Electron-Transfer Mechanisms for Organometallic Intermediates in Catalytic Reactions

Jay K. Kochi

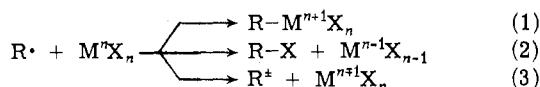*Department of Chemistry, Indiana University, Bloomington, Indiana 47401*

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Organometallic intermediates play a crucial role in a variety of organic and biochemical reactions, particularly those catalyzed by transition-metal complexes.[1] Although a number of qualitative mechanisms have been proposed, there is almost no fundamental insight into how bonds between carbon and metals are made and broken in organometallic species.

Organic reaction mechanisms are generally characterized by two-electron changes (*i.e.*, electron-pair processes), whether they proceed by ionic or free-radical pathways. In inorganic chemistry, on the other hand, one-electron changes (*i.e.*, electron-transfer processes) are well established in a variety of oxidation–reduction reactions. To bridge this dichotomy, we have felt that the concept of electron transfer should play an even wider role in the reactions of organometallic intermediates than heretofore suspected.[2]

We have emphasized the importance of one-electron processes in catalytic reactions by examining the reactions of organometallic model compounds. In this Account we wish to describe mainly our studies aimed at probing some of the problems presented in the study of alkyl transfers in organometallic intermediates.

Reactions involving discrete one-electron changes represent the most direct method for mechanistic studies of complex organometallic processes. Our initial approach to studying these reactions is to deal directly with various oxidation–reduction processes of the free-radical intermediates, which are necessarily constrained to one-equivalent changes as we described in a recent review.[3] Unambiguous methods for producing and reacting transient alkyl radicals are the basis for these studies. Thus, the reaction of an alkyl radical (R) with a metal complex (MX_n) may lead to the formation of an alkyl–metal bond, ligand transfer, or electron transfer, as described in reactions 1–3, respectively.[4]

$$R\cdot + M^nX_n \begin{cases} \longrightarrow R-M^{n+1}X_n & (1) \\ \longrightarrow R-X + M^{n-1}X_{n-1} & (2) \\ \longrightarrow R^{\pm} + M^{n+1}X_n & (3) \end{cases}$$

Jay K. Kochi was born in Los Angeles and educated at Cornell University and UCLA. He obtained his Ph.D. degree at Iowa State University with George Hammond in 1952. After an instructorship at Harvard University and NIH Special Fellowship at Cambridge University, he was at Shell Development Co. in Emeryville, Calif., until 1962. He reentered academic work at Case Institute of Technology (later Case Western Reserve University) and moved to Indiana University in 1969 where he is the Earl Blough Professor of Chemistry. His research has included mechanistic studies of organic reactions catalyzed by metal complexes, photochemistry of organometallic compounds, and application of esr spectroscopy to transient organic and organometallic free radicals and to the mechanism of homolytic reactions.

In each case, the metal nucleus undergoes a formal change in oxidation state of one. A homolytic substitution reaction shown in eq 4 is also possible

$$R\cdot + M^nX_n \longrightarrow R-M^nX_{n-1} + X\cdot \tag{4}$$
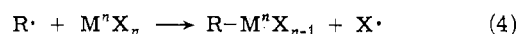
in which the oxidation state of the metal is unchanged.

Alkylation of metal complexes by alkyl radicals presented in eq 1 has been shown to occur in the reaction between copper(II) complexes and alkyl radicals, in which alkylcopper(III) species are important intermediates in the oxidation of alkyl radicals to alkenes given in eq 5.[3] Similarly, an alkylchromi-

$$R\cdot + Cu^{II}(OAc)_2 \longrightarrow [R-Cu^{III}(OAc)_2] \longrightarrow$$

$$R(-H) + Cu^{I}OAc + HOAc \tag{5a}$$
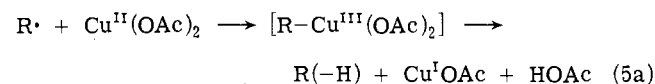
um(III) species is the key intermediate formed during the reduction of alkyl radicals by chromium(II) reagent to alkanes.[5] Finally, four-coordinate phosphoranyl(IV) intermediates arise during the reactions of phosphorous(III) compounds and free radicals, and such an addition–elimination sequence forms the basis of a number of ligand substitution reactions.[6] All of these examples represent facile reactions, with a second-order rate constant greater than 10^4 M^{-1} sec^{-1}, since they must compete with other radical reactions which generally limit the lifetimes of alkyl radicals in solution to less than a millisecond.[7]

The rise and fall of the oxidation state of the metal resulting from the attachment of a free radical to the metal nucleus followed by the subsequent loss of a ligand from the metastable organometallic intermediate constitute the basis for a number of catalytic

(1) M. M. Taqui Khan and A. E. Martell, "Homogeneous Catalysis by Metal Complexes," Vol. I and II, Academic Press, New York, N. Y., 1974; G. N. Schrauzer, Ed. "Transition Metals in Homogeneous Catalysis," Marcel Dekker, New York, N. Y., 1971.

(2) This notion merely represents a resuscitation of the Michaelis postulate which has been largely neglected by organic chemists after its universality was refuted (R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, New York, N. Y., 1964, p 6 ff).

(3) J. K. Kochi, "Free Radicals," Wiley-Interscience, New York, N. Y., 1973, Chapter 11; J. K. Kochi, A. Bemis, and E. L. Jenkins, *J. Amer. Chem. Soc.*, 90, 4616 (1968).

(4) Coordination around the metal center hereinafter will be largely unspecified unless required for the discussion (L and X generally denote neutral and anionic ligands, respectively). Oxidation numbers are included only as a bookkeeping device, and are not necessarily intended to denote actual changes in oxidation states (*cf.* (a) C. K. Jorgensen, "Oxidation Numbers and Oxidation States," Springer-Verlag, New York, N. Y., 1969; (b) J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968); (c) J. Halpern, *ibid.*, 3, 386 (1970).

(5) J. K. Kochi and D. D. Davis, *J. Amer. Chem. Soc.*, 86, 5264 (1964); J. K. Kochi and J. W. Powers, *ibid.*, 92, 137 (1970).

(6) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 91, 3944 (1969); K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971.

(7) K. U. Ingold, ref 3, Chapter 2.

processes. However, it is not necessary for all oxidation–reduction reactions to occur by inner-sphere processes at the metal site. Thus, the ligand transfer reaction[8] in eq 2 may proceed by a one-step process involving direct displacement on the ligand center by a free radical shown in eq 6. Such an inner-sphere

$$R\cdot + Cu^{II}Br_2 \longrightarrow [R\cdots Br\cdots CuBr]^* \longrightarrow$$

$$R-Br + Cu^{I}Br, \text{ etc.} \quad (6)$$
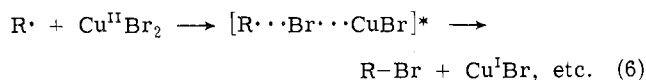
mechanism proceeding by the bridged activated complex has been described for a number of wholly inorganic systems.[9] The microscopic reverse process, *viz.*, the 1-equiv oxidation of a metal complex, is also a fairly common mode of reaction of organic halides, *e.g.*[5,10,11]

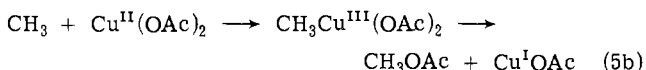$$Cr^{II} + R-Br \longrightarrow Cr^{III}Br + R\cdot \quad (7)$$
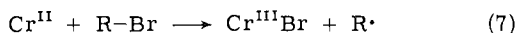
In a similar manner, the substitution reaction represented in eq 4 may proceed by two distinct pathways. A mechanism involving addition to form an organometallic intermediate $R-M^{n+1}X_n$ followed by elimination has been described for three-coordinate phosphorus and arsenic compounds by the observation of transient paramagnetic phosphorus(IV) and arsenic(IV) species by electron spin resonance (esr) spectroscopy.[12] Alternatively, alkyl radicals may react with a metal complex in a one-step process involving direct displacement of a ligand. Thus, no paramagnetic ^{11}B or ^{27}Al intermediates are observed by esr spectroscopy during the facile metathesis of *tert*-butoxy radicals and trialkylboranes and -alanes even when the reactions are carried out at temperatures as low as −100°.[13] The clear mechanistic dis-

$$(CH_3)_3B + t\text{-BuO}\cdot \longrightarrow t\text{-BuOB}(CH_3)_2 + CH_3\cdot$$
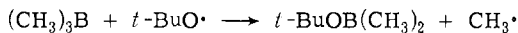
tinction between a substitution process proceeding by addition–elimination or direct displacement rests on the detection of a metal-centered intermediate by the use of esr techniques which can effectively probe for paramagnetic species present in concentrations less than 10^{-6} M and at low temperatures.[14] Substitution reactions such as reaction 4 form the basis of the radical-chain process for the efficient addition of

alkylboron and -aluminum compounds to unsaturated compounds.[15]

