(6) ^{1}H and ^{13}C NMR data consistent with these structures, as well as those of fragments IV–IX, were obtained and will be published later in a full paper. Structures of fragments I and VIII were confirmed by X-ray. The aromatic chlorine in II and III may just as well be on the equivalent position on the right-hand ring.

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A Radical-Chain Mechanism in Substitution Reactions of (Unsaturated Alkyl) Metal Carbonyl Complexes

Sir:

We have previously reported that reactions of the *monohapto*cyclopentadienyl complex, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(\eta^1\text{-C}_5\text{H}_5)$ (henceforth abbreviated FpCp), with phosphorus donor ligands, are atypical of (alkyl) metal carbonyl substitution reactions.[1] In addition to the formation of unexpected products in some cases, these reactions are unusually facile: FpCp reacts completely with a variety of phosphines and phosphites over periods varying from several minutes to several days (depending on ligand and solvent), whereas the methyl analogue FpMe is completely inert to all such ligands under the same conditions. Similar behavior has been reported for a number of (hydrido) metal carbonyl substitutions (including FpH[2]); mechanistic investigations on several of these have established that a radical-chain mechanism is responsible for these relatively rapid reactions.[3] We now present evidence that substitution reactions of (unsaturated alkyl) metal carbonyls, including FpCp, can proceed by a closely related radical-chain pathway.

FpCp reacts very slowly in the dark with P(OPh)_3 to give the substitution product, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(P(OPh)}_3)(\eta^1\text{-C}_5\text{H}_5)$ (Fp′Cp).[1] Irradiation with near-UV light does not cause any significant acceleration of the substitution reaction; instead FpCp is converted into ferrocene.[4] However, if the irradiated solution also contains a small amount of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}_2]_2$(Fp$_2$), substitution is markedly enhanced.[5] This result is similar to observations made for (hydrido) metal carbonyls[3] and suggests formulation of an analogous mechanism, viz:

$$\text{Q}\cdot + \text{FpCp} \rightarrow \text{QCp} + \text{Fp}\cdot \tag{1}$$

$$\text{Fp}_2 \xrightarrow{h\nu} 2\text{Fp}\cdot \tag{2}$$

$$\text{Fp}\cdot + \text{L} \xrightarrow{\text{fast}} \text{Fp}'\cdot + \text{CO} \tag{3}$$

$$\text{Fp}'\cdot + \text{FpCp} \rightarrow \text{Fp}'\text{Cp} + \text{Fp}\cdot \tag{4}$$

In this scheme initiation, either by adventitious impurities (1) or by photocleavage of a metal–metal bond (2) gives the 17-electron fragment Fp. Such 17-electron species have been shown to be highly labile toward substitution.[6] Steps 3 and 4 correspond to chain propagation. The crucial element of this scheme is step 4, which is a homolytic displacement reaction of an *unsaturated* alkyl group. Such a process should be relatively facile, by an addition–elimination sequence, whereas a similar reaction involving a *saturated* alkyl group, as in FpMe, would be highly unfavorable.[7] This would explain the different reactivities of the two complexes. According to this scheme, similar behavior would be anticipated for Fp(allyl) and was in fact found: Fp(allyl) reacts with P(OMe)_3 over several hours in the dark, to give the substituted Fp′(allyl);[12] irradiation causes only gradual conversion into $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(\eta^3\text{-allyl})$,[13] while irradiation with added Fp$_2$ gives complete substitution in 10 min. It is noteworthy that there does not appear to be any direct photosubstitution of either FpCp or Fp(allyl), in contrast to the behavior of saturated alkyl analogues;[14] photolysis under conditions not favoring the chain path leads only to the above-mentioned CO-elimination products, ferrocene and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)}(\eta^3\text{-allyl})$, respectively.

While the above provides strong support for the involvement of a radical-chain path, the specific scheme proposed and, in particular, the key step in which the unsaturated alkyl group is transferred from one metal to another remain to be demonstrated. Evidence for the alkyl transfer was obtained, under both photoactivation and dark substitution conditions, by the following crossover experiments.

