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**Preliminary communication**

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# Cyclobutadieneiron nitrosyl complexes

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## SUMMARY

The air stable yellow-orange complexes of cyclobutadieneiron dicarbonyl nitrosyl hexafluorophosphate, $[R_4C_4Fe(CO)_2NO]^+PF_6^-$; R = H, $CH_3$, Ph, were prepared by the reaction of $R_4C_4Fe(CO)_3$ and nitrosonium hexafluorophosphate. These complexes undergo facile monocarbonyl substitution reactions with various Lewis bases (L) to afford products of the type $[R_4C_4Fe(CO)(NO)L]^+PF_6^-$, R = H, L = $Ph_3P$, $Ph_3As$, $Ph_3Sb$ or R = Ph; L = $Ph_3P$, $Ph_3As$; a dicarbonyl substitution product of the type $[R_4C_4Fe(NO)L_2]^+PF_6^-$, R = Ph; L = $(PhO)_3P$, was also isolated and characterized.

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Metal complexes of cyclobutadiene and substituted cyclobutadienes have been reported with carbonyl[1], halides[1], hydride[2], phosphine[1], trifluoromethylthio[3], σ-phenyl[4] and various π-ligands[1]. The preparation of the parent and numerous partially and fully substituted cyclobutadieneiron tricarbonyl complexes is well documented[5]. However, little attention has been given to the study of their inorganic aspects. Except for $Me_4C_4Fe(CO)_2(CF_3)_2CO$[6], $C_4H_4Fe(CO)_2(MeOOCCH{=}CHCOOMe)$[7], $C_4H_4Fe(C_6H_6NCOOEt)$[8], $C_8H_6Fe(CO)_2(Ph_3P)$[5] and $Ph_4C_4Fe(CO)_2(Ph_3P)$[9], no other cyclobutadieneiron derivatives are known. This work describes the preparation of cyclobutadieneiron nitrosyl complexes: the first known complexes of this type.

The air stable yellow orange complexes of cyclobutadieneiron dicarbonyl nitrosyl hexafluorophosphate (I: R = H, $CH_3$, Ph) were prepared by the reaction of $R_4C_4Fe(CO)_3$ (II: R = H, $CH_3$, Ph) with nitrosonium hexafluorophosphate in acetonitrile solution at ambient temperature. The parent complex (I: R = H) undergoes a facile monocarbonyl substitution with L (L = $Ph_3P$, $Ph_3As$, $Ph_3Sb$) in boiling acetone solution to afford the respective complexes (III: R = H; L = $Ph_3P$, $Ph_3As$, $Ph_3Sb$). The phenyl analogue (I: R = Ph) reacts similarly with $Ph_3P$ and $Ph_3As$ in boiling benzene solution to give (III: R = Ph, L = $Ph_3P$, $Ph_3As$) while with $(PhO)_3P$ under identical conditions the disubstituted product (IV) is formed exclusively. Attempts to prepare the stibine analogue (III: R = Ph; L = $Ph_3Sb$)

TABLE 1

| Complex | Color | M.p. (°C) [b] | Yield (%) | Infrared ($cm^{-1}$) [c] | | | | Proton NMR ($\tau$) [d] | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $\nu(CO)$ | | $\nu(NO)$ | $\nu(PF)$ | $C_4H_4$ | $C_6H_5$ |
| $[C_4H_4Fe(CO)_2NO]^+PF_6^-$ [a] | yellow | dec. > 167 | 92 | 2133<br>(2144 | 2103<br>2076 | 1882<br>1865) | 832 | 3.86(s) | |
| $[C_4H_4Fe(CO)(NO)Ph_3P]^+PF_6^-$ | yellow | dec. > 171 | 50 | 2075<br>(2028 | | 1846<br>1787) | 840 | 4.60(d) [f] | 2.26(s) |
| $[C_4H_4Fe(CO)(NO)Ph_3As]^+PF_6^-$ | yellow | dec. > 183 | 72 | 2065<br>(2028 | | 1842<br>1788) | 834 | 4.45(s) | 2.31(s) |
| $[C_4H_4Fe(CO)(NO)Ph_3Sb]^+PF_6^-$ | yellow | dec. > 181 | 73 | 2046<br>(2029 | | 1836<br>1789) | 833 | 4.35(s) | 2.27(s) |
| $[Me_4C_4Fe(CO)_2NO]^+PF_6^-$ | yellow | dec. > 155 | 69 | 2102 | 2063 | 1828 | 838 | – [g] | – |
| $[Ph_4C_4Fe(CO)_2NO]^+PF_6^-$ | orange | dec. > 157 | 64 | 2105 | 2095 | 1853 | 840 | | 2.68(s) |
| $[Ph_4C_4Fe(CO)(NO)Ph_3P]^+PF_6^-$ | orange | 175 | 80 | 2078 | | 1819 | 838 | | 2.55(s) |
| $[Ph_4C_4Fe(CO)(NO)Ph_3As]^+PF_6^-$ | orange | 166 | 68 | 2060 | | 1811 | 838 | | 2.58(s) |
| $[Ph_4C_4Fe(NO)[(PhO)_3]_2]^+PF_6^-$ | pale-orange | 142 | 21 | | | 1817 | 842 | | 2.40(m)<br>2.75(m)<br>3.15(m) |

