Alkylrhodium Tetracarbonyl Derivatives as Catalytic Intermediates in Homogeneous Hydroformylation Reactions. An Infrared Spectroscopic Study[1]

R. B. King,* A. D. King, Jr., and M. Z. Iqbal[2]

Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602. *Received October 11, 1978*

Abstract: The rhodium-catalyzed hydroformylation of ethylene in *n*-tetradecane solution has been monitored by infrared spectroscopic examination of the ν(CO) region using a high-pressure cell-autoclave. Diverse rhodium(I) carbonyl derivatives, including $[Rh(CO)_2Cl]_2$, $C_5H_5NRh(CO)_2Cl$, $[CH_3CO_2Rh(CO)_2]_2$, and $C_5H_7O_2Rh(CO)_2$, generate systems that catalyze the hydroformylation of ethylene under mild conditions (e.g., 35 °C and 20-100 atm total pressure). In each of these systems absorption bands due to an unstable metal carbonyl derivative develop as the hydroformylation reaction proceeds. These absorption bands, which occur at the ν(CO) frequencies 2115 w, 2037 s, 2019 s cm^{-1}, are attributed to an unstable rhodium alkyl, presumably $C_2H_5Rh(CO)_4$, on the basis of the close agreement between these frequencies and those reported for $CH_3Co(CO)_4$ (2105 w, 2036 m, 2019 vs cm^{-1}).

Introduction

In a previous paper of this series[3] the reactions of CO and H_2 with relatively stable transition-metal alkyls of the types $RMn(CO)_4L$ (L = CO or trivalent phosphorus ligands), $RFe(CO)_2C_5H_5$, and $RMo(CO)_3C_5H_5$ were examined using infrared spectroscopy at elevated pressures to follow the courses of the reactions. This work indicated that the range of transition-metal alkyls with appropriate reactivity patterns to serve as catalytic intermediates in the homogeneous hydroformylation of olefins to aldehydes[4] was extremely limited.

We now report a different, more direct approach to the study of the homogeneous hydroformylation reaction using our previously described[3] high-pressure infrared cell. In this work we perform hydroformylation reactions in the infrared cell using ν(CO) frequencies to monitor the formation and destruction of both metal carbonyl species and the aldehyde. The specific hydroformylation reaction studied was the conversion of ethylene to propionaldehyde according to the equation

$$C_2H_4 + CO + H_2 \rightarrow C_2H_5C(O)H \qquad (1)$$

Use of ethylene has several advantages including a single possible hydroformylation product and the ability to add or remove ethylene easily in our high-pressure equipment. We selected rhodium as the catalyst metal because of its high catalytic activity.[5-8] In order to assess most fully the features of rhodium complexes that make them such effective catalyst precursors, several low oxidation state derivatives were investigated.

We found that a common feature of many of these rhodium-catalyzed hydroformylation reactions was the observation of a consistent set of new metal ν(CO) frequencies under conditions where propionaldehyde was also produced. This new rhodium carbonyl derivative was only stable under carbon monoxide pressure. Data are presented in this paper suggesting that these bands can be assigned to the previously unknown $C_2H_5Rh(CO)_4$. This work represents the first time that evidence has been obtained for the existence of an $RRh(CO)_4$ derivative, albeit under rather special conditions. Analogous $RCo(CO)_4$ derivatives (R = alkyl[9-11] or perfluoroalkyl[12,13]) have been known for some time.

Experimental Section

The infrared spectra at elevated pressures were run in the previously described[3] stainless steel high-pressure infrared cell with Irtran 1 windows and recorded on a Perkin-Elmer Model 281 grating spectrometer. Eastman highest purity *n*-tetradecane was used as the solvent for all of the spectra reported here. The rhodium compounds $[Rh(CO)_2Cl]_2$,[14] $Rh_4(CO)_{12}$,[15] $[C_8H_{12}RhCl]_2$,[16] $[C_8H_{12}RhCO_2CH_3]_2$,[16] [nor-$C_7H_8RhCl]_2$,[17] $[(C_2H_4)_2RhCl]_2$,[18] $(C_2H_4)_2Rh(C_5H_7O_2)$,[19] $C_6H_5NH_2Rh(CO)_2Cl$,[20] and $(CH_3CO_2)_4Rh_2 \cdot 2CH_3OH$[21] were prepared by the cited procedures. The apparently unreported yellow pyridine complex 1,5-$C_8H_{12}Rh(NC_5H_5)Cl$, mp 165–166 °C, was prepared by a standard method[16] involving reaction of $[C_8H_{12}RhCl]_2$ with excess pyridine in dichloromethane solution followed by crystallization from light petroleum or *n*-hexane; this product gave correct C, H, and N analyses.

