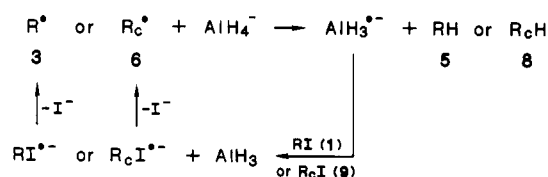
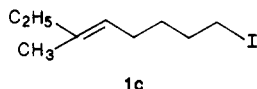


Scheme V



queness of **1b** as an invalid probe, we reacted LiAlH_4 with 8-iodo-3-methyl-3-octene (**1c**), thus replacing the



methoxy and cyano groups with methyl and ethyl groups, which do not affect the reduction potential of the double bond as would be expected for **1b**. We found that the *E/Z* ratio of the product does not change from that of the reactant, indicating that the double bond is not affected by these groups. Importantly, when **1c** was reduced with LiAlH_4 in ether, cyclized product **7c** was formed in 9.6% yield and when **1c** was reduced with LiAlD_4 , cyclized product **8c** was formed in 18.4% yield.

Since cyclized product would not be expected to come from cyclized iodide **9c**, it must come from radical **6c**. Additional convincing evidence comes from the reduction of **1c** by LiAlD_4 in ether. There is significant protium content not only in the cyclized product (11%) but also in the straight-chain product (5%). All of these data are clearly compatible with the mechanism shown in Scheme IV that we proposed in 1984.

Recently, in addition to the halogen atom radical chain process $6 \xrightarrow{1} 9$, which accounts for some of the cyclized products (**7**, **8**), we have found evidence to

support a hydrogen atom radical chain process to account for the conversion of **3** \rightarrow **5**, **6** \rightarrow **8**, and **9** \rightarrow **8** by reaction of radicals R^\bullet (**3**) and R_c^\bullet (**6**) with LiAlH_4 (Scheme V). Support for the hydrogen atom radical chain process is based on (1) the increased amount of **5** formed (3.3% to 9.4% to 15.2%) as the LiAlH_4 :**1** ratio is increased from 0.1:1 to 1:1 to 1:5, showing that radical **3** is quenched with LiAlH_4 at a faster rate in competition with reaction with SH , $\text{LiAlH}_4^{\bullet-}$, and the cyclization of **3** \rightarrow **6** and (2) the results of an entrainment experiment that shows that although the corresponding chloride of **1**, which does not react with LiAlH_4 in THF for 48 or 92 h, 28% reaction does take place over the same period of time in the presence of an equivalent amount of iodide (**1**). It has been shown that chloride is not converted to **1** by reaction with I^- . Both of these studies are consistent with a hydrogen atom radical chain process.

In conclusion, we believe that SET is indeed a major reaction pathway in organic chemistry and that even reactions heretofore thought to be classic $\text{S}_{\text{N}}2$ processes proceed, at least to some extent, via a SET pathway. This pathway is particularly important when $\text{X} = \text{I}$, but even when $\text{X} = \text{Br}$ and Cl when a super one-electron donor such as Me_3Sn^- is involved. Evidence has also been presented to support SET as a major reaction pathway in the reactions of aromatic ketones with certain nucleophiles. We continue to believe that the use of alkyl halide cyclizable radical probes does provide important information concerning the radical nature of reactions classified as nucleophilic aliphatic substitution.

We are indebted to the National Science Foundation (Grant No. CHE 8403024) for support of our work.

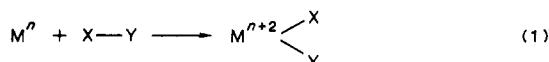
Organometallic Chemistry of Electrophilic Transition and Lanthanide Metal Ions. The Dominant Pathways for Reactions Involving C=C, C-C, and C-H Bonds

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The chemistry of electron-rich transition-metal centers has been studied extensively in recent years, and many of the characteristic reactions are, by now, well understood. The one reaction that appears to dominate this chemistry is oxidative addition (eq 1),¹ and the propensity to undergo this reaction *increases* with in-



common examples: X, Y = hydrocarbyls, H, and halogens

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creasing electron density on the metal. In contrast, with the important exceptions of (a) reactions involving nucleophilic attack on π -complexes² and (b) reactions involving early transition, lanthanide, and actinide metal hydrocarbyls,³ the mechanistic aspects of the

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(2) Review: ref 1, p 409.

