donors, another predominantly for aromatic donors, with least-squares slopes $-0.067 \pm 0.005$ mol/kcal and $-0.105 \pm 0.006$ mol/kcal, respectively. The rate constants for the most reactive compounds, **1**, **16**, and **10**, level off and may be approaching diffusion control. The values of slope are much lower than 0.74[14] observed in systems in which quenching of fluorescence occurs *via* complete electron transfer, while the rate constants span the same range, $10^6$–$10^{10}$ $M^{-1}$ sec$^{-1}$. Only small solvent effects are observed. Values of $k_{ir}$ for benzophenone–2-butylamine rise by a factor of 1.3 and for di-*n*-butyl sulfide by 2.0 in acetonitrile as compared with benzene, whereas the corresponding factor for fluorescence quenching involving full charge transfer is 13.[13] The reduction potential of benzophenone is 1.73 V,[20] and from eq 2 and 3 it may be calculated that activation energies for transfer of a full unit of charge from most of the donors would be too great to lead to the high observed values of $k_{ir}$. This, the slopes, and the solvent effects indicate that these interactions of excited benzophenone with electron donors involve only partial transfer of charge, and may be rapid because of mixing with partial transfer of $\alpha$ H. The low reactivity of the bicyclic amine Abco and of di-*tert*-butyl sulfide is consistent with such a mixed process. Their values of $k_{ir}$ increase by factors of 5.7 and 2.7, respectively, as solvent is changed from benzene to acetonitrile, indicating somewhat larger, but still partial charge transfer. Partial charge transfer enhances intersystem crossing from excited triplet to ground-state singlet, as it may enhance crossing from excited singlet to excited triplet.[21] That 2-propanol (**9**) lies on the line may further indicate that interaction with both $\alpha$ H and $n$ electrons is a general mechanism for interaction with such aliphatic compounds. Polar contribution to stabilization of the transition for abstraction of hydrogen from alcohols,[1] and abstraction of H from amines *via* CT interaction, may differ as the process starts and be similar at the transition state.

The aromatic compounds show lower ionization potentials and generally *lower* values of $k_{ir}$ than their aliphatic analogs. These values show more sensitivity to *IP*, indicating a higher degree of charge transfer. Interaction with aromatic donors may be predominantly with the $\pi$ electrons[22] of the highest occupied molecular orbital, with less interaction with $\alpha$ H, if that is present, in the transition state.

A related study of interaction of a $\pi,\pi^*$ excited triplet with a series of donors, and the application of the second relationship, $\log k_{ir} \approx (-{}^3\Delta E_{0,0} - E(A^-/A)) + C''$, to interaction of acceptors of varied excited state configurations with a constant donor will be published elsewhere.

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[22] D. W. Turner, *Advan. Phys. Org. Chem.*, 4, 31 (1966).

**Joseph B. Guttenplan, Saul G. Cohen***
*Department of Chemistry, Brandeis University*
*Waltham, Massachusetts 02154*

*Received October 12, 1971*

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## Reactions of Iron Atoms with Unsaturated Hydrocarbons

*Sir:*

We wish to outline the reactions of iron atoms with unsaturated hydrocarbons, to describe some new experiments which further illustrate the chemistry of metal atoms, and to report the synthesis of several novel organometallic compounds by the metal atom codeposition technique.

Iron atoms were obtained by resistively heating alumina or zirconium oxide crucibles containing iron powder (>99% Fe) to 1500° at a pressure of $10^{-3}$ Torr or less. The atoms then produced were cocondensed with hydrocarbons at −196° using the type of apparatus previously described for use in carbon atom reactions.[1]

When iron atoms and 1,3-butadiene are cocondensed at −196° and the reaction mixture is warmed to room temperature, no volatile organometallic compound is obtained. However, a dark residue remains from which, under various conditions, it is possible to synthesize organometallic compounds by displacement.[2] Thus, if the reaction mixture is warmed to −78°, stirred 1 hr (at which temperature the residue is in suspension in the butadiene), and cooled to −196°, $PF_3$ or CO is added, and the mixture is warmed to room temperature, compounds of structure Fe(1,3-$C_4H_6$)$_2$L can be isolated.

Bis(1,3-butadiene)trifluorophosphineiron(0) was obtained in 3.2% yield, as orange-yellow crystals: mp 185–192° dec (sealed tube); nmr ($C_6D_6$) multiplet $\tau$ 5.6 (4 H), multiplet 9.1 (4 H), multiplet 10.6 (4 H); mass spectrum (70 eV, 100°) $-m/e$ 252 (10%, $M\cdot^+$), 164 (55%), 110 (100%).