Finally, the outer-sphere electron-transfer process represented in eq 3 may be involved in the oxidation of radicals capable of producing more or less stable ionic entities such as trityl, tropyl, or pyryl.[3] More commonly, the formation of carbocations follows the heterolysis of an alkylmetal intermediate such as[16]

$$PhCH_2CH_2\cdot + Cu^{II} \longrightarrow PhCH_2CH_2Cu^{III} \longrightarrow$$
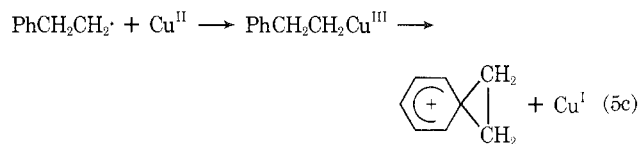
Similarly, except in unusual cases,[17] outer-sphere electron-transfer processes for the reduction of radicals by metal complexes directly to carbanions is not favored relative to the formation of an alkylmetal intermediate followed by reaction at the ligand site[18]

$$ClCH_2CH_2\cdot + Cr^{II} \longrightarrow$$

$$ClCH_2CH_2Cr^{III} \xrightarrow{H_3O^+} \begin{cases} ClCH_2CH_3 + Cr^{III} \\ CH_2{=}CH_2 + Cr^{III}Cl \end{cases}$$

With this background established for one-electron transfer reactions of free radicals and metal complexes, we wish now to examine the mechanisms of more complex organometallic reactions and catalytic processes in which 2-equiv changes may appear to be involved in the overall transformation.

Mechanistic Studies of Alkyl Transfers from Organometallics

There are a number of basic transformations which are of primary importance in the reactions of organometallic intermediates, including: (1) alkyl transfer and aromatic metallations, (2) oxidative addition, (3) reductive elimination, and (4) β elimination and its reverse, addition.[19-21] Most of these processes are commonly considered to proceed by two-electron pathways. In this section we wish to present alternative one-electron mechanisms for these processes, with the principal emphasis on establishing some criteria for distinguishing among various mechanisms.

A. Electrophilic and Electron-Transfer Mechanisms in Alkyl Transfer and Aromatic Substitution. The dichotomy between two-electron and one-electron mechanisms in organometallic reactions is well-illustrated in this Account by two processes: (1) alkyl transfer from σ-alkylmetals and (2) aromatic substitution.

1. Alkyl Transfer from Organometals. Electrophilic processes represent by far the most common path-

(8) J. K. Kochi and D. M. Mog, *J. Amer. Chem. Soc.*, **87**, 522 (1965).

(9) (a) H. Taube, *Advan. Inorg. Chem., Radiochem.*, **1**, 1 (1959). (b) The mechanisms drawn for the two inner-sphere processes, one occurring at the metal center in eq 5 and the other on the ligand site in eq 6, are not readily differentiated, however, since there are examples in which the alkylmetal intermediate undergoes reductive elimination as shown.[10]

$$CH_3 + Cu^{II}(OAc)_2 \longrightarrow CH_3Cu^{III}(OAc)_2 \longrightarrow$$
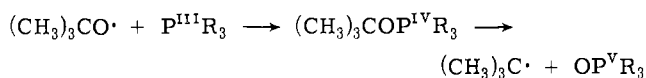
$$CH_3OAc + Cu^{I}OAc \quad (5b)$$

(10) C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 843, 856 (1972).

(11) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **91**, 582 (1969).

(12) P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6033 (1972); A. G. Davies, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, **38**, C8 (1972).
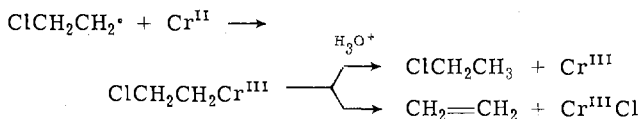
(13) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 3942 (1969); K. U. Ingold, *J. Chem. Soc., Perkin Trans. 2*, 420 (1973); A. G. Davies and B. P. Roberts, ref 3, Chapter 10.

(14) (a) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, **24**, 147 (1970). (b) A less direct indication of the formation of the formation of a metastable adduct lies in the observation of β-cleavage shown below for phosphoranyl(IV) species.[12]

$$(CH_3)_3CO\cdot + P^{III}R_3 \longrightarrow (CH_3)_3COP^{IV}R_3 \longrightarrow$$

$$(CH_3)_3C\cdot + OP^{V}R_3$$

(15) H. C. Brown, M. M. Midland, and G. W. Kabalka, *J. Amer. Chem. Soc.*, **93**, 1024 (1971); G. W. Kabalka and R. F. Daley, *ibid*, **95**, 4428 (1973).

(16) J. K. Kochi, *Pure Appl. Chem.*, **4**, 377 (1971).

(17) K. Okamoto, K. Komatsu, O. Murai, and O. Sakaguchi, *Tetrahedron Lett.*, 4989 (1972).

(18) J. K. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, **24**, 3503 (1968); *J. Amer. Chem. Soc.*, **89**, 6547 (1967); **90**, 1582 (1968).

(19) See ref 4b, c.

(20) P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, **2**, 271 (1973); M. C. Baird, *J. Organometal. Chem.*, **64**, 289 (1974); W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 533 (1972).

(21) Various types of insertion reactions and rearrangements should also be included.

Table I
Rates of Acetolysis of CH_3–Pb and CH_3CH_2–Pb Bonds at 20°

Bond	Compound	Rate constant, 10^6 sec^{-1}		Relative rate[b]	
		k	k'[a]	Found	Calcd[c]
CH_3–Pb	$(CH_3)_4Pb$	7.3	1.8	1.00	1.00
	$(CH_3)_3PbCH_2CH_3$	10	3.3	1.8	1.8
	$(CH_3)_2Pb(CH_2CH_3)_2$	13	6.5	3.6	3.4
	$CH_3Pb(CH_2CH_3)_3$	11	11	6.1	6.2
CH_3CH_2–Pb	$(CH_3CH_2)_4Pb$	4.9	1.2	1.00	1.00
	$(CH_3CH_2)_3PbCH_3$	2.1	0.70	0.56	0.57
	$(CH_3CH_2)_2Pb(CH_3)_2$	0.88	0.44	0.35	0.33
	$CH_3CH_2Pb(CH_3)_3$	0.21	0.21	0.17	0.18

[a] Normalized for each alkyl group. [b] Per alkyl group based on $R_4Pb = 1.00$. [c] Constant multiplicative factor of 1.84 for CH_3–Pb and 1.75 for CH_3CH_2–Pb.

way by which carbon–metal bonds are cleaved.[22] We have chosen organolead compounds for the study of alkyl-transfer reactions, because they incorporate the best features of organometallic systems, *i.e.*, they are reactive but sufficiently substitution stable and well behaved in solution to allow for quantitative study.

(a) Tetraethyllead in acetic acid solutions undergoes protonolysis according to eq 8 with a pseudo-

$$Et_4Pb + HOAc \longrightarrow Et_3PbOAc + EtH \quad (8)$$
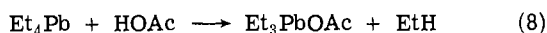
first-order rate constant of 4.9×10^{-6} sec^{-1} at 20° and shows a deuterium kinetic isotope effect of 9.[23] The trends in Table I for a series of methyl and ethyllead compounds indicate that the rates of acetolysis of a particular alkyl–lead bond increase as the methyl groups are successively replaced with ethyl groups in the trialkyllead leaving group.[23] Thus, the reactivity of an ethyl–lead bond is the greatest in tetraethyllead and the least in ethyltrimethyllead. Similarly, the CH_3–Pb bond is the least reactive in tetramethyllead and most reactive in methyltriethyllead. In fact, a constant multiplicative factor S separates the rates of acetolysis between any two contiguous members in the series $(CH_3)_{4-n}Pb(CH_2CH_3)_n$ where $n = 0, 1, 2, 3$, or 4, as listed in the fifth column of Table I. This correlation represents a linear free energy relationship in which the factor S is the sensitivity of the particular alkyl–lead cleavage to methyl or ethyl substitution in the departing trialkylplumbonium ion, *i.e.*

$$k(R) = k_0(R)S^m = k_0(R) \exp(m\Delta\Delta F^*/RT) \quad (9)$$

in which $k_0(R)$ represents the cleavage rate of R_4Pb (where $R = CH_3$ or CH_3CH_2), m is the number of ethyl groups, and $\Delta\Delta F^*$ is the change in the free energy of activation as a result of an ethyl substitution. In particular, the replacement of each methyl group by an ethyl group leads to an approximate doubling of the rate of acetolysis or lowering the free energy of the transition state by about 0.4 kcal mol^{-1}.