Results and Discussion

1. $Rh_4(CO)_{12}$. A solution of $Rh_4(CO)_{12}$ in *n*-tetradecane (ν(CO) 2068 vs, 2042 s, 1883 s cm^{-1}) is unaffected upon treatment at room temperature with 35 atm of a 1:1:1 $CO/H_2/C_2H_4$ mixture for 9 h. Heating this solution above ~60 °C leads to the formation of $Rh_6(CO)_{16}$ identified by its infrared ν(CO) frequencies at 2072 vs and 1818 s cm^{-1} (lit.[22] 2073 s, 2026 m, and 1800 s cm^{-1} in KBr) in accord with previous observations.[15,23] Cooling the resulting solution of $Rh_6(CO)_{16}$ below 60 °C while maintaining the $CO/H_2/C_2H_4$ pressure results in the regeneration of $Rh_4(CO)_{12}$, thereby indicating the reversibility of this reaction. No evidence for the formation of propionaldehyde (ν(CO) 1738 cm^{-1}) was found from reactions of $Rh_4(CO)_{12}$ with a 1:1:1 $CO/H_2/C_2H_4$ mixture in *n*-tetradecane solution under these conditions even at temperatures of 150 °C. This indicates that $Rh_4(CO)_{12}$ is not an active ethylene hydroformylation catalyst under these specific conditions, although it has been shown to serve as a hydroformylation catalyst for 1-heptene and related liquid substituted olefins[24] under different conditions and as a stoichiometric rather than catalytic hydroformylation reagent with H_2 under mild conditions.[25] Our observations may be regarded as a control experiment indicating that $Rh_4(CO)_{12}$ is not an active ethylene hydroformylation catalyst under the specific conditions where the experiments with other rhodium compounds were carried out.

2. $[Rh(CO)_2Cl]_2$. A solution of $[Rh(CO)_2Cl]_2$ in *n*-tetradecane (ν(CO) 2087 s, 2031 s cm^{-1}; see Figure 1, upper left) gradually forms $Rh_4(CO)_{12}$ with 90 atm of 1:1 CO/H_2 at 35 °C over a period of hours. A similar experiment using 96 atm of 1:1:1 $CO/H_2/C_2H_4$ likewise first forms $Rh_4(CO)_{12}$ (Figure 1, upper right) but subsequently forms propionaldehyde, identified by its ν(CO) frequency at 1738 cm^{-1} (Figure 1, lower left). The formation of propionaldehyde was accompanied by two new relatively strong rhodium carbonyl ν(CO) frequencies at 2037 and 2019 cm^{-1} and a weak ν(CO) frequency at 2115 cm^{-1} (see especially Figure 1, lower right,

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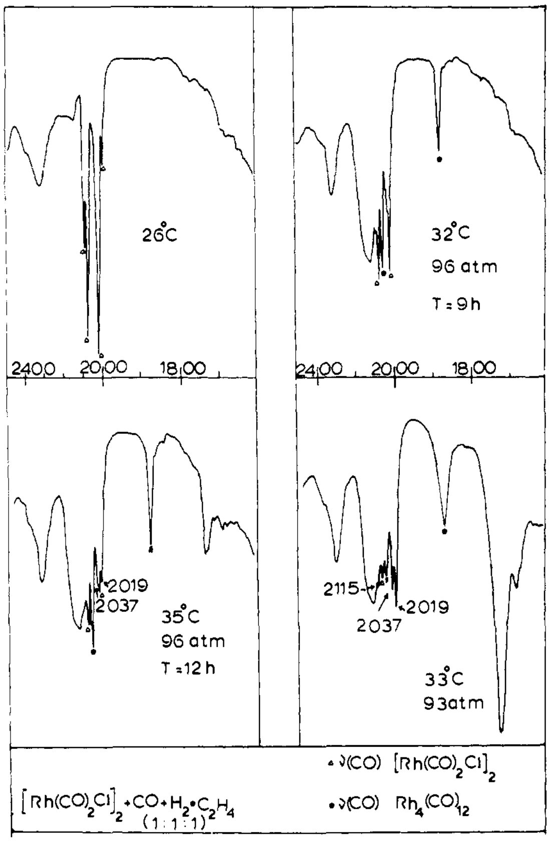

Figure 1. Infrared spectra obtained during the reaction of $[Rh(CO)_2Cl]_2$ with a 1:1:1 $CO/H_2/C_2H_4$ mixture.

