One of the simplest systems in which this mechanism appears to operate is in the low-temperature protonation of dieneiron tricarbonyl complexes. Young, Holmes, and Kaesz[2] have reported that when butadieneiron tricarbonyl, III, is dissolved in excess fluosulfonic acid (SO_2 solvent), a new species is formed which they have assigned to a diprotonated structure, V. The formation of V is presumed to occur by attack of a second proton H_j on the saturated carbon of the π-allyl complex IV with shift of H_h from saturated carbon to iron. The species assumed to be V exhibits chemical shifts as follows (τ values): H_a, 3.05; H_b, 3.56; H_c, 6.37; H_d, 8.33; H_e, 9.00; H_f, 10.86; H_h, 24.59. Important coupling constants are $J_{fh} = 22$ Hz, $J_{eh} = 14$ Hz, $J_{bd} = 11.7$ Hz, $J_{cd} = 3.7$ Hz, $J_{bc} = 7.8$ Hz, $J_{ab} = 6.5$ Hz, and $J_{ef} \simeq 7$ Hz. The H_j proton is proposed to be in rapid equilibrium with solvent acid and is thus not observed by nmr, yet H_c, H_d must *remain distinct* from H_f, H_e. By deuteration in DSO_3F and by nmr line broadening it was demonstrated that protons H_h, H_f, and H_e show rapid equilibration presumably *via* deprotonation back through species IV as an intermediate in which the three protons of the methyl group become equivalent. Using the monodeuterium label generated by deuteration in DSO_3F it was shown that on a longer time scale deuterium equilibrates over positions c, d, h, f, and e but *not* with acid or with positions a and b. The slower scrambling was presumed to be due to the following reaction sequence coupled with the more rapid three proton scrambling



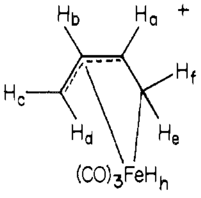
IV V



V V

In addition to III, protonations of other acyclic irondiene tricarbonyl complexes and the cyclohexadieneiron tricarbonyl complex are reported.[2] All show similar phenomena which are explained using diprotonated species analogous to V.

By reformulating the diprotonated species as the monoprotonated σ,π species VI, an alternative and simpler explanation for the observations can be made.[3] The nmr of the observed species is in good agreement with structure VI. Using II as a model and noting that C_1 is σ bound to iron, J_{fh} (22 Hz) and J_{eh} (14 Hz) are not unexpectedly large. In addition, the upfield shifts of H_e (τ 9.00) and H_f (τ 10.86) are in accord with an iron-C_1 σ bond. As noted previously,[2] the coupling constants J_{cd}, J_{bc}, and J_{ab} are consistent with those expected for π-allyl systems.[4] The proton scrambling phenomena can readily be accounted for by the σ,π species VI. The three-proton scrambling of H_f, H_e, and H_h can occur *via* equilibration with a small concentration of the methyl-π-allyl species IV. This scrambling



VI

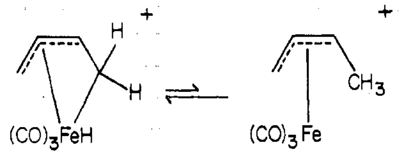
---

(1) M. Brookhart, D. L. Harris, and R. C. Dammann, *J. Chem. Soc., Chem. Commun.*, 187 (1973).

(2) D. A. T. Young, J. R. Holmes, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 91, 6968 (1969).

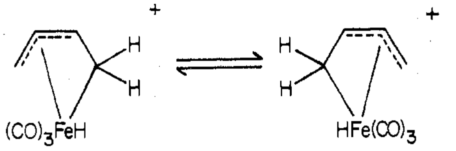
(3) Young, Holmes, and Kaesz[2] have noted that the equilibrium between the π-allyl complex III and the "new species" assigned structure V is highly solvent dependent. Upon addition of the *ca.* 1.4 mol of HSO_3F/mol of complex III, both the π-allyl species and the new species V are formed and the concentration of the new species is proportional to excess acid. Our explanation of this observation is that at low acid concentrations the fluorosulfonate anion is probably coordinated to the π-allyl complex (not free as indicated by IV) and the function of excess acid is to ionize this coordinated group to produce the unsaturated complex IV which may then rearrange to the saturated σ,π species VI. Note Added in Proof. In support of this explanation, T. H. Whitesides and R. W. Arhart (unpublished data) have shown experimentally that the σ,π species generated in HBF_4-CF_3COOH is monoprotonated not diprotonated.

(4) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, 3, 1 (1965).



VI IV

is intramolecular as required and involves no exchange of protons with solvent acid. The slower intramolecular scrambling of H_c, H_d, H_e, H_f, and H_g can be accounted for by equilibration *via* σ-π rearrangement of the two degenerate species VIa and VIb coupled with the faster three-proton scrambling.