When the relative reactivities of methyl and ethyl

groups are compared under conditions of constant leaving group (R_3Pb^+), we find that the ratios of rates of methyl and ethyl cleavage are more or less invariant among all the methylethyllead compounds. This rate ratio (R_0) measures the intrinsic difference between the rates of CH_3–Pb and CH_3CH_2–Pb cleavage. The values of R_0 can also be obtained under conditions in which the absolute rate constants $k(R)$ are unknown and unobtainable. Thus, the following four relative rates can be obtained from studies involving three intramolecular comparisons together with one intermolecular competition (M = methyl, E = ethyl), and it can be shown that

$$[R(M_4/E_4)][R(ME_3)][R(M_2E_2)][R(M_3E)] = R_0^4 \quad (10)$$

The value of R_0 for the acetolysis of methylethyllead compounds computed in this manner is in good agreement with the value obtained from the absolute rate measurements. The procedure outlined in eq 10 can be used to obtain R_0 for the protonolysis of CH_3–Pb and CH_3CH_2–Pb bonds by triflic acid which is too fast to measure accurately by absolute methods. The same general method can also be applied to the cleavage of tetraalkyllead by other electrophiles such as copper(I) and copper(II).[23,24] In every case, CH_3–Pb cleavage is significantly faster than CH_3CH_2–Pb, as shown by the values of R_0 in Table II, and this factor represents a mechanistic criterion for electrophilic cleavage of an alkyl–lead bond. The change of electrophile from CH_3CO_2H to $CH_3CO_2H_2^+$ (triflic acid) is accompanied by a large increase in rate (Table II), but there is also a parallel increase in selectivity, R_0. This trend is opposite to that expected on the basis of a direct proton transfer from the acid to the tetraalkyllead moiety *via* an open transition state. According to the Hammond postulate, the stronger acid in such a formulation should lead to a decrease in selectivity relative to the weaker acid, since bond making (*i.e.*, R⋯H) will not have progressed as far in the transition state. From such a basis, we conclude that the conjugate base X must also be involved directly in the proton-transfer process, as represented in a closed four-centered transition state,[25] and it would be supported by a

(22) F. R. Jensen and B. Rickborn, "Electrophilic Substitution in Organomercurials," McGraw-Hill, New York, N. Y., 1968; M. H. Abraham, *Compr. Chem. Kinet.*, 12, 1 (1972).

(23) N. A. Clinton, and J. K. Kochi, *J. Organometal. Chem.*, 42, 229 (1972); N. A. Clinton, H. C. Gardner, and J. K. Kochi, *ibid.*, 56, 227 (1973).

(24) N. A. Clinton and J. K. Kochi, *J. Organometal. Chem.*, 42, 241 (1972); *ibid.*, 56, 243 (1973).

Table II
### Intrinsic Reactivities of CH_3–Pb and CH_3CH_2–Pb Bonds in Electrophilic Cleavages in Acetic Acid Solutions

Electrophile	Rate constant,[a] l. mol⁻¹ sec⁻¹	R_0	S
HOAc	2.8×10^{-5}	8.7	1.80
HOTf(H_2OAc^+)	$>2 \times 10^{-1}$	48	1.77
Cu^IOAc	3.3×10^{-2}	~56	1.85
$Cu^{II}Cl_2$	10^{-1}	26	1.8
(Mass Spectral Cracking)		0.3	0.7

[a] For reaction of tetraethyllead.

Table III
Reactivity Parameters for $PbMe_nEt_{4-n}$ and $IrCl_6^{2-}$

$PbMe_nEt_{4-n}$	k,[a] l. mol⁻¹ sec⁻¹	Alkyl chloride (mmol)		EtCl/MeCl	IP,[b] eV	E,[c] V
		EtCl	MeCl			
$PbEt_4$	25	0.101			8.13	1.67
$PbEt_3Me$	11	0.104	0.0015	24	8.26	1.75
$PbEt_2Me_2$	3.3	0.101	0.0040	25	8.45	1.83
$PbEtMe_3$	0.57	0.092	0.012	24	8.65	2.00
$PbMe_4$	0.02		0.105		8.90	2.13

[a] Second-order rate constant. [b] Ionization potential. [c] Electrochemical oxidation potential.

$$R_4Pb + HX \longrightarrow \left[R_3Pb \overset{R}{\underset{X}{\diagdown}}H \right] \longrightarrow R_3PbX + HR$$
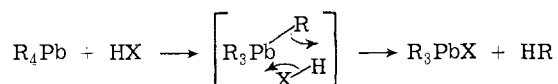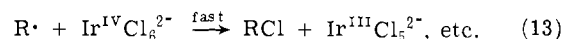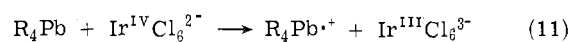
stereochemical study. The catalytic cleavage of alkyllead by copper(I) complexes represents a similar electrophilic process.[23]

(b) Electrophilic processes, however, are not the only routes available for alkyl transfers. Thus, facile alkyl transfers also occur from the same series of organoleads to hexachloroiridate(IV), which is known to participate in outer-sphere oxidations involving one-electron changes.[26] For example, the oxidative cleavage of tetraalkyllead by $2Ir^{IV}Cl_6^{2-}$ occurs rapidly to afford alkyl chloride and $2Ir^{III}$. The kinetics

$$R_4Pb + 2Ir^{IV}Cl_6^{2-} \xrightarrow{HOAc} R_3PbOAc + RCl + 2Ir^{III}$$
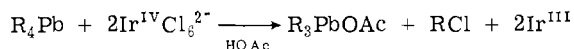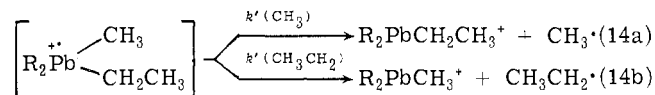
are first order in each reactant. Two important criteria can be used to distinguish this alkyl transfer from the more conventional electrophilic processes described above. First, the rate of reaction of $PbMe_nEt_{4-n}$ with $IrCl_6^{2-}$ increases successively as methyl is replaced by ethyl groups (see $n = 4$ to 0 in Table III, column 2). Second, a given ethyl group is cleaved approximately 25 times faster than a methyl group (column 5). Both of these reactivity trends are diametrically opposed to those established for an electrophilic cleavage as discussed above in Tables I and II. These results suggest that the rate-limiting step with $IrCl_6^{2-}$ occurs prior to alkyl transfer; we propose the mechanism given in Scheme I in which the slow step in eq 11 involves charge transfer. Indeed, there is a linear correlation of the rates (log k)

(25) M. H. Abraham and J. A. Hill, *J. Organometal. Chem.*, 7, 11 (1967).
(26) H. C. Gardner and J. K. Kochi, *J. Amer. Chem. Soc.*, 96, 1982 (1974).

Scheme I

$$R_4Pb + Ir^{IV}Cl_6^{2-} \longrightarrow R_4Pb^{\cdot+} + Ir^{III}Cl_6^{3-} \quad (11)$$

$$R_4Pb^{\cdot+} \xrightarrow{fast} R\cdot + R_3Pb^+ \quad (12)$$

$$R\cdot + Ir^{IV}Cl_6^{2-} \xrightarrow{fast} RCl + Ir^{III}Cl_5^{2-}, etc. \quad (13)$$

of $PbMe_nEt_{4-n}$ with the one-electron oxidation potentials, which are related to the electron-detachment process, $R_4Pb \rightarrow R_4Pb^{\cdot+} + \epsilon$. There is also a striking relationship with the vertical ionization potentials of R_4Pb determined by He(I) photoelectron spectroscopy shown in Figure 1.[26] Selectivity in the transfer of alkyl groups according to Scheme I occurs during fragmentation of the cation radical in a fast subsequent step which is consistent with a mass

$$\left[R_2Pb \overset{\cdot+}{\underset{CH_2CH_3}{\overset{CH_3}{\diagdown}}} \right] \begin{array}{l} \xrightarrow{k'(CH_3)} R_2PbCH_2CH_3^+ + CH_3\cdot (14a) \\ \xleftarrow{k'(CH_3CH_2)} \\ \xrightarrow{} R_2PbCH_3^+ + CH_3CH_2\cdot (14b) \end{array}$$
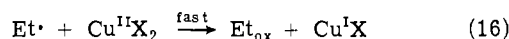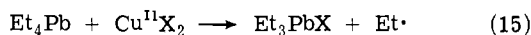
spectral study (Table II) and in accord with expectations based on differences in bond strengths of ethyl and methyl compounds.

Examination of the electron spin resonance spectrum during the reaction with $IrCl_6^{2-}$ did not reveal the presence of the cation radical $PbEt_4\cdot^+$, which must be a highly unstable intermediate even at temperatures as low as $-20°$. Nonetheless, the formation of ethyl radicals in high yields is evident from spin-trapping experiments with nitrosoisobutane. The use of $IrCl_6^{2-}$ as efficient scavenger in the ligand-transfer oxidation of alkyl radicals is implied in Scheme I (eq 13) by the isolation of alkyl chlorides in high yields (even in the presence of a hundredfold excess of bromide ion). Strikingly, separate experiments show that ethyl radicals generated unambiguously from the thermolysis of propionyl peroxide are quantitatively converted by $IrCl_6^{2-}$ to ethyl chloride.