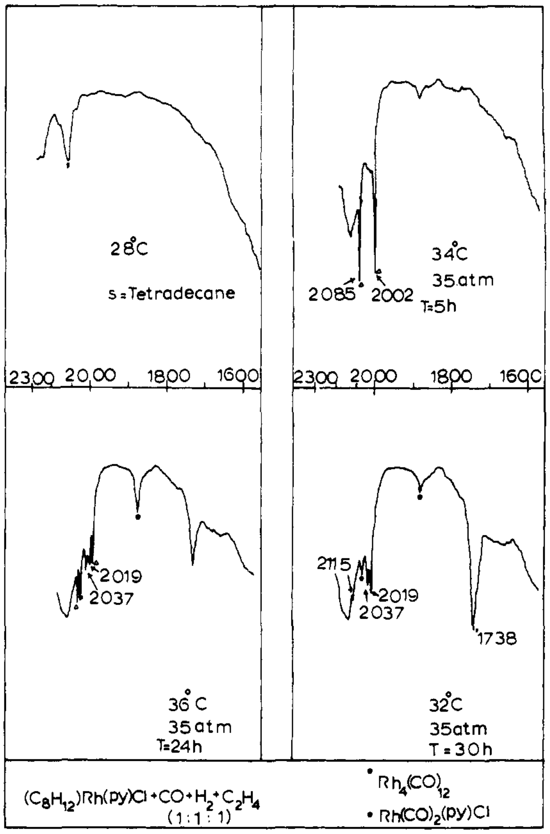

Figure 2. Infrared spectra obtained during the reaction of $C_8H_{12}Rh(NC_5H_5)Cl$ with a 1:1:1 $CO/H_2/C_2H_4$ mixture.

taken after a 34-h reaction time). These new ν(CO) frequencies disappeared upon reducing the pressure to 1 atm.

Comparison of these new ν(CO) frequencies with those of appropriate model compounds suggests that they come from an $RRh(CO)_4$ derivative. Thus their positions are very close to those reported[11] for $CH_3Co(CO)_4$ (i.e., 2105 w, 2036 m, 2019 vs cm^{-1}). Furthermore, the observation by previous workers[23] as well as in our own work that a similar species is not formed by reaction of $Rh_4(CO)_{12}$ with a CO/H_2 mixture in the absence of ethylene suggests that ethylene is an essential component of this $RRh(CO)_4$ derivative. Accordingly, the new ν(CO) frequencies at 2037 s, 2019 s, and 2115 w cm^{-1} are assigned to the previously unreported $C_2H_5Rh(CO)_4$. The observed instability of $C_2H_5Rh(CO)_4$ is consistent with the reported[9-11] instability of $RCo(CO)_4$ derivatives (R = hydrocarbon alkyl such as methyl or ethyl) and the lower stability of metal-carbonyl bonds involving 4d transition metals relative to corresponding 3d transition metals.[26] This work thus represents a new application of infrared spectroscopy at elevated pressures for the detection of unstable reaction intermediates.

These observations suggest that $[Rh(CO)_2Cl]_2$ can react with a $CO/H_2/C_2H_4$ mixture according to the following equation:

$$[Rh(CO)_2Cl]_2 + 4CO + 2H_2 + 2C_2H_4 \rightarrow 2C_2H_5Rh(CO)_4 + 2HCl \quad (2)$$

The same system can also be generated from other rhodium(I) derivatives. Thus the diene-rhodium(I) complexes [(diene)-$RhCl]_2$ (diene = 1,5-cyclooctadiene and norbornadiene) were found to react with CO at room temperature and 1-4 atm with displacement of the diolefin to give $[Rh(CO)_2Cl]_2$. Similarly the aniline complex $C_6H_5NH_2Rh(CO)_2Cl$ (ν(CO) 2082 s, 2008 s cm^{-1}) gradually forms $[Rh(CO)_2Cl]_2$ at 42 °C and 20 atm of 1:1 CO/H_2 after several hours. Subsequent reactions of all of these systems, including formation of propionaldehyde, $Rh_4(CO)_{12}$, and the presumed $C_2H_5Rh(CO)_4$, parallel those of $[Rh(CO)_2Cl]_2$ discussed above.