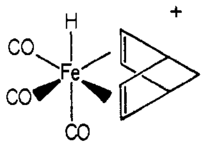


VIa VIb

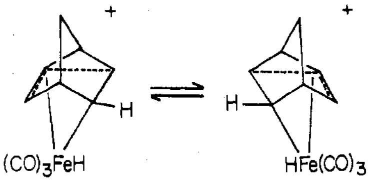
The butadiene complex, III, has been considered in detail; application of analogous reactions can explain observations made for the other dieneiron tricarbonyl complexes reported.[2,5]

Additional cases involving protonation of dieneiron tricarbonyl complexes where σ,π species must now be considered as possible intermediates are the reports by Whitesides of the stereospecific deuterium exchange of the endo protons of cyclohexadieneiron tricarbonyl[6] and the exchange of the terminal protons of dieneiron tricarbonyl complexes[7] in trifluoroacetic-d_1 acid. The observed sites of exchange result if the scrambling processes described above are coupled with proton (deuterium) exchange with the trifluoroacetic acid.

The structure of protonated norbornadieneiron tricarbonyl[8] can also be formulated in terms of a σ,π species. The nmr spectral data, in which the coupling of the iron-bound proton with two olefinic protons of the ring is 13 Hz, are consistent both with the structure VII as proposed by Lillya and Rausch[8] and with a rapidly equilibrating σ,π species VIII in which the π-allyl moiety is a homoallyl system.



VII



VIII VIII

Other cases in which σ,π species may likely play a role as intermediates include the proton scrambling processes in the protonated cyclohexadiene(cyclopentadienyl)rhodium,[9] the stereospecific endo protonation of cyclooctatetraenemolybdenum tricarbonyl,[10] and the 1,4 hydrogen shifts and deuterium-exchange reactions of π-allyliron tetracarbonyl cations.[11]

Acknowledgments. This work was supported in part by the National Science Foundation (Grant GP-29580) and the Materials Research Center, University of North Carolina, under Grant No. GH-33632 from the National Science Foundation.

---

[5] The only datum reported which is not in agreement with the proposed scheme is the integrated area of the methylene region for the species produced by protonation of cyclohexadieneiron tricarbonyl in excess HSO_3F. The reported integral corresponds to 6 H; our mechanism predicts a 5 H integral. However, the corresponding integral (4.7 H) in DSO_3F is in accord with our mechanism (4.5 H).

[6] T. H. Whitesides and R. W. Arhart, *J. Amer. Chem. Soc.*, 93, 5296 (1971).

[7] T. H. Whitesides, R. W. Arhart, and R. W. Slaven, *J. Amer. Chem. Soc.*, 95, 5792 (1972).

[8] D. R. Falkowski, D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Amer. Chem. Soc.*, 89, 6387 (1967).

[9] (a) B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J. Chem. Soc., Chem. Commun.*, 235 (1972); (b) B. F. G. Johnson, J. Lewis and D. J. Yarrow, *J. Chem. Soc., Dalton Trans.*, 2084 (1972).

[10] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, 87, 3267 (1965).

[11] D. H. Gibson and R. L. Vonnahme, *J. Chem. Soc., Chem. Commun.*, 1021 (1972).

Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

Maurice Brookhart*
David L. Harris

Received November 14, 1973

Mechanism of Insertion of Olefins into Platinum-Hydrogen Bonds

AIC30846A

Sir:

The uncatalyzed insertion of C_2H_4 into *trans*-$PtHClL_2$ (**1**), where $L = P(C_2H_5)_3$, to form the corresponding ethylplatinum complex (**2**) according to eq 1, has been reported to

$$trans\text{-}PtHClL_2 + C_2H_4 \rightleftarrows \underset{\mathbf{2}}{trans\text{-}Pt(C_2H_5)ClL_2} \qquad (1)$$

occur only slowly even under vigorous conditions (20 hr, 100°, 80 atm).[1,2] On the other hand the corresponding reactions of C_2H_4 with *trans*-$PtH(NO_3)L_2$ (**3**) [to form *trans*-$Pt(C_2H_5)(NO_3)L_2$ (**4**)] and with *trans*-PtH(acetone)L_2^+ (**5**) (to form **2** after work-up with methanolic LiCl) occur readily at room temperature and atmospheric pressure, as does reaction 1 in the presence of catalytic amounts of $AgPF_6$.[3]

The latter observations have been interpreted in terms of the cationic intermediate *trans*-$PtH(C_2H_4)L_2^+$ (**6**) formed through the facile replacement by C_2H_4 of the weakly bound trans NO_3^- and acetone ligands of **3** and **5**, respectively, or through the corresponding Ag^+-assisted displacement of the trans Cl^- ligand of **1**. Salts of **6**, for example, [*trans*-$PtH(C_2H_4)L_2]^+BPh_4^-$, have in fact been isolated and the trans configuration of the cation in solution has been established by nmr spectroscopy.[3,4]

This interpretation is consistent with the widely accepted view that insertion of olefins into transition metal-hydrogen bonds requires prior coordination of the olefin to the metal ion but not, on the face of it, with the further implied requirement of cis rather than trans disposition of the hydride and olefin ligands.[5] The purpose of this communication is to examine this apparent inconsistency and to suggest possible explanations for its origin. Two such explanations that have occurred to us and that we have examined are encompassed by the mechanistic Schemes I and II, respectively (where S = solvent and $X^- = NO_3^-$, etc.).[6]

---

[1] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

[2] J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. A*, 190 (1968).

[3] H. C. Clark and H. Kurosawa, *Inorg. Chem.*, 11, 1275 (1972).

[4] A. J. Deeming, B. F. G. Johnson and J. Lewis, *Chem. Commun.*, 598 (1970).

[5] See for example, R. F. Heck, *Advan. Chem. Ser.*, No. 49, 181, 208 (1965).