Bis(1,3-butadiene)carbonyliron(0) was isolated in similar yield: orange-red crystals; mp 130–137° dec (lit. 130–135°); mass spectrum and ir spectrum as reported.[3]

If the displacing $\pi$-acceptor ligand is removed at −78°, then volatile compounds containing more than one iron atom are also obtained. We believe that these may contain bridging butadiene ligands, which are displaced at higher temperatures, and that the dark involatile residue obtained if no $\pi$-acceptor ligand is added consists to a certain extent of chains of iron atoms bridged with butadiene ligands. In this way the iron atoms produced by vaporization are prevented from recombining and the residues obtained remain active toward reagents which do not react with bulk metal at these temperatures.

When iron is cocondensed with 1,3-cyclohexadiene and the mixture is warmed to −20° and stirred for 1 hr, catalytic disproportionation of the hydrocarbon to cyclohexene and benzene occurs. In a typical run, 4.4 mmol of iron was vaporized and converted 120 mmol of the cyclohexadiene into a mixture containing 33.4% cyclohexene, 30.2% cyclohexadiene, and 36.4% benzene. The known complex benzene(1,3-cyclohexadiene)iron(0) is also produced: red crystals; 1.7%

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[1] P. S. Skell, L. D. Wescott, Jr., J.-P. Goldstein, and R. R. Engel, *J. Amer. Chem. Soc.*, 87, 2829 (1965).

[2] After removal of excess butadiene by pumping at −78°, treatment of the residue with water releases 0.93 mmol of $C_4$ hydrocarbons/mmol of iron deposited in the reaction zone.

[3] E. Koerner von Gustorf, J. Buchkremer, Z. Pfajfer, and F. W. Grevels, *Angew. Chem., Int. Ed. Engl.*, 10, 260 (1971).

yield; mp 102–104° (lit. 102–104°); nmr as published.[4]

Iron complexes have also been produced by displacement reactions on the products of codeposition with aromatics. Timms has reported the possible existence of bis-$\pi$-arene–iron complexes at low temperatures.[5] When iron and toluene were cocondensed and warmed to $-94°$, stirred 1 hr, and cooled to $-196°$, and $PF_3$ was added and the resultant mixture warmed to room temperature, a volatile red liquid bis(trifluorophosphine)tolueneiron(0) was obtained (20% yield): nmr ($C_6D_6$) multiplet $\tau$ 5.2 (5 H), singlet 8.2 (3 H); mass spectrum (70 eV, 70°) —$m/e$ 324 (6%, $M\cdot^+$), 236 (6%), 148 (33%), 92 (78%), 91 (100%).

1,3-Butadiene may also be used as a displacing reagent. Typically, iron and toluene were codeposited at $-196°$, 1,3-butadiene was added after vaporization of iron was completed, and the mixture was warmed to $-15°$. A volatile red liquid 1,3-butadiene(toluene)iron(0) could be pumped off (10–20% yield): nmr ($(CD_3)_2CO$) multiplet $\tau$ 4.8 (5 H), multiplet 5.5 (2 H), singlet 7.9 (3 H), doublet 9.05 (2 H), doublet 11.1 (2 H); mass spectrum (70 eV, 100°) —$m/e$ 202 (23%, $M\cdot^+$), 148 (50%), 92 (70%), 91 (100%).

From this series of reactions it thus becomes clear that the codeposition technique could be very useful for the synthesis of organometallics difficult to obtain by other routes. In particular, it is now possible to synthesize a wide variety of metal–hydrocarbon–$PF_3$ complexes. We have already obtained complexes of this type from Co, Ni, and Cr and these will be reported at a later date.

**Acknowledgment.** The financial support of the Air Force Office of Scientific Research (1983) is acknowledged with gratitude. L. R. Wolf thanks the National Science Foundation for a Graduate Fellowship.

(4) E. O. Fischer and J. Muller, *Z. Naturforsch. B*, **17**, 776 (1962).

(5) P. L. Timms, *Chem. Commun.*, 1033 (1969).

**D. L. Williams-Smith, L. R. Wolf, P. S. Skell***
*Department of Chemistry, The Pennsylvania State University*
*University Park, Pennsylvania 16802*

*Received March 20, 1972*

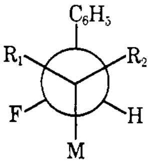
## Oxidative Addition to Iridium(I). A Free-Radical Process

*Sir:*

Two general mechanisms have been proposed for the oxidative addition of alkyl halides to square Ir(I) complexes: (i) an $S_N2$ process in which Ir(I) acts as a nucleophile;[1,2] (ii) a concerted, three-center addition.[3] We wish to present evidence which indicates that oxidative addition to Ir(I) can proceed *via* a free-radical pathway.