3. $C_8H_{12}Rh(NC_5H_5)Cl$. Reaction of $C_8H_{12}Rh(NC_5H_5)Cl$ with 6 atm of 1:1 CO/H_2 at 39 °C results in the fairly rapid (~15 min) displacement of the 1,5-cyclooctadiene ligand with CO to give $C_5H_5NRh(CO)_2Cl$ (ν(CO) 2085 s and 2002 s cm^{-1}). A slower reaction under these conditions gives $Rh_4(CO)_{12}$. Reaction of $C_8H_{12}Rh(NC_5H_5)Cl$ with 35 atm of 1:1:1 $CO/H_2/C_2H_4$ at 35 °C (Figure 2) gives slowly $Rh_4(CO)_{12}$, propionaldehyde, and the proposed $C_2H_5Rh(CO)_4$ indicated ultimately by the 2115 w, 2037 s, and 2019 s cm^{-1} ν(CO) pattern noted above. This system led to the spectrum proposed for $C_2H_5Rh(CO)_4$ containing the minimum amount of other metal carbonyl impurities (Figure 2, lower right). This last spectrum contained the expected strong 1738-cm^{-1} propionaldehyde band but no ν(CO) bands assignable to acyl carbonyl groups, thereby excluding an alternative formulation of this $RRh(CO)_4$ derivative as the propionyl $C_2H_5CORh(CO)_4$. Assuming that the $C_2H_5Rh(CO)_4$ proposed to account for the above ν(CO) bands is indeed an intermediate in a series of chemical reactions leading to propionaldehyde, then the absence of any acyl carbonyl ν(CO) frequencies suggests that the rhodium-carbon (alkyl) bond in this $RRh(CO)_4$ derivative is relatively strong in comparison with the rhodium-carbon (acyl) bond in the corresponding acyl derivative which is also an expected intermediate resulting from alkyl migration. These observations may also relate to our previously observed inability[3] to carbonylate $CH_3Re(CO)_5$ to $CH_3CORe(CO)_5$ and to the apparent instability of the metal-alkyl bond in the 3d transition metal derivative $CH_3Cr(CO)_3C_5H_5$ relative to the corresponding 4d and 5d transition metal derivatives $CH_3M(CO)_3C_5H_5$ (M = Mo and W).[27]

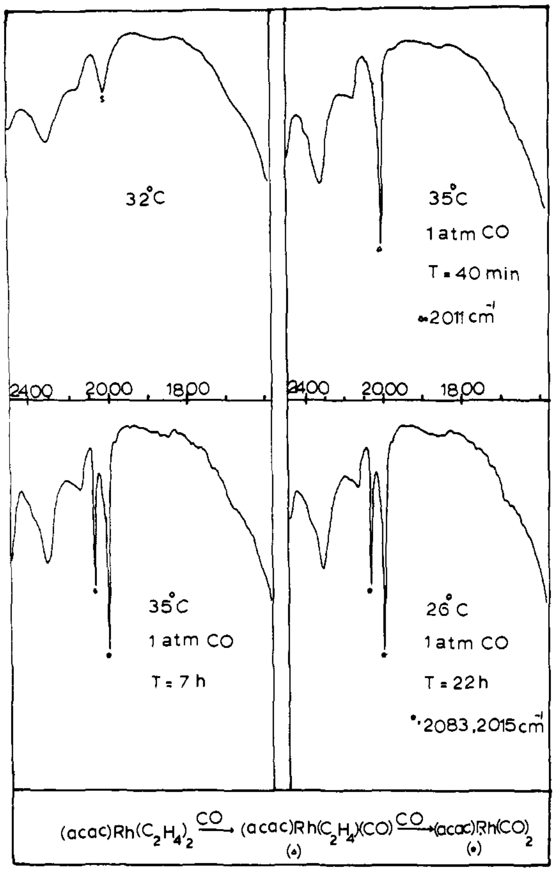

Figure 3. Infrared spectra obtained during the stepwise reaction of $(C_2H_4)_2RhC_5H_7O_2$ with CO at atmospheric pressure.