(c) The subtle distinction between electrophilic and charge-transfer processes in alkyl transfers from organometallics is also shown in the very rapid reductions of copper(II) acetate, triflate, and chloride by tetraethyllead which proceed at widely different rates in acetic acid.[24] In all of these cases the ethyl group suffers an overall 2-equiv oxidation such that two Cu(II) are required, *i.e.*
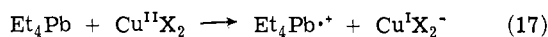
$$Et_4Pb + 2Cu^{II}X_2 \longrightarrow Et_3PbX + 2Cu^IX + Et_{ox}$$
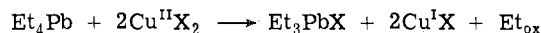
where Et_{ox} = ethylene, ethyl acetate, and ethyl chloride. It is noteworthy that the products (Et_{ox}) are identical with those obtained from the unique reductions of the same Cu(II) complexes by ethyl radicals generated by independent methods developed in earlier studies.[3] We conclude that the ethyl radical is the prime intermediate formed in the reaction of tetraethyllead with Cu(II) as it is with hexachloroiridate above. Moreover, the stoichiometry of the two reactions is the same in that the oxidation of each tetraethyllead requires 2 equiv of copper(II) and iridium(IV).

$$Et_4Pb + Cu^{II}X_2 \longrightarrow Et_3PbX + Et \cdot \qquad (15)$$

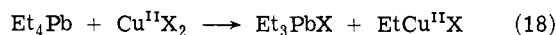$$Et \cdot + Cu^{II}X_2 \xrightarrow{fast} Et_{ox} + Cu^IX \qquad (16)$$

There are essentially two mechanisms by which ethyl radicals can be formed during the reduction of Cu(II) by tetraethyllead (eq 15). An outer-sphere electron transfer in Scheme II is equivalent to the

Scheme II

$$Et_4Pb + Cu^{II}X_2 \longrightarrow Et_4Pb \cdot^+ + Cu^IX_2^- \qquad (17)$$

$$Et_4Pb \cdot^+ \xrightarrow{fast} Et_3Pb^+ + Et \cdot, \text{ etc.} \qquad (12)$$

mechanism previously shown for the stoichiometrically analogous reduction of hexachloroiridate(IV) in Scheme I. Alkyl transfer from tetraethyllead to Cu(II) by an electrophilic process represented in eq 19 is an alternative pathway for reduction. The alkyl radical is formed in this mechanism by a rapid homolysis of an alkylcopper(II) intermediate. In order

Scheme III

$$Et_4Pb + Cu^{II}X_2 \longrightarrow Et_3PbX + EtCu^{II}X \qquad (18)$$

$$EtCu^{II}X \xrightarrow{fast} Et \cdot + Cu^IX, \text{ etc.} \qquad (19)$$
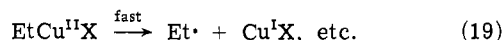
to distinguish between Schemes II and III for the reduction of copper(II), selectivity studies were carried out with various methylethyllead compounds (Table II). An electrophilic pattern consistent only with Scheme III is clearly established in the facile reaction of tetraalkyllead compounds with copper(II) chloride. Therefore, the formation of alkyl radicals during the reduction of copper(II) is associated with the ready homolysis of a metastable alkylcopper(II) intermediate in a subsequent step (eq 19). These conclusions are enlightening in view of prejudices favoring Scheme II by its expected relationship to the mechanism of hexachloroiridate reduction.

2. Aromatic Substitution. Metalation of alkenes and arenes represents a general method of electro-
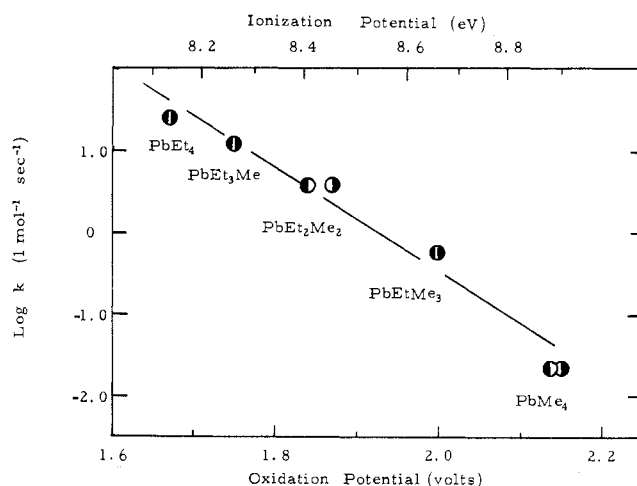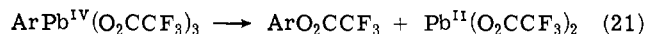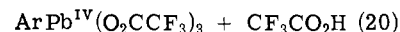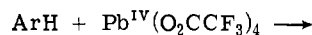

Figure 1. Correlation of the rates of oxidation of $PbMe_nEt_{4-n}$ by $IrCl_6^{2-}$ in acetonitrile with the electrochemical oxidation potential, ● (lower scale), and the vertical ionization potential, ○ (upper scale).

philic catalysis in substitution reactions at trigonal carbon centers. A particularly relevant example is the oxidative substitution of arenes by Pb(IV), in which the detection and isolation of aryllead(IV) intermediates support a mechanism such as[27]

Scheme IV

$$ArH + Pb^{IV}(O_2CCF_3)_4 \longrightarrow$$

$$ArPb^{IV}(O_2CCF_3)_3 + CF_3CO_2H \qquad (20)$$

$$ArPb^{IV}(O_2CCF_3)_3 \longrightarrow ArO_2CCF_3 + Pb^{II}(O_2CCF_3)_2 \qquad (21)$$

Oxidative substitution by this scheme requires the metal oxidant to initially effect electrophilic addition. Indeed, arenes can be metalated by a number of metal carboxylates, such as those derived from mercury(II), thallium(III), lead(IV), and palladium(II). The high yields of aryl esters obtained from the oxidation of arenes including toluene with lead-(IV) trifluoroacetate are traced directly to the reductive elimination from the aryllead(IV) intermediate in eq 21.

Benzene is also readily oxidized by cobalt(III) in high yields to phenyl trifluoroacetate in trifluoroacetic acid solutions at room temperature according to eq 22.[28] The kinetics of the oxidative substitu-

$$C_6H_6 + 2Co^{III}(O_2CCF_3)_3 \longrightarrow$$

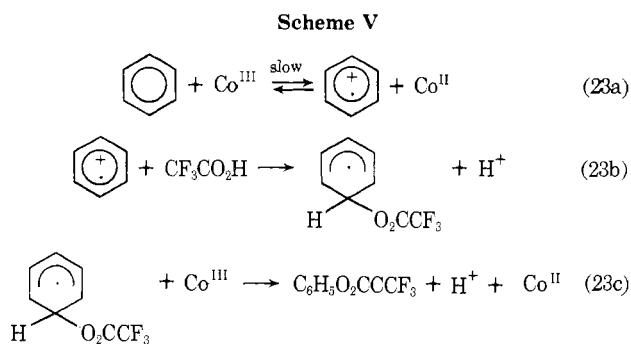$$C_6H_5O_2CCF_3 + 2Co^{II}(O_2CCF_3)_2 \qquad (22)$$
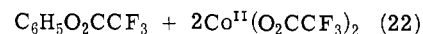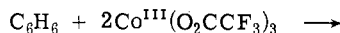
tion, however, indicate that only one Co(III) is involved in, or prior to, the rate-limiting transition state. The kinetic isotope effect, retardation by Co(II), and esr studies support a mechanism involving two successive one-electron transfers such as that presented in Scheme V.

The electron-transfer Scheme V cannot be distinguished *a priori* from the electrophilic Scheme IV. Both mechanisms depend on π-electron availability. For example, the formation of arene cation radicals in Scheme V is determined by the ionization poten-

(27) J. R. Campbell, J. R. Kallman, J. T. Pinhey, and S. Sternhell, *Tetrahedron Lett.*, 1763 (1972); 5369 (1973).

(28) J. K. Kochi, R. T. Tang, and T. Bernath, *J. Amer. Chem. Soc.*, 95, 7114 (1973).