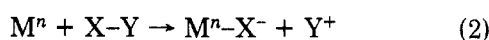
(3) Leading references for "four-center" electrophilic activation of hydrocarbons by early transition metal, lanthanide, and actinide complexes: (a) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* 1988, 110, 976. (b) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santasiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* 1987, 109, 203. (c) Watson, P. L. *J. Am. Chem. Soc.* 1983, 105, 6491. (d) Teuben, J. H. In *Fundamentals and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds.; NATO ASI Series; D. Reidel: Boston, 1985; p 195. (e) Smith, G. M.; Carpenter, J. D.; Marks, T. J. *J. Am. Chem. Soc.* 1986, 108, 6805.

Table I

ion	promotion energy, ^a eV	electron affinity, eV
Rh(I)	1.6	7.31
Ir(I)	2.4	7.95
Pd(II)	3.05	18.56
Pt(II)	3.39	19.42
Cu(I)	8.25	7.72
Ag(I)	9.94	7.59
Zn(II)	17.1	17.96
Cd(II)	16.6	16.9
Hg(II)	12.8	18.75

$$^a nd^x \rightarrow nd^{x-1}(n+1)p^1.$$

chemistry of electrophilic metal ions remain less explored, despite the extensive organic chemistry of electrophilic metals such as silver⁴ and palladium.⁵ This is surprising in view of the literature precedents which indicate that the important reaction pathways in this type of chemistry are very different from those observed with electron-rich metals. For example, the heterolytic cleavage of bonds appears to be the dominant reaction with electrophilic metal centers (eq 2). We shall demonstrate several examples of this class of reactions and show that the propensity to undergo such reactions decreases with increasing electron density on the metal.



common examples: X, Y = hydrocarbyls, H

The catalytic and stoichiometric activation of C=C, C—C, and C—H bonds by transition and lanthanide metals are important problems in organometallic chemistry, and in this account we discuss the role of electrophilic metal centers in such activation processes. In addition, we will indicate how the electrophilicity, and hence the reactivity, of the metal center in this class of compounds can be varied in a systematic way by the appropriate choice of the ligands and the central metal ion.

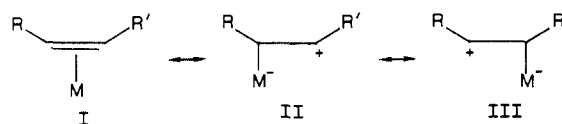
In order to compare the chemistry of electrophilic metal ions from different parts of the periodic table, we have examined the reactivity pattern of the following series of complexes: [Pd(MeCN)₄](BF₄)₂ (1),⁶ [M(MeCN)₆](BF₄)₂ (M = Ni (2), Co (3)),⁷ [M(NO)₂(MeCN)₄](BF₄)₂ (M = Mo (4), W (5)),⁷ and [Eu(MeCN)₃(BF₄)₃]_x (6).⁸ They are all cationic complexes incorporating the weakly ligating MeCN ligand. These compounds are readily soluble in polar organic solvents such as MeCN and MeNO₂ but insoluble in less polar media. Except in compound 6, the BF₄⁻ ions are non-coordinating in solution and do not appear to participate in the chemistry. Compound 6 is dimeric in solution, and studies indicate that two of the three BF₄⁻

ions (per Eu(III) ion) coordinate to the metal through the F atoms and thus function as bridging ligands.⁸ However, the coordinated BF₄⁻ ions are held weakly and are easily displaced by other ligands.

Before examining the organic chemistry of transition-metal electrophiles, it is worthwhile to compare them with the traditional main-group Lewis acids. As Table I illustrates,⁹ the electron affinity of Pd(II) is comparable to those of Zn(II) and Hg(II). However, the Pd(II) ion has a smaller electron promotion energy, and this results in stronger initial binding with organic substrates like alkenes because of more efficient back-bonding. This mode of interaction is energetically unfavorable for most common Lewis acids, and this constitutes the principal difference between transition-metal electrophiles on one hand and the more traditional main-group electrophiles on the other.