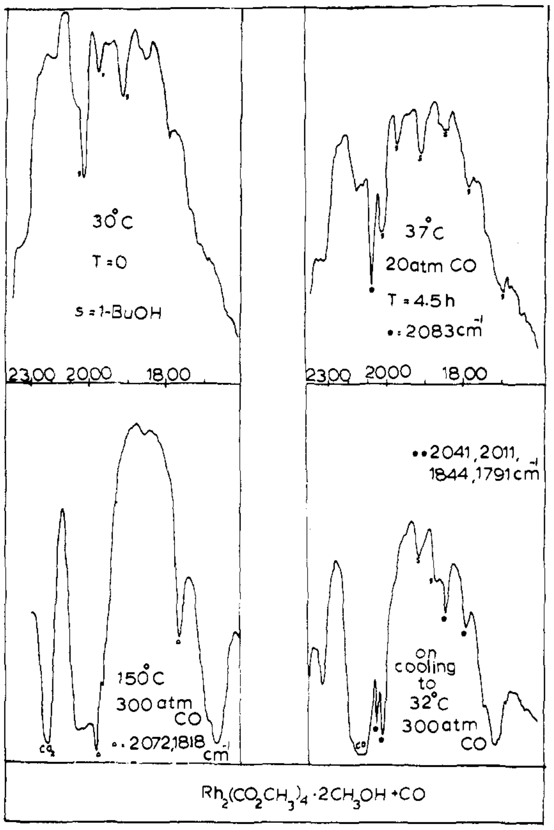

Figure 4. Infrared spectra obtained during the carbonylation of $[Rh(CO_2CH_3)_2]_2 \cdot 2CH_3OH$. The peaks marked S arise from the 1-butanol solvent.

4. Rhodium(I) Carbonyl Acetates. A solution of $[CH_3CO_2Rh(CO)_2]_2$[28] (ν(CO) 2091 m, 2067 m, 2027 s cm^{-1}) was prepared by treating a hexane solution of $[Rh(CO)_2Cl]_2$ with excess solid potassium acetate. This product was found to form $Rh_4(CO)_{12}$ readily upon treatment with 30 atm of 1:2 CO/H$_2$ at temperatures below 40 °C with no evidence for the production of any $Rh_6(CO)_{16}$. This contrasts with similar reported[15] reactions of $[CH_3CO_2Rh(CO)_2]_2$ with 1 atm of CO in methanol which gives a high yield of $Rh_6(CO)_{16}$. Reaction of $[CH_3CO_2Rh(CO)_2]_2$ with 60 atm of 1:1:1 CO/H$_2$/C$_2$H$_4$ at 33 °C results in the production of propionaldehyde.

A tetradecane solution of $[CH_3CO_2RhC_8H_{12}]_2$ reacts with 25 atm of 4:1 CO/H$_2$ at 36 °C to give a pair of bands at 2070 and 2004 cm^{-1} which may tentatively be assigned to a mononmetallic rhodium dicarbonyl derivative such as possibly $CH_3CO_2Rh(CO)_2$. Further reaction under these conditions gives $[CH_3CO_2Rh(CO)_2]_2$ and $Rh_4(CO)_{12}$.

5. Rhodium Carbonyl Acetylacetonates. The known complex[29,30] $Rh(CO)_2C_5H_7O_2$ ($C_5H_7O_2$ = acetylacetonate) with ν(CO) at 2083 s and 2015 s cm^{-1} (lit.[29] ν(CO) 2083 s and 2015 s cm^{-1}) can easily be generated by displacement of the coordinated olefins in $C_8H_{12}RhC_5H_7O_2$ or $(C_2H_4)_2RhC_5H_7O_2$ with CO at 30 °C and 1-6 atm. In the case of $(C_2H_4)_2RhC_5H_7O_2$ (Figure 3) an intermediate monocarbonyl $(C_2H_4)Rh(CO)(C_5H_7O_2)$ is indicated by a single ν(CO) frequency at 2011 cm^{-1} after the reaction has been allowed to proceed for a short time. The $Rh(CO)_2C_5H_7O_2$ system was again an active catalyst for the hydroformylation of ethylene at 35 °C. Again the ν(CO) frequencies assigned to $C_2H_5Rh(CO)_4$ (2115 w, 2037 s, and 2019 vs cm^{-1}) were observed during such a hydroformylation at 38 °C and 40 atm of 1:1:1 CO/H$_2$/C$_2$H$_4$.