Scheme V

$$\text{C}_6\text{H}_6 + \text{Co}^{III} \underset{\text{slow}}{\rightleftharpoons} \text{C}_6\text{H}_6^{+} + \text{Co}^{II} \qquad (23a)$$

$$\text{C}_6\text{H}_6^{+} + \text{CF}_3\text{CO}_2\text{H} \longrightarrow \underset{\text{H}\ \ \ \ \text{O}_2\text{CCF}_3}{} + \text{H}^+ \qquad (23b)$$

$$\underset{\text{H}\ \ \ \ \text{O}_2\text{CCF}_3}{} + \text{Co}^{III} \longrightarrow \text{C}_6\text{H}_5\text{O}_2\text{CCCF}_3 + \text{H}^+ + \text{Co}^{II} \qquad (23c)$$
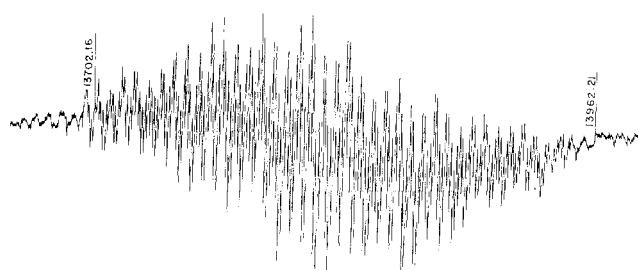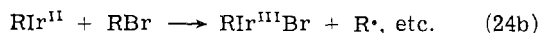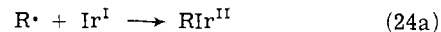

Figure 2. Esr spectrum obtained during the reaction of lead(IV) trifluoroacetate with 2,5-dimethyl-2,4-hexadiene in trifluoroacetic acid at 25°. Proton nmr field markers are in kHz.

tials of the respective arenes, which are directly related to the easily measurable absorption frequencies of the charge-transfer complexes. In turn, the rates of electrophilic substitution of arenes in Scheme IV can also be related to charge-transfer frequencies by a Hammett relationship (using σ^+), provided the substituent causes only a small perturbation on the benzene ring. Thus, ionization potentials and Hammett parameters are indirectly related in these benzenoid systems insofar as the orbital from which the electron is removed by charge transfer has the same symmetry as the orbital which participates in electrophilic attack. In other words, mechanistic distinctions between rate-limiting electron transfer (eq 23a) and electrophilic addition (eq 20) cannot easily be made on the basis of substituent effects. Electron-releasing substituents facilitate and electron-attracting substituents hinder both oxidation processes. Although the differences between the two mechanistic schemes appear to be slight, they can be distinguished in individual cases such as toluene, in which the toluene radical cation reacts differently than the tolylmetal intermediate in Schemes V and IV, respectively.[28]

Judging by this dichotomy, it is not surprising, therefore, to find examples of oxidative substitutions of arenes which proceed competitively *via* both mechanisms. Indeed, reaction of arenes with Tl(III), which is a well-established 2-equiv oxidant like Pb(IV), is generally considered to be an electrophilic process since the one-electron route involves the highly metastable Tl(II) species.[29] Nonetheless, a variety of arene cation radicals detectable by esr are generated under thallation conditions and may be implicated as reaction intermediates in an apparently electrophilic metalation process.[30] The metalation of olefins may involve similar 1-equiv processes, since the esr spectrum of the alkene cation radical can be derived by mixing them with thallium(III) or lead(IV) trifluoroacetates as shown in Figure 2. Finally, the concept of electron transfer in organometallic reactions should not be restricted to electrophilic processes. The generalization to nucleophilic processes with the roles of donors and acceptors reversed has been discussed recently.[30b]

B. Alkylation of Metal Complexes by Oxidative Addition. Alkylation of metal centers may be

achieved by oxidative addition of alkyl derivatives in which the increase in the coordination number of the metal by addition of an alkyl group is accompanied by an increase in its oxidation state.[19] Oxidative addition by free radicals leading to 1-equiv changes was described in the introduction to this Account. Those reactions of alkyl halides involving overall 2-equiv changes (*i.e.*, the alkyl group is electrophilic) have been postulated to proceed *via* an SN2 process, a concerted three-center addition, or a free-radical chain process to conform to the observation of inversion, retention or racemization at the alkyl center.[31] Inversion is a usual consequence of the SN2 process and requires the metal to act as a nucleophile, although displacement of a radical is also possible.[32,33] A three-center process leading to retention of configuration, however, is formally akin to an attack by a metal acting as an electrophilic species,[34] and it is unexpected in a process involving oxidation of the metal acting as an electrophilic species,[34] and it is obscure such a limitation.[33] Indeed, the facility with which successive 1-equiv chain reactions take place may have been underestimated due to their high sensitivity to adventitious impurities, particularly molecular oxygen, which may cause inhibition, retardation, or catalysis.[31] The recent reports of a radical chain process in oxidative addition of alkyl bromides to Ir(I) and Pt(0) complexes are particularly relevant examples, in which the propagation sequence involves a ligand transfer reaction (eq 24b).[35] We are

$$\text{R·} + \text{Ir}^{I} \longrightarrow \text{RIr}^{II} \qquad (24a)$$

$$\text{RIr}^{II} + \text{RBr} \longrightarrow \text{RIr}^{III}\text{Br} + \text{R·, etc.} \qquad (24b)$$

seeking evidence for transient alkyliridium(II) and platinum(I,III) species by esr studies.

C. Reductive Elimination from Alkylmetals:

(29) A. McKillop and E. C. Taylor, *Advan. Organometal. Chem.*, 11, 147 (1973).

(30) (a) I. H. Elson and J. K. Kochi, *J. Amer. Chem. Soc.*, 95, 5061 (1973). (b) The limitation of space does not permit a discussion of electron-transfer processes in nucleophilic reactions of organometals. For a recent report, see W. A. Nugent, F. Bertini, and J. K. Kochi, *J. Amer. Chem. Soc.*, 96, 4945 (1974).

(31) J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970); R. C. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, 92, 5519 (1970); J. A. Labinger, A. V. Kramer, and J. A. Osborn, *ibid.*, 95, 7908 (1973).

(32) R. E. Dessy and L. A. Bares, *Accounts Chem. Res.*, 5, 415 (1972); F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, 92, 1414 (1970).

(33) *Cf.* M. D. Johnson, *et al.*, *J. Chem. Soc., Chem. Commun.*, 685 (1972); 163 (1973); J. H. Espenson and T. D. Sellers, *J. Amer. Chem. Soc.*, 96, 94 (1974); K. M. Nicholas and M. Rosenblum, *ibid.*, 95, 4449 (1973).

(34) D. S. Matteson, "Organometallic Reaction Mechanisms," Academic Press, New York, N. Y., 1974.

(35) J. S. Bradley, D. E. Connor, D. Dolphin. J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, 94, 4043 (1972); J. A. Osborn in "Prospects in Organotransition Metal Chemistry," Plenum Press, New York, N. Y., in press. *Cf.* also M. Lappert and P. W. Lednor, *J. Chem. Soc., Chem. Commun.*, 948 (1973). We have recently shown that typical diamagnetic d^{10} complexes such as those of nickel(0) and platinum(0) are capable of undergoing facile one-electron transfers (I. H. Elson, D. G. Morrell, and J. K. Kochi, to be published).
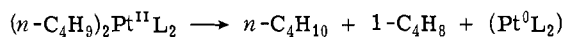
Coupling and Disproportionation. Reductive elimination as the reverse of oxidative addition involves both the reduction of the oxidation number as well as the coordination number of the organometallic intermediate. Conceptually, homolysis of an alkyl-metal bond represents the simplest example of a 1-equiv process in reductive elimination. Thermodynamic data on the strengths of transition-metal-alkyl bonds are scarce, but indirect evidence suggests that the bond dissociation energies are relatively high, being more generally like those of the main group metals.[36] The facile homolysis of alkylcopper(II) described earlier in eq 19 appears to be an exception rather than the rule.

Reductive elimination of alkylmetals involving an overall 2-equiv transformation can proceed in a concerted manner without the involvement of alkyl free radicals.[20,37] Thus, in a series of trialkyl(triphenylphosphine)gold(III) complexes, a pair of cis alkyl groups are reductively coupled to alkane by a first-order elimination process involving a prior dissociation of the phosphine ligand.[38] The absence of alkene

$$CH_3CH_2Au^{III}(CH_3)_2L \longrightarrow CH_3CH_2CH_3 + CH_3Au^{I}L \quad (25)$$
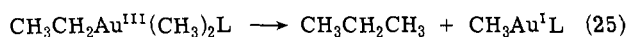
and products derived from attack on solvent indicate that alkyl radicals are not intermediates in the reductive coupling. Analogous reductive eliminations have been observed in platinum(IV) and nickel(II) complexes.[39]

Reductive elimination of alkylmetals may also proceed by disproportionation of the alkyl groups. Thus, the thermolysis of di-*n*-butylbis(triphenylphosphine)platinum(II) occurs by a first-order intramolecular process and affords an equimolar mixture of butane and butene-1, but no octane obtains as a result of reductive coupling.[40] A three-coordinate

$$(n\text{-}C_4H_9)_2Pt^{II}L_2 \longrightarrow n\text{-}C_4H_{10} + 1\text{-}C_4H_8 + (Pt^0L_2)$$

platinum(II) intermediate similar to that in the isoelectronic gold(III) complex above has been postulated.

Reductive elimination by a 2-equiv coupling or disproportionation of the alkyl derivative of Ni(II), Pt(IV,II), Au(III), and similar metal complexes by various intramolecular processes is not mechanistically unreasonable,[20] since the reduced metal species is available as a fairly stable entity, *i.e.*, Ni(0), Pt(II,0), Au(I), etc.[41] However, there are a number of alkylmetals such as those of Cu(I), Ag(I), Au(I), Ir(I), etc., in which the metal cannot readily sustain

a 2-equiv reduction. The overall reduction requires two metal centers as will be shown for alkylcopper(I), -silver(I), and -gold(I) complexes.