Reactions Involving C=C Bonds

We have proposed⁶⁻⁸ that the dominant mode of interaction between an electrophilic metal center and an alkene involves the transfer of a significant amount of charge density from the π-bond to the metal, concomitant with the formation of an incipient carbocationic center at the alkene. Such an interaction may be visualized as resulting from significant contributions from the canonical structures II and III in the following bonding picture.



Such a transfer of charge should be particularly facile for alkenes possessing strong electron-releasing substituents. An alkene that meets this requirement is tetra-*p*-anisylethylene (TAE), which has a low ionization potential of 6 eV¹⁰ and which is known to form charge-transfer complexes with main-group electrophiles.¹¹ The addition of TAE to a solution of 1 in MeCN caused an immediate development of intense blue color with an absorption maximum at 566 nm. An attempt to ascertain the stoichiometry of this reaction through a spectral titration was unsuccessful since the successive additions of TAE to 1 caused a monotonic increase in absorbance without leveling off, indicating the existence of an equilibrium. A similar blue solution with an absorption maximum at 564 nm was formed when Br₂ was added to a solution of TAE in CHCl₃, a reaction that is known to generate a TAE-Br₂ charge-transfer complex.¹⁰ Thus, it is clear that there is a significant degree of charge-transfer from the olefin to the metal when TAE interacts with 1. Hg(II), a well-studied electrophile, is also known to form charge-transfer complexes with alkenes,¹² and, indeed, the addition of TAE to a solution of HgCl₂ in a MeCN-CHCl₃ mixture caused a slow (hours versus seconds for 1) development of blue color with an absorption maximum at 564 nm. The formation of a charge-transfer complex was, however, not observed when TAE was

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Table II

cat.	substrate	substrate/cat.	solvent	temp, °C	time	product	yield, %
Pd(MeCN) ₄ ^{2+a}	2,3-DM1B ^f	10	MeNO ₂	25	20 min	2,3-DM2B ^h	90 ^f
Pd(MeCN) ₄ ^{2+a}	2,3-DM1B ^f	10	MeCN	25	20 min	2,3-DM2B ^h	90 ^f
Mo(NO) ₂ (MeCN) ₄ ^{2+b}	2,3-DM1B ^f	10	MeNO ₂	25	20 min	2,3-DM2B ^h	90 ^f
W(NO) ₂ (MeCN) ₄ ^{2+b}	2,3-DM1B ^f	10	MeNO ₂	25	20 min	2,3-DM2B ^h	90 ^f
W(NO) ₂ (MeCN) ₄ ^{2+b}	2,3-DM1B ^f	10	MeCN	25	20 min	2,3-DM2B ^h	20
Co(MeCN) ₆ ^{2+c}	2,3-DM1B ^f	20	MeNO ₂	25	2 days	2,3-DM2B ^h	40
Co(MeCN) ₆ ^{2+c}	2,3-DM1B ^f	20	MeCN	25	2 days	2,3-DM2B ^h	0
Ni(MeCN) ₆ ^{2+c}	2,3-DM1B ^f	20	MeNO ₂	25	3 days	2,3-DM2B ^h	30
Ni(MeCN) ₆ ^{2+c}	2,3-DM1B ^f	10	MeCN	25	3 days	2,3-DM2B ^h	0
Pd(MeCN) ₄ ^{2+d}	PhCH=CH ₂	100	MeNO ₂	25	5 min	(-CH(Ph)CH ₂) _n	95
Pd(MeCN) ₄ ^{2+d}	PhCH=CH ₂	100	MeCN	25	5 min	(-CH(Ph)CH ₂) _n	95
Mo(NO) ₂ (MeCN) ₄ ^{2+e}	PhCH=CH ₂	250	MeNO ₂	25	4 hrs	(-CH(Ph)CH ₂) _n	95
W(NO) ₂ (MeCN) ₄ ^{2+e}	PhCH=CH ₂	250	MeNO ₂	25	4 hrs	(-CH(Ph)CH ₂) _n	85
W(NO) ₂ (MeCN) ₄ ^{2+e}	PhCH=CH ₂	250	MeCN	25	4 hrs	(-CH(Ph)CH ₂) _n	0
Co(MeCN) ₆ ^{2+c}	PhCH=CH ₂	100	MeNO ₂	25	2 days	(-CH(Ph)CH ₂) _n	75
Co(MeCN) ₆ ^{2+c}	PhCH=CH ₂	100	MeCN	25	2 days	(-CH(Ph)CH ₂) _n	0
Ni(MeCN) ₆ ^{2+c}	PhCH=CH ₂	100	MeNO ₂	25	3 days	(-CH(Ph)CH ₂) _n	40
Ni(MeCN) ₆ ^{2+c}	PhCH=CH ₂	100	MeCN	25	3 days	(-CH(Ph)CH ₂) _n	0