6. Rhodium(II) Acetate (Figure 4). Rhodium(II) acetate has been shown[31] to exist as a dimer $[Rh(CO_2CH_3)_2]_2$ containing a metal-metal bond. Furthermore, it readily forms adducts of the type $[Rh(CO_2CH_3)_2]_2L_2$ with a variety of donor ligands (e.g., L = water, methanol, tetrahydrofuran, acetonitrile, dimethyl sulfoxide, dimethyl sulfide, trimethylamine, ammonia, nitric oxide, and ethylenediamine).[21] Reaction of the methanol adduct $[Rh(CO_2CH_3)_2]_2 \cdot 2CH_3OH$ with 20 atm of CO in 1-butanol solution results in the appearance of a strong 2083-cm^{-1} band (Figure 4, upper right) suggesting the formation of the dicarbonyl $[Rh(CO_2CH_3)_2]_2(CO)_2$. Releasing the CO pressure causes this ν(CO) frequency to disappear indicating that this adduct is unstable at atmospheric pressure. Further heating of a solution containing this CO adduct under 300 atm of CO results in the formation of $Rh_6(CO)_{16}$ above 120 °C (e.g., Figure 4, lower left). A band assignable to CO$_2$ is also observed in this spectrum, suggesting that CO is the reducing agent converting $[Rh(CO_2CH_3)_2]_2L_2$ to $Rh_6(CO)_{16}$. Cooling this solution of $Rh_6(CO)_{16}$ so generated from $[Rh(CO_2CH_3)_2]_2 \cdot 2CH_3OH$ and CO results in the formation of new ν(CO) frequencies at 2041 s, 2011 s, 1844 m, and 1791 m cm^{-1} (solid circles in Figure 4, lower right). This new species is tentatively formulated as the acetate derivative $[Rh_6(CO)_{15}OCOCH_3]^-$ by analogy with reported[31] ν(CO) frequencies of $[Rh_6(CO)_{15}Cl]^-$ (2095 w, 2060 s, 2028 w, 1822 w, 1790 s, and 1785 sh cm^{-1}). A species $[Rh_6(CO)_{15}OCOCH_3]^-$ is likely to be formed by reaction of $Rh_6(CO)_{16}$ with acetate ion present in the reaction solution similar to reported[32] reactions of $Rh_6(CO)_{16}$ with nucleophiles.

A 1-butanol solution of $[Rh(CO_2CH_3)_2]_2 \cdot 2CH_3OH$ is inactive as a hydroformylation catalyst at 34 °C and 40 atm of 1:1:1 CO/H$_2$/C$_2$H$_4$.

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References and Notes

(1) Portions of this work were presented at the Symposium on Rhodium in Homogeneous Catalysis, Veszprém, Hungary, Sept 1978, Proceedings, p 84.

(2) Postdoctoral Research Associate, 1976–1978.

(3) R. B. King, A. D. King, Jr., M. Z. Iqbal, and C. C. Frazier, *J. Am. Chem. Soc.*, **100**, 1687 (1978).

(4) A. J. Chalk and J. F. Harrod,*Adv. Organomet. Chem.*, **6**, 119 (1968).

(5) D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 3133 (1968).

(6) C. K. Brown and G. Wilkinson, *J. Chem. Soc. A*, 2753 (1970).

(7) J. H. Craddock, A. Hershman, F. E. Paulik, and J. F. Roth, *Ind. Eng. Chem., Prod. Res. Dev.*, **8**, 291 (1969).

(8) J. Falbe, *J. Organomet. Chem.*, **94**, 213 (1975).

(9) W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch. B*, **13** 192 (1958).

(10) R. F. Heck and D. S. Breslow, *Chem. Ind.* (*London*), 467 (1960).

(11) L. Marko, G. Bor, G. Almasy, and P. Szabó, *Brennst.-Chem.*, **44**, 184 (1963).

(12) W. R. McClellan, *J. Am. Chem. Soc.*, **83**, 1598 (1961).

(13) W. Hieber, W. Beck, and E. Lindner, *Z. Naturforsch. B*, **16**, 229 (1961).

(14) J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, **8**, 211 (1965).

(15) P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 315 (1969).

(16) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

(17) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

(18) R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

(19) R. Cramer, *J. Am. Chem. Soc.*, **86**, 217 (1964).

(20) M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Organomet. Chem.*, **40**, 393 (1972).

(21) S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, **2**, 960 (1963).

(22) (a) W. Beck and K. Lottes, *Ber.*, **94**, 2578 (1961); (b) E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963).

(23) R. Whyman, *J. Chem. Soc., Dalton Trans.*, 1375 (1972).