Alkyl(triphenylphosphine)gold(I) complexes are amenable to kinetic study since they are relatively stable and exist in solution as monomeric species.[44] *n*-Alkylgold(I) complexes undergo reductive coupling similar to the silver(I) analogs in very high yields according to eq 26. The rates of the decomposition

$$2CH_3CH_2AuL \longrightarrow CH_3CH_2CH_2CH_3 + 2Au^0 + 2L \quad (26)$$
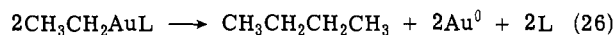
of $CH_3(PPh_3)Au$ in decalin solution follow first-order kinetics for approximately two half-lives. The first-order rate constant is independent of the concentration of $CH_3(PPh_3)Au$ in the range of 0.01–0.04 M and the presence of oxygen, but the rate is retarded by the addition of triphenylphosphine. The formation of ethane in near-quantitative yields as the sole hydrocarbon product even in the presence of hydrogen donor solvents and molecular oxygen strongly supports a molecular process for the methyl coupling. The monomeric nature of $CH_3(PPh_3)Au$ in solution, the first-order thermolysis, and the retardation suggest a rate-limiting loss of ligand. Rapid reaction of the coordinatively unsaturated methylgold(I) species with another CH_3AuPPh_3 in a subsequent step would account for all the known facts,

$$CH_3AuL \xrightarrow{k_1} CH_3Au + L$$

$$CH_3Au + CH_3AuL \longrightarrow CH_3CH_3 + 2Au^0 + L$$
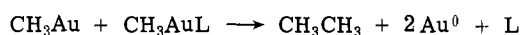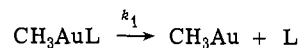
but a further description of the coupling process is undefined. One or several transients such as the binuclear $CH_3AuAuCH_3(L)$ and $Au(CH_3)_2AuL$ are likely intermediates.[42] Alkylsilver(I) complexes similarly afford coupled products on reductive elimination.[43,44]

D. β Elimination from Alkylmetals. The thermal decomposition of alkylcopper(I) differs from that of the silver(I) and gold(I) analogs in that no alkyl coupling is observed, and only products of disproportionation result, as represented in eq 27.[45] The ab-

$$2CH_3CH_2Cu^{I} \longrightarrow CH_3CH_3 + CH_2{=\!=}CH_2 + 2Cu^0 \quad (27)$$
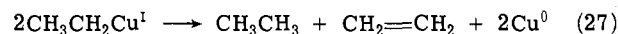
sence of coupled dimer in the decomposition of ethylcopper(I) species in eq 27 indicates alkyl radicals *per se* are not prime intermediates, since the bimolecular disproportionation and combination of ethyl radicals are relatively invariant with the medium and favor coupling, *i.e.*, $k_d/k_c = 0.18$.[46] Free-radical routes for decomposition are available, however, in those alkylcopper(I) analogs such as the more thermally stable neophyl derivatives which have no available β hydrogens.[47] Labeling studies with β,β-dideuteriobutylcopper(I) in ether show a specific intermolecular transfer of a β deuterium, which has been accommodated by a two-step mechanism in-

(36) N. J. Friswell and B. G. Gowenlock, *Advan. Free Radical Chem.*, 1, 39 (1965); 2, 1 (1967). *Cf.* also D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 165 (1972); M. C. Baird, *J. Organometal. Chem.*, 64, 289 (1974); P. S. Braterman and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 657 (1972); P. J. Davidson, M. F. Lappert, and R. Pearce, *Accounts Chem. Res.*, 7, 209 (1974).

(37) However, for a radical chain mechanism in the 2-equiv reductive elimination of alkylmercury(II), see G. M. Whitesides, *et al., J. Amer. Chem. Soc.*, 92, 6611 (1970); 96, 870 (1974).

(38) A. Tamaki, S. A. Magennis, and J. K. Kochi, *J. Amer. Chem. Soc.*, 95, 6487 (1973).

(39) M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J. Organometal. Chem.*, 49, C61 (1973); T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 93, 3350 (1971).

(40) G. M. Whitesides, J. G. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 94, 5258 (1972). See also *ibid.*, 95, 4451 (1973).

(41) The alkene-induced homolysis of dialkylplatinum(II) is noteworthy [N. G. Hargeaves, R. J. Puddephatt, L. H. Sutcliffe, and P. J. Thomson, *J. Chem. Soc., Chem. Commun.*, 861 (1973)]. *Cf.* also ref 39b.

(42) A. Tamaki and J. K. Kochi, *J. Organometal. Chem.*, 61, 441 (1973).
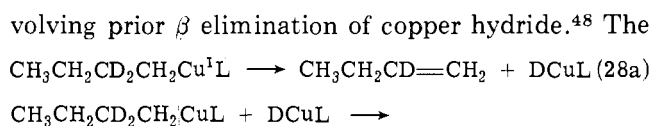
(43) M. Tamura and J. K. Kochi, *J. Amer. Chem. Soc.*, 93, 1483 (1971).

(44) (a) G. M. Whitesides, D. Bergbreiter, and P. E. Kendall, *J. Amer. Chem. Soc.*, 96, 2806 (1974); (b) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *ibid.*, 93, 1379 (1971).
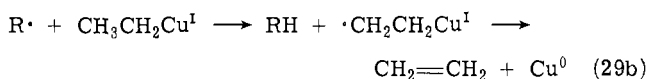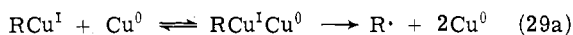
(45) M. Tamura and J. K. Kochi, *J. Organometal. Chem.*, 42, 205 (1972).

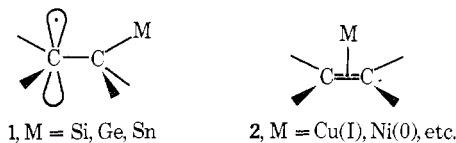(46) M. J. Gibian and R. C. Corley, *Chem. Rev.*, 73, 441 (1973).

(47) G. M. Whitesides, E. J. Panek, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, 94, 232 (1972).

volving prior β elimination of copper hydride.[48] The

$$CH_3CH_2CD_2CH_2Cu^IL \longrightarrow CH_3CH_2CD{=}CH_2 + DCuL \quad (28a)$$

$$CH_3CH_2CD_2CH_2CuL + DCuL \longrightarrow$$

$$CH_3CH_2CD_2CH_2D + 2Cu^0 + 2L \quad (28b)$$

reactivity of alkylcopper to reductive protonolysis in eq 28b is, however, relatively insensitive to structure and increases from *n*-butyl to *sec*-butyl to *tert*-butyl in the order 1:1.3:3.3.[47] Aggregation of alkylcopper species may contribute to this apparent lack of selectivity, and indeed reductive elimination may even proceed directly within the cluster itself.[49] Alkylcopper(I) species are more stable in THF solutions compared to ether, but otherwise afford the same products on decomposition. The rates in THF show an unusual and marked inhibition and autocatalysis. The esr spectrum obtained during the thermolysis has been attributed to a transient Cu^ICu^0 mixed-valence intermediate which we incorporated as a catalytic species in the Whitesides formulation.[50] However, there are several attractive mechanistic implications in an alternative free-radical *chain* process, in which autocatalysis is due to labilization of an alkylcopper(I) bond by Cu(0) in eq 29a, followed by abstraction of a β hydrogen in eq 29b.

$$RCu^I + Cu^0 \rightleftharpoons RCu^ICu^0 \longrightarrow R{\cdot} + 2Cu^0 \quad (29a)$$

$$R{\cdot} + CH_3CH_2Cu^I \longrightarrow RH + {\cdot}CH_2CH_2Cu^I \longrightarrow$$

$$CH_2{=}CH_2 + Cu^0 \quad (29b)$$

The driving force for the removal of a reactive hydrogen located in a β position relative to a metal, as shown in eq 29b, has been previously explored in esr studies of the main-group derivatives such as Si, Ge, and Sn.[51] The resulting β-metal-substituted alkyl radicals have rather unique conformational and structural properties which are related to hyperconjugative and homoconjugative interactions between the metal substituent and the radical center on carbon shown in **1**. The distinction between these structures (1) and the common diamagnetic π-olefin complexes of transition metals[52] such as Ni(0) and Cu(I) illustrated by **2** involves a rather subtle movement of the metal to a symmetrical bridging position. Indeed, the paramagnetic β-copperethyl radical presented in eq 29b as a hypothetical intermediate in

the decomposition of ethylcopper(I) may represent the missing link between structures such as **1′** and **2′**.[52b] Although these structures remain speculative

at this juncture, we think that they introduce the provocative notion that paramagnetic metal species may be viable intermediates in other organometallic processes such as the addition of metal hydrides to olefins, *i.e.*

$$M{-}C{-}C{\cdot} + MH \longrightarrow M{-}C{-}C{-}H + M{\cdot} \quad (30a)$$

$$M{\cdot} + C{=}C \rightleftharpoons M{-}C{-}C{\cdot}, \text{ etc.} \quad (30b)$$

and the reverse process, β elimination.[53] Esr spectroscopy represents the ideal technique to probe for these metastable structures, and we are engaged in the pursuit of such intermediates in catalytic reactions.