^a[] = 9×10^{-2} M. ^b[] = 8.6×10^{-2} M. ^c[] = 5×10^{-2} M. ^d[] = 1.1×10^{-2} M. ^e[] = 1.7×10^{-1} M. ^fAt equilibrium, the ratio of 2,3-dimethyl-2-butene to 2,3-dimethyl-1-butene is ~90:10. ^g2,3-Dimethyl-1-butene. ^h2,3-Dimethyl-2-butene.

added to solutions of either AgNO₃ or AgBF₄. This is not surprising since Ag(I) is a weaker electrophile than Pd(II) and Hg(II) (Table I) and is known to bind alkenes less strongly than does Hg(II).¹³ Finally, the neutral Pd(II) compound, Pd(PhCN)₂Cl₂, which is expected to be less electrophilic than 1, did not form a TAE charge-transfer complex even in a noncoordinating solvent such as CHCl₃, although this compound is known to form alkene complexes by the displacement of PhCN under these conditions.¹⁴

Whereas the formation of the charge-transfer complex between 1 and TAE was observed in both MeCN and MeNO₂, the corresponding charge-transfer complexes with 4–6 were only observed in MeNO₂, and 2 and 3 did not form complexes with TAE in either solvent. This pronounced solvent effect is best understood in terms of the coordinating ability of MeCN and MeNO₂. The latter is a significantly poorer ligand. For example, while all or part of the coordinated MeCN molecules of 1, 4, and 5 were observed to exchange with solvent MeCN within seconds at 25 °C, no analogous exchange was observed over hours at 25 °C when MeNO₂ was used as the solvent. The MeCN ligands in 2 and 3 are held particularly tightly since, in MeCN, 2 and 3 did not react with Ph₃P while 1 formed Ph₃P-substituted products under these conditions. Thus, the greater propensity to form a charge-transfer complex with TAE in MeNO₂ indicates that a close approach of TAE to the metal center is required for complex formation. Consistent with this conclusion was the observation of a strong correlation between the formation of a charge-transfer complex with TAE and the ability of the metal species to cause electrophilic activation of alkenes. Thus, as Table II indicates, the ability of the metal compounds 1–6 to isomerize 2,3-dimethyl-1-butene and polymerize styrene in MeCN and MeNO₂ is directly related to the ability of the compound to form a TAE complex in that solvent. With the exception of 1, the reactivity of all other metal species was significantly attenuated in MeCN when compared to MeNO₂.

The predominance of the canonical structure II or III (depending on the nature of R and R') in the bonding of alkenes to electrophilic metal ions has several physical ramifications. For example, with complexes of monosubstituted alkenes bearing electron-donating substituents, one would expect that the metal-carbon distance to the unsubstituted carbon would be significantly shorter than that to the substituted carbon since the incipient carbocation would be located on the carbon with the electron-donating substituent. Furthermore, the magnitude of this structural asymmetry should decrease with decreasing donor ability of the substituent. This expectation was borne out by crystal structure studies on CpFe(CO)₂(CH₂=CHX)⁺ (X = NMe₂, OMe),¹⁵ CpPd(PPh₃)(CH₂=CHC₆H₄X-p)⁺ (X = OMe, H, Cl),¹⁶ and PtCl₂(py)(CH₂=CHC₆H₄X-p) (X = NMe₂, H, NO₂)¹⁷ complexes. In the latter two series, the difference in metal-carbon distances to the two ends of the alkene (i.e., the asymmetry in the metal-alkene structure) decreased with decreasing donor ability of X. In addition, for the same alkene (X = H), the structural asymmetry was significantly greater for the cationic Pd(II) complex when compared to the neutral Pt(II) analogue although the difference in auxiliary ligands present precludes a proper comparison.

