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-π-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 τ 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 τ 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.

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

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

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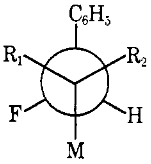
Oxidative Addition to Iridium(I). A Free-Radical Process

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).

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(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°.

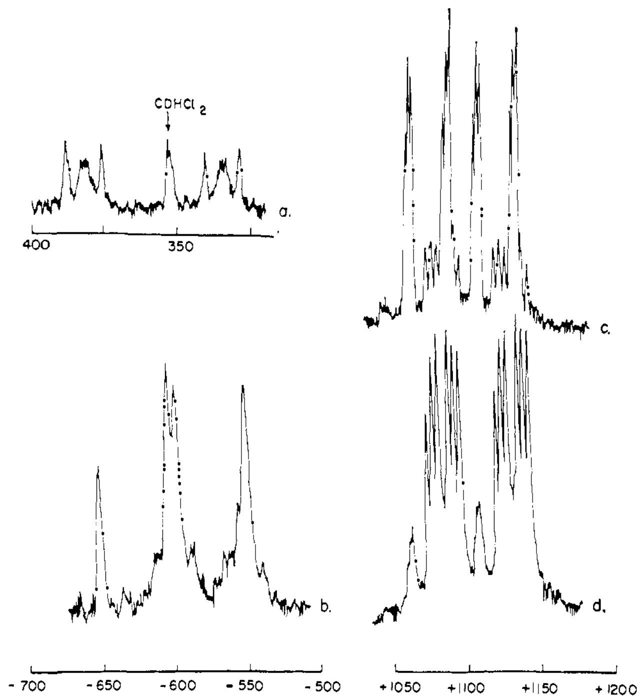

Figure 1. (a) ^1H spectrum of adduct of I with IIb or IIc; recorded at 60 MHz in CD_2Cl_2; shift relative to external TMS. (b) ^{19}F spectrum of same adduct. (c) ^{19}F spectrum of IIc. (d) ^{19}F spectrum of IIb. All ^{19}F spectra recorded at 94.1 MHz in CH_2Cl_2; shift relative to external C_6F_6.

and $^3J_{F-D} < 10$ Hz (unresolved)).[10] These data are only consistent with the formation of approximately equimolar quantities of the two diastereomers IIIb and IIIc from either IIb or IIc.

(iv) The addition of *trans*- or *cis*-1-bromo-2-fluorocyclohexane to I is efficiently initiated by oxygen to give the Ir(III) adducts which were isolated in high yield and fully characterized.[11] The products from both trans and cis show identical ^{19}F spectra also indicating loss of configuration at carbon during this process. Although an unambiguous structural assignment cannot be made from the observed spectra,[12] our original claim that these reactions occurred with stereospecific inversion of configuration is incorrect.[2]

(v) Competitive experiments with or without initiator indicate the following relative reactivity sequence: II > 1-bromo-2-phenylethane ~ *trans*-1-bromo-2-fluorocyclohexane ~ *cis*-1-bromo-2-fluorocyclohexane > bromocyclohexane. The accelerating effect of an electron-withdrawing substituent in these reactions has precedent in related radical processes involving alkyl halides.[13]

In analogy with related reactions of alkyl halides with complexes of Co(II) and Cr(II) which occur *via* radical pathways,[14] an attractive mechanism presents itself for oxidative addition to Ir(I).

$$\begin{aligned} \mathrm{Ir^{I}} + \mathrm{Q}\cdot &\longrightarrow \mathrm{Ir^{II}\text{–}Q} \\ \mathrm{Ir^{II}\text{–}Q} + \mathrm{R\text{–}Br} &\longrightarrow \mathrm{Br\text{–}Ir^{III}\text{–}Q} + \mathrm{R}\cdot \qquad (\mathrm{Q}\cdot = \text{initiator}) \\ \mathrm{Ir^{I}} + \mathrm{R}\cdot &\longrightarrow \mathrm{Ir^{II}\text{–}R} \\ \mathrm{Ir^{II}\text{–}R} + \mathrm{RBr} &\longrightarrow \mathrm{Br\text{–}Ir^{III}\text{–}R} + \mathrm{R}\cdot \end{aligned}$$

However, it is noteworthy that CH_3I reacts extremely rapidly with I (unlike systems known to follow a radical path[14b]) even in the presence of radical inhibitors, indicating that an alternate pathway(s) can be operative for certain substrates.

Investigations are proceeding toward determining the scope of free-radical processes in oxidative addition and the potential utility of such processes in synthesis and catalytic behavior in transition metal chemistry.

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[10] A deuterium isotope effect on the ^{19}F chemical shift of IIIb and c (*ca.* 26 Hz) and IIb and c (10.5 Hz) is evident (Figure 1b–d). Spectra measured at 56.45 MHz confirm the presence of two species.

[11] Despite extreme precautions we find that adduct formation still occurs (albeit slowly) in the absence of initiator. This is contrary to other observations.[5] This uninitiated reaction is, however, inhibited by duroquinone. These differing observations therefore may result from the presence of a trace of inhibitor or initiator under differing experimental conditions.

[12] Unlike the solution ^{19}F data previously reported,[2] the spectra of the isolated adducts are most consistent with the presence of two species with almost coincident chemical shifts.

[13] L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).

[14] (a) J. Kochi, *Rec. Chem. Progr.*, 27, 207 (1966); (b) J. Halpern, *Accounts Chem. Res.*, 3, 386 (1970), and references cited therein.

[15] National Science Foundation Predoctoral Fellow.

Some Ring Size Effects in the Intramolecular Transannular Cyclizations of Macrocyclic Alkadiynes with Iron Carbonyls

Sir:

Recent work[1,2] has shown that macrocyclic alkadiynes of the type I ($m = 4$, $n = 4$, 5, or 6; $m = 5$, $n = 5$ or 6) undergo an intramolecular transannular cyclization reaction with $C_5H_5Co(CO)_2$ to give the tricyclic cyclobutadiene derivatives II of stoichiometry C_5H_5Co(alkadiyne). Previous work[3] has also shown that the macrocyclic alkadiyne 1,8-cyclotetradecadiyne (I, $m = n = 5$) reacts with $Fe(CO)_5$ to undergo a different type of intramolecular transannular cyclization reaction resulting in the formation of the tricyclic cyclopentadienyl derivative $[C_{14}H_{19}Fe(CO)_2]_2$ of structure III ($m = 4$; $n = 5$). This communication reports other intramolecular transannular cyclization reactions of macrocyclic alkadiynes of the type I with iron carbonyls. Of particular interest is the observation of a strong dependence of the nature of the intramolecular transannular cyclization product on the number of methylene groups (m and n in I) bridging each side of the pair of carbon–carbon triple bonds, an effect not observed in the previously reported[1,2] intramolecular transannular cyclizations of the same macrocyclic alkadiynes (I) with $C_5H_5Co(CO)_2$.

The macrocyclic alkadiyne 1,7-cyclotetradecadiyne (I, $m = 4$; $n = 6$) unlike the isomeric but more sym-

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[1] R. B. King and A. Efraty, *J. Amer. Chem. Soc.*, **92**, 6071 (1970).

[2] R. B. King and A. Efraty, *ibid.*, **94**, 3021 (1972).

[3] R. B. King and C. W. Eavenson, *J. Organometal. Chem.*, **16**, P75 (1969).