Alkyl Transfers from Organometallic Intermediates in Catalytic Processes

The oxidation–reduction reactions of organometallic intermediates presented in the foregoing description can be applied, in combination, to a variety of catalytic processes. We apply them in this Account to the metal-catalyzed alkyl-transfer reactions of Grignard reagents originally investigated by Kharasch and coworkers.[54] The catalytic reactions between labile organometals [RM] and alkyl halides [RX] can be generally classified into two categories, coupling in eq 31a and disproportionation in eq 31b,

$$R{-}m + R{-}X \xrightarrow{\text{cat.}} \begin{cases} R{-}R + mX \quad (31a) \\ RH + R(-H) + mX \quad (31b) \end{cases}$$
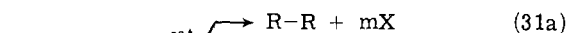
depending on the catalyst. For example, silver(I) and copper(I) are effective catalysts in the coupling of alkyl groups, whereas iron effects only disproportionation except when aryl and vinylic halides are employed. Each catalyst shows unique features which are best described within the following mechanistic context.

A. Homo Coupling with Silver(I). Silver is an effective catalyst for the coupling of Grignard reagents and alkyl halides, and it is especially useful when both alkyl groups are the same.[55] When different alkyl groups are employed, a mixture of three coupled products is obtained. Disproportionation be-

$$RMgX + RX \xrightarrow{Ag^I} R{-}R + MgX_2$$
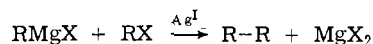
comes increasingly important with secondary and tertiary groups, independently of whether they are derived from the Grignard reagent or the alkyl halide. The rate of production of butane from ethyl-

1, M = Si, Ge, Sn   2, M = Cu(I), Ni(0), etc.

(48) G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Fillippo, Jr., *J. Amer. Chem. Soc.*, **92**, 1426 (1970). *Cf.* also J. Schwartz and J. B. Cannon, *ibid.*, **96**, 2276 (1974), for alkyliridium(I).
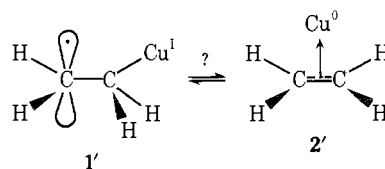
(49) M. Tamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 1485 (1971).

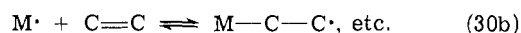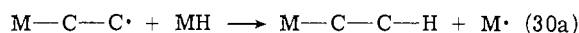(50) K. Wada, M. Tamura, and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 6656 (1970).

(51) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 6161 (1969); **93**, 846 (1971); T. Kawamura, P. Meakin, and J. K. Kochi, *ibid.*, **94**, 8065 (1972); T. Kawamura and J. K. Kochi, *ibid.*, **94**, 648 (1972); *J. Organometal. Chem.*, **47**, 79 (1973).

(52) (a) E. O. Fischer, *et al.*, "Metal π-Complexes," Vol. I and II, Elsevier, Amsterdam, 1966, 1972; R. G. Salomon and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 1889 (1973). (b) Hg(I) may be another example for σ and π interactions [F. R. Jensen and H. E. Guard, *J. Amer. Chem. Soc.*, **90**, 3250 (1968); P. A. W. Dean, *et al.*, *J. Chem. Soc., Chem. Commun.*, 626 (1973)]. See ref 34, p 298.

(53) Trapping or observation of radical intermediates in chain reactions will depend on the efficiency of the propagation sequence such as eq 29 or 30. These metal hydride and alkylmetal species may be excellent chain-transfer agents, as shown for group IVb hydrides [*cf.* H. G. Kuivila, *Accounts Chem. Res.*, 1, 299 (1968)].
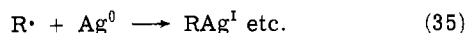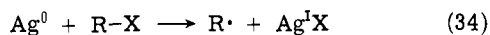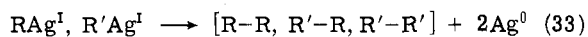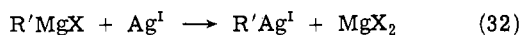
(54) M. S. Kharasch and O. Reinmuth, "Grignard Reagents of Nonmetallic Substances," Prentice-Hall, New York, N. Y., 1954.

(55) M. Tamura and J. K. Kochi, *Synthesis*, 303 (1971).

magnesium bromide and ethyl bromide is roughly first order in silver and ethyl bromide, but zero order in Grignard reagent.[43a] The reactivity of alkyl halides follows the order: *tert*-butyl > isopropyl > *n*-propyl bromide in the ratio 20:3:1. Structural variations in the Grignard reagent show no apparent systematic trend.

The results can be accommodated by Scheme VI, in which the coupling arises from alkylsilver(I) intermediates generated *via* two largely independent pathways.

Scheme VI

$$R'MgX + Ag^I \longrightarrow R'Ag^I + MgX_2 \tag{32}$$

$$RAg^I, R'Ag^I \longrightarrow [R-R, R'-R, R'-R'] + 2Ag^0 \tag{33}$$

$$Ag^0 + R-X \longrightarrow R\cdot + Ag^IX \tag{34}$$

$$R\cdot + Ag^0 \longrightarrow RAg^I \text{ etc.} \tag{35}$$

The rate-limiting step in this mechanism is given by eq 34 in which the alkyl halide is responsible for the reoxidation of silver(0) produced in eq 33. The reactivity of alkyl halides in eq 34 follows the order of stability of alkyl radicals, *i.e.*, tertiary > secondary > primary. This slow step is closely akin to the production of alkyl radicals by the ligand-transfer reduction of alkyl halides with other reducing metal complexes described earlier in eq 7.[5,10]

Previous studies have shown that alkyl radicals are not involved in the reductive dimerization of alkylsilver(I) in eq 33.[42,43] More direct evidence for the selective formation of alkyl radicals from the alkyl halide is shown by trapping experiments as well as stereochemical studies. Thus, the catalytic reaction of *cis*-propenylmagnesium bromide with methyl bromide yielded *cis*-butene-2, in accord with the retention of stereochemistry during the reductive coupling of vinylsilver(I) complexes.[43] On the other hand the
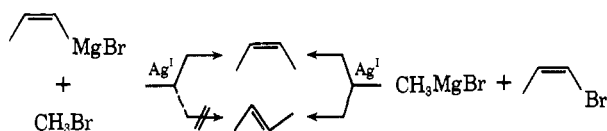
reverse combination, *cis*-propenyl bromide and methylmagnesium bromide, is catalytically converted to a mixture of *cis*- and *trans*-butene-2, consistent with the formation and rapid isomerization of the 1-propenyl radical in Scheme VI.

B. Cross-Coupling with Copper(I). Copper(I) specifically catalyzes the cross-coupling between Grignard reagents and alkyl bromides when carried out in THF solutions at 0° or lower.[45] The yield of homo-

$$RMgX + R'X \xrightarrow{Cu^I} R-R' + MgX_2$$
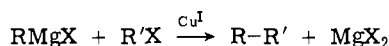
dimers, R–R and R'–R', under these conditions is negligibly small. This cross-coupling reaction is most facile with primary alkyl halides, but, unlike silver(I) catalysis, the secondary and tertiary alkyl halides are generally inert and give poor yields of coupled products and mainly disproportionation. The structure of the Grignard reagent is not as important, in analogy with the cross-coupling observed with lithium dialkylcuprates.[56]

(56) *Cf.* A. E. Jukes, *Advan. Organometal. Chem.*, **12**, 215 (1974), and C. R. Johnson and G. A. Dutra, *J. Amer. Chem. Soc.*, **95**, 7783 (1973).