| Complex | Mössbauer (mm/sec) [e] | |
|---|---|---|
| | *IS* | *QS* |
| $[C_4H_4Fe(CO)_2NO]^+PF_6^-$ | 0.135 | 1.161 |
| $[C_4H_4Fe(CO)(NO)Ph_3P]^+PF_6^-$ | 0.130 | 1.299 |
| $[C_4H_4Fe(CO)(NO)Ph_3As]^+PF_6^-$ | 0.138 | 1.275 |
| $[C_4H_4Fe(CO)(NO)Ph_3Sb]^+PF_6^-$ | 0.148 | 1.203 |
| $[Me_4C_4Fe(CO)_2NO]^+PF_6^-$ | | |
| $[Ph_4C_4Fe(CO)_2NO]^+PF_6^-$ | | |
| $[Ph_4C_4Fe(CO)(NO)Ph_3P]^+PF_6^-$ | | |
| $[Ph_4C_4Fe(CO(NO)Ph_3As]^+PF_6^-$ | | |
| $[Ph_4C_4Fe(NO)[(PhO)_3]_2]^+PF_6^-$ | | |

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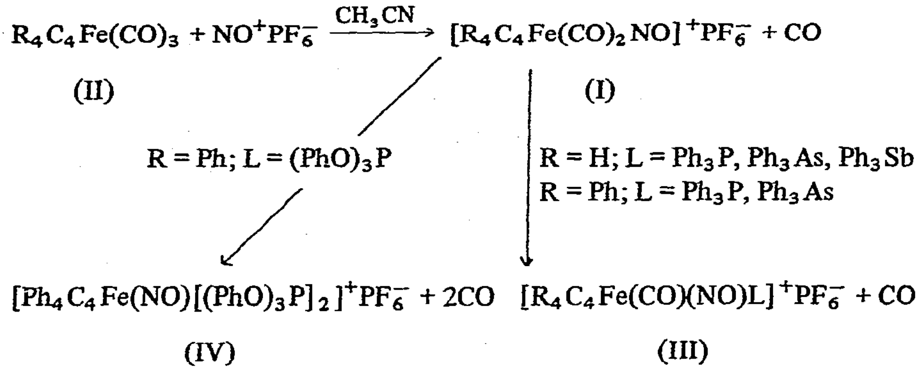
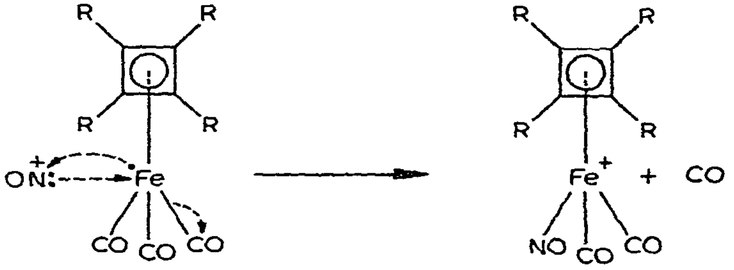
[a] Satisfactory elemental analyses were obtained for all these new complexes. [b] Melting and decomposition (dec.) points are uncorrected. [c] Infrared spectra were taken in KBr pellets on a Perkin–Elmer 225 grating spectrometer, the carbonyl and nitrosyl stretching frequencies of the related manganese complexes are indicated in parentheses. [d] Proton NMR spectra were run in *d*-acetone solution with TMS as an internal standard on a Varian T-60 or a JNM-MH-100 spectrometer. Abbreviations: s, singlet; d, doublet; m, multiplet. [e] Mössbauer spectra were taken at liquid nitrogen temperature and the *IS* values are given with respect to the center of a room temperature spectrum of NBS SRM metallic iron. *IS* and *QS* are given within ± 0.003 and ± 0.006 mm/sec accuracy, respectively. [f] *J*(PF) 2Hz. [g] Insufficient solubility in *d*-acetone prevented from obtaining the proton NMR spectrum.