(i) A solution containing equimolar amounts of FpCp and $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Fe(CO)}_2]_2$ (MeFp$_2$) in benzene was irradiated for 1 h; the NMR showed about a 75% decrease in FpCp and much more complex patterns in the regions for both η^5-Cp ring and CH$_3$ protons. Chromatography on alumina gave three fractions, corresponding to ferrocene, FpCp, and Fp$_2$, respectively. However, ^{1}H NMR showed that *each* fraction contained both unsubstituted $(\eta^5\text{-C}_5\text{H}_5)$ and methyl-substituted $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)$ compounds. This indicates that the following transfer scheme is taking place:

$$\text{MeFp}_2 \overset{h\nu}{\rightleftarrows} 2\text{MeFp}\cdot \tag{5}$$

$$\text{MeFp}\cdot + \text{FpCp} \rightleftarrows \text{MeFpCp} + \text{Fp}\cdot \tag{6}$$

$$2\text{Fp}\cdot \underset{h\nu}{\rightleftarrows} \text{Fp}_2 \tag{7}$$

$$\text{FpCp (+ MeFpCp)} \xrightarrow{h\nu} \text{ferrocenes} + 2\text{CO} \tag{8}$$

(ii) A benzene solution containing equimolar amounts of MeFpCp and Fp(allyl) was treated with P(OMe)_3. After 20 min no starting complexes remained; new NMR peaks were present corresponding to Fp′(allyl) as well as the product previously characterized in the reaction of FpCp with P(OMe)_3, $\text{CpFe(CO)[P(OMe)}_3][\text{PO(OMe)}_2]$.[1,15,16] Concentration and extraction with hexane left the latter, which was shown by NMR to be an approximately equimolar mixture of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)[P(OMe)}_3][\text{PO(OMe)}_2]$ and $(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{Fe(CO)[P(OMe)}_3][\text{PO(OMe)}_2]$. This result demonstrates both the transfer of the η^1-Cp group between metal centers and the existence of a common intermediate in the substitution reactions of the two complexes.

Further support for the intermediacy of radicals can be found in reactions of FpCp with PMePh$_2$. In acetone, the major identifiable product is Fp$_2$;[1] in an acetone–chloroform mixed solvent,[18] the major product is $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe(CO)(PMePh}_2)_2]\text{Cl}$, which was isolated as the PF$_6$ salt.[12] Abstraction of halogen from halocarbons is typical of metal-centered radicals,[19] including Fp·.[20] No FpCl, Fp′Cl, or

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$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(PMePh_2)]Cl$ could be detected. This indicates that Fp undergoes CO replacement with phosphine much faster than Cl abstraction from chloroform, consistent with earlier observations.[21] It also suggests that the reaction of Fp′· with chloroform is an outer-sphere electron transfer rather than an inner-sphere atom abstraction, since the latter would lead to Fp′Cl which would undergo chloride substitution to the observed product only slowly.[23]

A substantial body of chemistry of (unsaturated alkyl) metal complexes, especially Fp(allyl), has been generated by taking advantage of the capacity of the unsaturated group to undergo electrophilic attack.[24] The homolytic displacement mechanism shown here offers the potential for further expanding the scope of such systems, with regard to both mechanistic understanding[25] and new synthetic methods.