Many alkyl halides are found to undergo addition to *trans*-$Ir(PMe_3)_2COCl$ (I) at greatly enhanced rates if small quantities of molecular oxygen or radical initiator are present. The reaction is highly sensitive to adventitious impurities (which may cause catalysis or inhibition) and very careful purification procedures are necessary to obtain consistent results.[4] This may explain apparently contradictory observations recently reported.[2,5]

Typical of the reactions studied is that between I and the primary halides[6] IIa–c. II (1.0 mmol) in $CH_2Cl_2$ or $C_6H_6$ (1.0 ml) was thoroughly degassed on a vacuum line and added to I (0.5 mmol); 5 mol % (based on iridium) of oxygen was admitted. The reaction was complete in *ca.* 15 min at 25° as indicated by the disappearance of the carbonyl stretching band of I at 1945 $cm^{-1}$ and the growth of the adduct, III, absorption[8] at 2037 $cm^{-1}$. Work-up of the reaction mixture yielded III as a pale cream solid (in 75% yield) which was recrystallized from $CH_2Cl_2$–*n*-hexane as colorless needles (mp 147–150° dec). This compound exhibits a strong band at 2037 $cm^{-1}$ and has been fully characterized by elemental analysis, mass spectroscopy, and $^1H$ and $^{19}F$ nmr data (*vide infra*).



II, M = Br
III, M = $Ir(PMe_3)_2COClBr$

a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = D$
c, $R_1 = D$; $R_2 = H$

Evidence that these reactions proceed *via* a free-radical pathway is indicated as follows.

(i) The addition can be similarly initiated[9] by radical sources such as AIBN or benzoyl peroxide. These studies were carried out in sealed tubes with 5 mol % initiator present after four freeze-pump-thaw cycles at $10^{-6}$ Torr. The adducts obtained are identical in every respect with those produced by oxygen initiation.

(ii) The presence of small quantities of radical scavenger such as duroquinone or hydroquinone retards addition.

(iii) There is loss in stereochemistry at carbon in products III. This is evident from the observation that the $^1H$ and $^{19}F$ spectra of the products of I with *either* IIb *or* IIc *are identical.* The $^1H$ spectrum of the proton gem to fluorine in the product consists of two superimposed patterns (Figure 1a): a doublet of doublets resulting from IIIb ($^2J_{H-F} = 48$ Hz, $^3J_{H-H} = 12$ Hz; $^3J_{H-D} < 1$ Hz), and a doublet of multiplets corresponding to the same proton in IIIc ($^2J_{H-F} = 48$ Hz, $^3J_{H-H}$ and $^3J_{H-D} < 3$ Hz (unresolved)). The protons gem to iridium are obscured by the $PMe_3$ resonances. The $^{19}F$ spectrum (Figure 1b) shows a double doublet for IIIc ($^2J_{F-H} = 48$ Hz, $^3J_{F-H} = 53$ Hz, $^3J_{F-D} < 3$ Hz (unresolved)) superimposed upon an equally intense doublet of multiplets for IIIb ($^2J_{F-H} = 48$ Hz, $^3J_{F-H}$

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(1) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966).

(2) J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970).

(3) R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970).

(4) *trans*-$Ir(PMe_3)_2COCl$ was sublimed three times *in vacuo* before use; alkyl halides were purified by distillation at reduced pressure through an adiabatic annular Teflon spinning-band column; $CH_2Cl_2$ was distilled from $CaH_2$ under argon; $C_6H_6$ was distilled from sodium under argon.

(5) F. R. Jensen and B. Knickel, *J. Amer. Chem. Soc.*, **93**, 6339 (1971).

(6) These compounds were prepared by treating the appropriate styrene[7a,b] with *N*-bromoacetamide in liquid HF.[7c] The $^{19}F$ spectra of IIb and c are shown in Figure 1c,d and indicate the deuterio compounds to be isomerically pure to *ca.* >85%.

(7) (a) J. W. Cornforth, J. W. Redmond, H. Eggerer, W. Buckel, and C. Gutschow, *Eur. J. Biochem.* **14**, 1 (1970); (b) M. Buza and E. I. Snyder, *J. Amer. Chem. Soc.*, **88**, 1161 (1966); (c) F. L. M. Pattison, D. A. V. Peters, and F. A. Dean, *Can. J. Chem.*, **43**, 1689 (1965).

(8) It has been reported[5] that this new band results from the interaction of I with molecular oxygen. This is incorrect since oxygen reacts with I to give several products, but none show an absorption between 2020 and 2040 $cm^{-1}$.

(9) Reactions initiated by AIBN were carried out at 60°.