(24) B. Heil and L. Markó, *Ber.*, **101**, 2209 (1968); **102**, 2238 (1969).

(25) P. Chini, S. Martinengo, and G. Garlaschelli, *J. Chem. Soc., Chem. Commun.*, 709 (1972).

(26) R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).

(27) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(28) D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1900 (1965).

(29) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964).

(30) F. Bonati and R. Ugo, *J. Organomet. Chem.*, **7**, 167 (1967).

(31) M. A. Porai-Koshits and A. S. Antsyshkina, *Dokl. Akad. Nauk SSSR*, **146**, 1102 (1962).

(32) P. Chini, S. Martinengo, and G. Giordano, *Gazz. Chim. Ital.*, **102**, 330 (1972).

Fluxional Behavior and Substituent Site Preferences in Cationic Monosubstituted Tropyliumiron Tricarbonyl Complexes

C. P. Lewis,[1a] W. Kitching,[1b] A. Eisenstadt,[1c] and M. Brookhart*[1a]

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514, the Department of Chemistry, University of Queensland, St. Lucia, Brisbane, Queensland, 4067, Australia, and the Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel.

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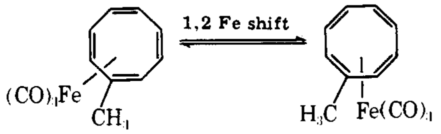
Abstract: The fluxional monosubstituted tropyliumiron tricarbonyl complexes, $RC_7H_6Fe(CO)_3^+$ (R = methyl, isopropyl, cyclopropyl, and phenyl), have been studied by variable temperature ^1H and ^{13}C NMR. Static systems can be observed at low temperatures (ca. −100 °C) and reveal the isomer distributions in the various ions studied and thus the substituent site preferences. For R = methyl, the 2-methyl, 3-methyl, and 6-methyl (vinyl substituted) ions can be observed in a ratio of ca. 43:7:50 at −100 °C. For R = isopropyl, no 3 isomer is observed and the 2-isopropyl:6-isopropyl ratio is ca. 15:85. When R = phenyl, the vinyl-substituted 6 isomer is the only species observed, while in contrast for R = cyclopropyl the 2 isomer predominates (80%) with the 6-cyclopropyl isomer as the minor component (20%). The substituent site preferences indicate that there is relatively little charge on the carbons of the metal-complexed pentadienyl ring, but among the three different sites, most positive charge resides at C_2, C_4. A fine balance of electronic vs. steric factors control the C_2:C_6 isomer ratio. The dynamic behavior of the complexes was studied at higher temperatures and, in general, three dynamic processes all occurring via 1,2 iron shifts could be observed. In order of increasing activation energies, these processes were (1) degenerate isomerization of the 2 isomer with its enantiomer via the symmetrical 3 isomer, (2) degenerate interconversion of the 6 isomer with its enantiomer, and (3) the interconversion of the equilibrating 2 and 3 isomers with the 6 isomer via the unobserved 1 isomer. Detailed rates and free energies of activation for these processes are given.

Introduction

Stereochemical nonrigidity is frequently encountered in transition metal π complexes in which the metal is bonded to a fragment of a completely conjugated cyclic polyolefin.[2] For such mononuclear complexes, the fluxionality is associated with a rapid metal migration around the ring, resulting in a number of thermally accessible degenerate configurations. This results in the "averaging" of all ring carbon and attached proton sites in the system, if migration is sufficiently rapid on the NMR time scale. Such metal migration is overwhelmingly of the 1,2 type, with concomitant π-bond reorganization.[2,3] When the polyene is substituted, structures generated by metal shifts are no longer degenerate, and are likely to differ in stability and hence be present in unequal amounts. Apparently only one thorough study of such a system has been conducted, that being the examination of monosubstituted cyclooctatetraene-$Fe(CO)_3$ (COT-$Fe(CO)_3$) complexes.[4] Anet demonstrated that methyl-COT-$Fe(CO)_3$ exists very largely (>90%) with the methyl group occupying the inside site of the bound diene unit as shown below.[4a,c] Other monosubstituted COT-$Fe(CO)_3$ complexes were examined and different substituents were found to prefer different sites.[4c] These results for an uncharged system suggested that the determination of site preferences in other systems could be quite illuminating with respect to the electronic properties of the bound unsaturated moiety.



Pentadienyl-$Fe(CO)_3$ cations are remarkably stable and have been subjected to extensive experimental[5,6] and theo-

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