The coupling of ethylmagnesium bromide and ethyl bromide to *n*-butane follows overall third-order kinetics, being first order in each component and the copper(I) catalyst.[45] There is no evidence for alkyl radicals in the copper(I)-catalyzed coupling process, and we propose the following two-step mechanism

Scheme VII

$$RMgBr + Cu^IBr \longrightarrow RCu^I + MgBr_2 \tag{32'}$$

$$RCu^I + R'Br \longrightarrow R-R' + Cu^IBr \tag{36}$$
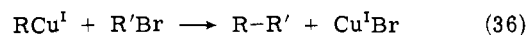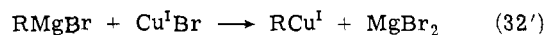
The rate-limiting step 36 can be shown independently by examining the stoichiometric reaction of alkylcopper(I) directly with organic halides. However, the extent to which *decomposition* of the alkylcopper(I) intermediate (described earlier in eq 27) competes with the catalytic coupling reaction introduces disproportionation products. The latter involves a copper(0)-catalyzed sequence[49] similar to that observed with iron (*vide infra*), and it is especially important with secondary and tertiary alkyl systems. The effects of structural variation are consistent with a rate-limiting step involving nucleophilic displacement of halide in eq 36.[56] The involvement of a nucleophilic copper(I) center, *i.e.*, oxidative addition, followed by reductive elimination has direct analogy to the mechanism which has been established with the analogous gold(I) catalyst.[57] Organo-

$$RCu^I + R'X \longrightarrow R(R')Cu^{III}X \tag{37a}$$

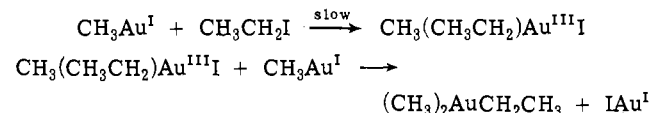$$R(R')Cu^{III}X \longrightarrow R-R' + Cu^IX \tag{37b}$$
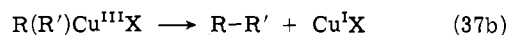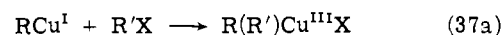
copper(III) intermediates presented in eq 37 are formally related to the species discussed earlier (eq 5) in the association of alkyl radicals with copper(II) complexes, with both showing a marked propensity for reductive elimination. Although the direct observation of these highly metastable intermediates is unlikely, the analogous organogold intermediates are more stable and can be isolated or observed directly by nmr.[59]

Catalysis by Iron. Alkyl disproportionation is the sole reaction observed during the iron-catalyzed reaction of ethylmagnesium bromide and ethyl bromide.[60] The catalyst is a reduced iron species formed

$$CH_3CH_2MgBr + CH_3CH_2Br \xrightarrow{Fe^I}$$
$$CH_3CH_3 + CH_2{=}CH_2 + MgBr_2$$
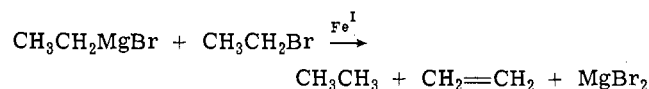
(57) Oxidative addition of alkyl halides to alkyl(triphenylphosphine)-gold(I) follows the expected pattern: $CH_3I > EtI > i\text{-}PrI$, *e.g.*[58]

$$CH_3Au^I + CH_3CH_2I \xrightarrow{slow} CH_3(CH_3CH_2)Au^{III}I$$
$$CH_3(CH_3CH_2)Au^{III}I + CH_3Au^I \longrightarrow$$
$$(CH_3)_2AuCH_2CH_3 + IAu^I$$

The subsequent reductive elimination of trialkylgold(III) complexes to coupled dimer was described earlier (*cf.* eq 25.)

(58) A. Tamaki and J. K. Kochi, *J. Chem. Soc., Dalton Trans.*, 2620 (1973); *J. Organometal. Chem.*, **64**, 411 (1974).
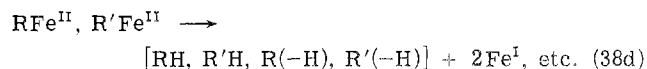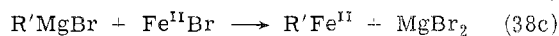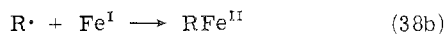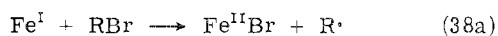
(59) The parallel between copper(I) and gold(I) is further shown in the behavior of the corresponding cuprate(I) and aurate(I) complexes. Thus, alkylgold(I) reacts with an equimolar amount of alkyllithium to afford an isolable lithium dialkylaurate(I). The anionic dimethylaurate(I) species formed in this manner is at least 10^6 times more reactive to oxidative addition of methyl iodide than the neutral methyl(triphenylphosphine)gold(I).[58] The same pattern is qualitatively established with organocopper(I) species in comparing the coupling reaction in eq 36 with that reported for lithium dialkylcuprates.[56]

(60) M. Tamura and J. K. Kochi, *J. Organometal. Chem.*, **31**, 289 (1971); *Bull Chem. Soc. Jap.*, **44**, 3063 (1971).

in situ by the reaction of iron(II,III) with Grignard reagent, and effective in concentrations as low as 10^{-5} *M*. Although the reaction has limited synthetic utility, it merits study since it can provide insight into some of the complications involved with organometallic intermediates.

The rate of reaction shows first-order dependence on the concentration of iron and ethyl bromide, but is independent of the concentration of ethylmagnesium bromide. The rate, however, varies with the structure of the Grignard reagent, and disproportionation usually results except when the alkyl group is methyl, neopentyl, or benzyl, none of which possesses β hydrogens. The reactivities of the alkyl bromides (*tert*-butyl> isopropyl > *n*-propyl) as well as the kinetics are the same as the silver-catalyzed coupling described above and suggest a similar mechanism.[60,61]

Scheme VIII

$$Fe^I + RBr \longrightarrow Fe^{II}Br + R\cdot \qquad (38a)$$

$$R\cdot + Fe^I \longrightarrow RFe^{II} \qquad (38b)$$

$$R'MgBr + Fe^{II}Br \longrightarrow R'Fe^{II} + MgBr_2 \qquad (38c)$$

$$RFe^{II}, R'Fe^{II} \longrightarrow$$
$$[RH, R'H, R(-H), R'(-H)] + 2Fe^I, etc. \qquad (38d)$$

According to this postulate, the difference between coupling with silver and disproportionation with iron rests on the decomposition of the alkylmetal intermediate. Indeed, it has been shown separately that the decomposition of alkylsilver(I) proceeds by reductive coupling. Unfortunately, the highly unstable alkyliron intermediate in Scheme VIII is not yet accessible to independent study, but the somewhat analogous dialkylmanganese(II) species undergoes similar reductive disproportionation by a mechanism[62] reminiscent of alkylcopper(I) described in eq 27. Selective trapping of alkyl radicals from the alkyl halide component during the course of the catalytic disproportionation is the same as the previous observation with silver,[42] and it indicates that the prime source of radicals in the Kharasch reaction lies in the oxidative addition of alkyl halide to reduced iron in eq 38a. Separate pathways for reaction of isopropyl groups derived from the organic halide and the Grignard reagent are also supported by deuterium labeling studies which show that they are not completely

equilibrated.[63] Furthermore, the observation of CIDNP (AE multiplet effect) in the labeled propane and propene derived only from the alkyl halide component can be attributed to a bimolecular disproportionation of isopropyl radicals arising from diffusive displacements. However, the latter can only be a minor fate of the alkyl radicals derived from the alkyl halide, since the coupled dimer is not formed in amounts required by the bimolecular reaction of alkyl radicals.[62,64]

Cross-coupling of Grignard reagents with 1-alkenyl halides, in marked contrast to alkyl halides, occurs readily with the reduced iron catalyst, especially that derived from tris(dibenzoylmethido)iron(III), as well as a recently reported nickel catalyst.[65,66] *n*-Propyl- and *n*-hexylmagnesium bromides react with vinyl bromide to afford pentene-1 and octene-1, respectively. Similarly, cyclohexylmagnesium bromide

$$RMgBr + \quad \diagup C=C \diagdown^{Br} \xrightarrow{Fe^I} \diagup C=C \diagdown^{R} + MgBr_2$$
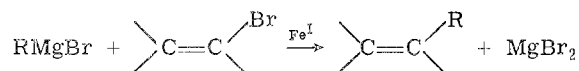
produces propenylcyclohexane in high yields from propenyl bromide. The reaction is stereospecific, since *cis*- and *trans*-propenyl bromides afford *cis*- and *trans*-butene-2, respectively. Secondary and even tertiary alkyl Grignard reagents can be coupled in excellent yields with other 1-alkenyl bromides including β-bromostyrene.[65] The iron-catalyzed reaction of Grignard reagents with 1-alkenyl halides can be differentiated from the reaction with alkyl halides. Thus, a mixture of propenyl bromide and ethyl bromide on reaction with methylmagnesium bromide afforded butene-2, but no crossover products such as pentene-2 or propylene. The latter certainly would have resulted if a propenyliron species *per se* were involved in the catalytic process. Cross-coupling under these circumstances clearly merits further study.

(61) The oxidation number in the reduced iron species has not been established. We tentatively favor iron(I) based on some recent studies. Reductive elimination may then proceed from mono- and dialkyliron(II) in eq 38d.

(62) M. Tamura and J. K. Kochi, *J. Organometal. Chem.*, **29**, 111 (1971).

(63) R. B. Allen, R. G. Lawler, and H. R. Ward, *J. Amer. Chem. Soc.*, **95**, 1692 (1973).

(64) The large enhancement possible in CIDNP may not reflect its chemical importance until they are *quantitatively* related. A small amount of radical combination leading to CIDNP may have been overlooked in the chemical studies.

(65) M. Tamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 1487 (1971); S. Neumann, unpublished results.

(66) K. Tamao, K. Sumitani, and M. Kumada, *J. Amer. Chem. Soc.*, **94**, 4374 (1972). See also J. Klein and R. Levene, *ibid.*, **94**, 2520 (1972); M. F. Semmelhack and L. Ryono, *Tetrahedron Lett.*, 2967 (1973).

Additions and Corrections

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Page 356. In column 2, line 20 should read as follows:

metal. Electron-transfer contributions, however, may