by a similar route were unsuccessful. The methyl substituted complex (I: R = $CH_3$) is apparently the least reactive of the series since all attempts to afford carbonyl substitution with $Ph_3P$ in different boiling solvents such as acetone, methanol and benzene were unsuccessful. Probably, this is due to the marginal solubility of (I: R = $CH_3$) in the above mentioned solvents.



The assigned structures of the new complexes, outlined in Table 1, are in full accord with their spectroscopic properties. The infrared spectra in the 2200–1700 $cm^{-1}$ region confirmed the presence of terminal metal carbonyl and/or nitrosyl groups, while a strong band in the 832–842 $cm^{-1}$ region, characteristic of the hexafluorophosphate anion, supports the ionic nature of these new complexes. The proton NMR spectra of (I: R = H) and (III: R = H; L = $Ph_3As$, $Ph_3Sb$) exhibit sharp singlet at $\tau \sim 4$ due to the equivalent protons of the cyclobutadiene ring. In the case of the spectrum of the phosphine derivative (III: R = H; L = $Ph_3P$) the cyclobutadiene protons resonance is split into a doublet by the phosphorus atom ($J(PF) \approx 2$Hz). The phenyl proton resonances were observed in their normal region and when appropriate the ratio of the different protons, obtained by integration, agreed with the calculated value. The presence of only one kind of iron atom in the parent cyclobutadieneiron complexes (I: R = H) and (III: R = H) was confirmed from the Mössbauer parameters at liquid nitrogen temperature. The $\nu(CO)$ and $\nu(NO)$ stretching frequencies of the complexes can be related to the nature of the ligand L. The systematic decrease of these frequencies is in accord with the established $\pi$-acidity sequence of $CO \gg Ph_3P > Ph_3As > Ph_3Sb$. The iron complexes (I: R = H) and (III: R = H) are closely related structurally to the manganese series $[C_5H_5Mn(CO)(NO)L]^+PF_6^-$ (L = CO, $Ph_3P$, $Ph_3As$, $Ph_3Sb$)[10,11]. Interestingly, the $\nu(CO)$ and $\nu(NO)$ frequencies of the iron complex series are substantially higher than their manganese counterparts (Table 1). A direct comparison between the two series is not strictly valid since the metals, their formal oxidation states, and their *d*-electron configurations, are different. However, since the iron atom attains a lower oxidation state than the manganese atom in the respective complexes, a greater degree of back-bonding interaction and thus lower carbonyl and nitrosyl stretching frequencies were expected to be observed for the iron series. The present results imply that the cyclobutadiene ligand is by far a better $\pi$-electron acceptor than is the cyclopentadienyl ligand[4,12]. To date, these results are the most convincing illustration of the π-acceptor property of the cyclobutadiene ligand.

Previously, attempts to prepare cyclobutadienemetal nitrosyl complexes by a direct synthesis from cyclobutadienemetal derivatives and nitric oxide were unsuccessful[13]. Apparently, nitric oxide oxidatively displaces the cyclobutadiene ring from its complexes. These results are not unexpected since even mild oxidizing agents like $FeCl_3$ and $(NH_4)_2Ce(NO_3)_6$ are known to oxidatively displace the cyclobutadiene ring from a relatively stable complex as (II: R = H)[14]. Therefore, the preparation of cyclobutadienemetal nitrosyls should not be regarded a trivial extention of the related chemistry of cyclopentadienylmetal nitrosyl complexes. The nitrosonium ion, in spite of being a much stronger oxidizing agent than either $Fe^{III}$ or $Ce^{IV}$, does not oxidatively displace the cyclobutadiene ring from its complexes. Unlike the reaction between (II: R = H) and $Ce^{IV}$ or $Fe^{III}$ which are believed to involve a free cyclobutadiene (singlet ground state) intermediate[8,14] the reaction of the former with nitrosonium could be best explained in terms of a concerted oxidative substitution mechanism. Such a process would involve an electronically and coordinatively saturated iron atom and therefore no substantial weakening of the cyclobutadiene–iron bond should occur.



(II) (III)

## ACKNOWLEDGEMENT

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