Several studies have indicated that the structural asymmetry in alkene complexes of electrophilic metal ions is not confined to the solid state but persists in solution. For example, a significant contribution of the canonical structure II or III in CpFe(CO)₂(CH₂=CHNMe₂)⁺ was supported by the observation of a low rotational barrier (10.5 kcal/mol) about the C=C bond in solution.¹⁵ In addition, for the series of compounds Pt(η³-CH₂CMeCH₂)(PPh₃)(CH₂=CHC₆H₄X)⁺ (X = NMe₂, OMe, Me, H, Cl, NO₂), the *J*_{Pt-C} value for the alkene carbon bearing the substituent was significantly smaller than that for the unsubstituted carbon.¹⁸ Moreover, the difference in *J*_{Pt-C} values for the two alkene carbons decreased with decreasing donor ability

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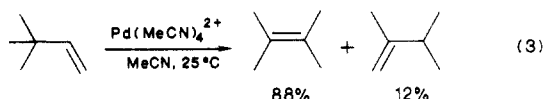
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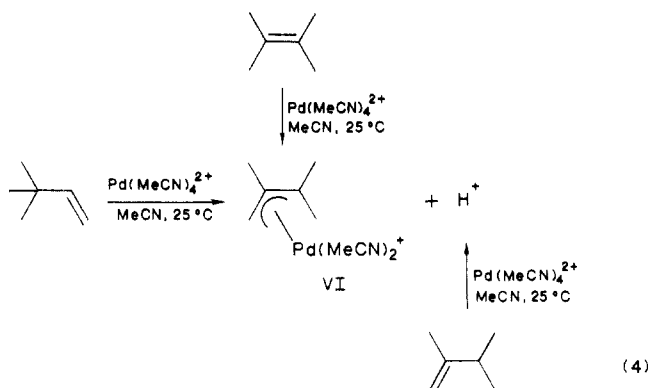
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of X. Finally, as might be expected for alkene complexes of electrophilic metal ions, the equilibrium for alkene coordination in the above series of compounds *decreased* with *decreasing* donor ability of X.¹⁸ Note that this trend is the *opposite* of that observed for low-valent electron-rich metal centers where the importance of "back-bonding" was demonstrated by the enhanced coordinating ability of electron-deficient alkenes.¹⁹

Since the interaction of alkenes with electrophilic metal ions results in the formation of incipient carbocations due to alkene-to-metal charge transfer, such electrophilic metal species would be expected to catalyze carbocationic rearrangements of appropriately substituted alkenes. Thus, 1 was found to catalyze the skeletal rearrangement of *tert*-butylethylene to an equilibrium mixture of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene both in MeCN and in MeNO₂ at 25 °C (eq 3).^{6d} A mechanism for this transformation is



shown in Scheme I. The secondary carbocation IV may be formed by the "slippage" of the metal fragment along the C=C bond, as postulated by Hoffmann for reactions involving nucleophilic attack on coordinated alkenes.²⁰ The species IV would then be expected to rearrange to the more stable tertiary carbocation V, which would eventually lead to the observed products. The Pd compound that was formed in the course of the catalytic skeletal rearrangement is the π -allyl compound VI. In fact, this compound could be generated by adding either *tert*-butylethylene, 2,3-dimethyl-2-butene, or 2,3-dimethyl-1-butene to a solution of 1 in MeCN (eq 4). Note that earlier work by Beak, Trost, and others has also demonstrated the formation of π -allyl complexes by the interaction of Pd(II) with alkenes.²¹