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(4) A small initial acceleration of Fp′Cp formation (~5% in 5 min) is observed, but this quickly ceases. In the presence of a small amount of added galvinoxyl—an effective radical scavenger—even this initial enhancement is suppressed. All irradiations were carried out in thin-walled Pyrex NMR tubes, using a low-intensity, long-UV (λ_{max} ~3600 Å) lamp.
(5) With 10% Fp_2 (based on FpCp) added, a 25% conversion into Fp′Cp after 5 min is observed. On further irradiation, disappearance of FpCp continues at about the same rate, but appearance of Fp′Cp slows while ferrocene formation increases, indicating the rate of photoconversion of Fp′Cp into ferrocene has become nearly equal to the rate of its formation. Irradiation for very prolonged periods gives virtually complete conversion into ferrocene.
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(16) Formation of this product is believed to arise from an intramolecular Arbuzov-like rearrangement of the intermediate substitution product, with a free double bond on the $\eta^1\text{-}C_5H_5$ acting as nucleophile; $C_5H_5CH_3$ is also formed.[1] A model for this transformation can be seen in the rearrangement of $CpM(CO)_2(EMe_2)[P(OMe)_3]$ to $CpM(CO)_2(EMe_3)[PO(OMe)_2]$ (M = Mo, W; E = As, Sb) which similarly involves transformation of trimethyl phosphite to a phosphonate ligand.[17]
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(21) Based upon data obtained from competition experiments,[22] the rate constant for the reaction of Fp· with chloroform is estimated as ~1 $mol^{-1}\ s^{-1}$; under conditions used here, this would give a pseudo-first-order rate constant of 2.5 s^{-1}. The rates for substitution of Fp· have not been measured, but the corresponding first- or pseudo-first-order rate constant for phosphine substitution in $Mn(CO)_5$· is at least several orders of magnitude higher.[6] Reaction with chloroform involves net oxidation of the metal and hence should be much more facile for the more electron-rich phosphine-substituted radical.
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(25) For example, it has been noted that $Fp(CH_2CH{=}CD_2)$ readily equilibrates under mild conditions to a 1:1 mixture with its isomer $Fp(CD_2CH{=}CH_2)$;[26] while no mechanism was proposed, it is tempting to ascribe this loss of regiochemistry to the homolytic displacement process, since in an addition–elimination mechanism for displacement each transfer would change the end of the allyl group bonded to iron. Also, the insertion of SO_2 into M–R bonds has recently been found to go by a closely related radical-chain path in certain cases.[27]
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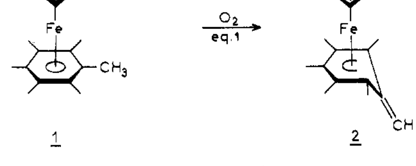
Novel Reactions of Dioxygen in Organometallic Chemistry. Hydrogen Atom Abstraction vs. Dimerization of the 19-Electron Complexes η^5-Cyclopentadienyliron(I) η^6-Arene

Sir:

Stoichiometric and catalytic activation of arenes has attracted much interest.[1] For example the reactivity of η^6-arene-$Cr(CO)_3$ complexes has proved of considerable help in organic synthesis.[2] On the other hand the interaction of $^3O_2$, $^1O_2$, and O_2^-· with organic and organometallic compounds is becoming a subject of increasing attention since it is relevant to synthesis of models and biological processes. Yet the known modes of reaction involve the attachment of one or two oxygen atoms onto the metal or onto an organic moiety. In particular when simple electron transfer occurs with a complex (A) according to $A + {}^3O_2 \rightarrow A^+ + O_2^-\cdot$, further interaction between these two latter species is not known.[3] We report now two peculiar reactions of O_2 on the 19-electron complexes η^5-CpFe–η^6-arene: the hydrogen atom abstraction by O_2 from a methyl group in $\eta^5\text{-}C_5H_5Fe\text{–}\eta^6\text{-}C_6(CH_3)_6$ and the O_2-induced dimerization of $\eta^5\text{-}C_5H_5Fe\text{–}\eta^6$-arene when the benzene ligand bears less than six methyl groups.

The green 19-electron complex $\eta^5\text{-}C_5H_5Fe\text{–}\eta^6\text{-}C_6(CH_3)_6$[4] (**1**) instantaneously reacts with 0.25 mol of O_2 or more simply contact with dry air (25 °C) in pentane or DME affords 0.5 mol of H_2O and the novel red diamagnetic complex (**2**) (eq 1)



in 90% crude yield (60% of crystals by slowly cooling down the filtered pentane solution to −40 °C). Anal. Calcd for $FeC_{17}H_{22}$: Fe, 19.79; C, 72.35; H, 7.86. Found: Fe, 19.61; C, 72.32; H, 8.07.

Minute amounts of H_2O_2 and of a precipitate of $\eta^5\text{-}C_5H_5Fe\text{–}\eta^6\text{-}C_6(CH_3)_6{}^+OH^-$ (≃10%) are also formed. The

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