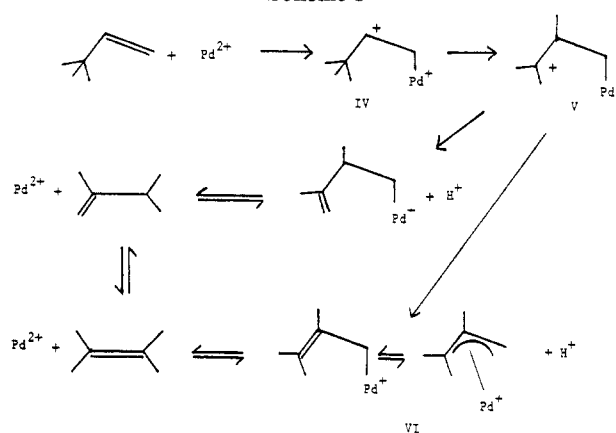
It is significant that the compounds Pd(MeCN)₂Cl₂ and Pd(MeCN)_{4-n}(PPh₃)_n²⁺ (*n* = 2, 3), which are expected to be weaker electrophiles than 1, did not catalyze the above skeletal rearrangement. Compounds 4–6 were also found to mediate the skeletal rearrangement but only in MeNO₂ and only in low yields. It is possible that the rate of skeletal rearrangement was a

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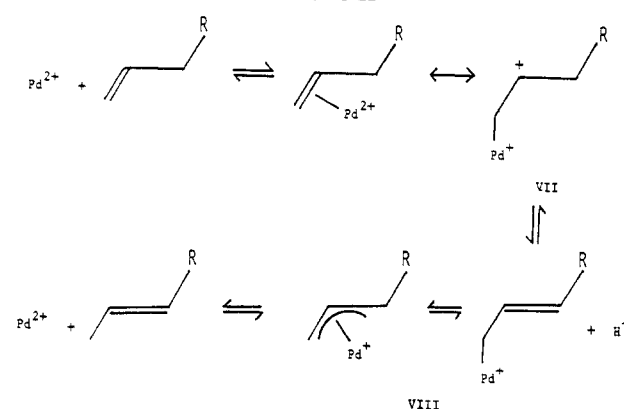
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Scheme I



Scheme II



function of the relative freedom of the carbocation formed initially (e.g., species IV, Scheme I). Reactions that proceed via carbocationic mechanisms do not necessarily require the same degree of carbocationic character in the intermediates involved. Thus it has been proposed²² that in the acid-catalyzed isomerization of 2-methylpent-2-ene, the methyl group migration requires more carbocationic character in the intermediate than does C=C bond migration. In our own work, we have consistently observed that, for a given electrophilic metal center, the catalysis of C=C bond isomerization proceeded more readily than skeletal rearrangements (*vide infra*).

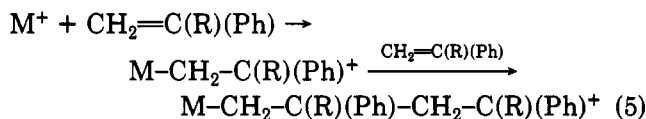
Compounds 1 in MeCN or MeNO₂ was found to rapidly C=C bond isomerize a variety of alkenes at 25 °C.^{6a} On the other hand, compounds 2–6 were found to catalyze the isomerization of 2,3-dimethyl-1-butene to 2,3-dimethyl-2-butene at varying rates primarily in MeNO₂ with very little, if any, activity in MeCN^{7,8} (Table II). The accepted mechanism for C=C bond isomerization of alkenes by electron-rich transition-metal compounds involves the initial oxidative addition of an allylic C–H bond to form a metal-allyl hydride intermediate.²³ However, such a step is highly unlikely for an electron-deficient metal center, and we have proposed an alternative mechanism involving the heterolytic cleavage of an allyl C–H bond by the electrophilic metal center (Scheme II).^{6a} There are several lines of evidence in support of this mechanism. First, consistent with a mechanism involving electrophilic attack, the rate of C=C bond isomerization was found

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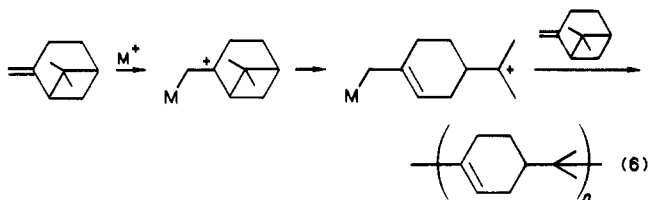
(23) Heck, R. F. *Organotransition Metal Chemistry*; Academic: New York, 1974; p 80.

to decrease with increasing electron density on the metal. For example, in the isomerization reactions catalyzed by 1, the incremental addition of basic tertiary phosphines resulted in gradual attenuation of catalytic activity.^{6a} In addition, the neutral Pd(II) analogue Pd(PhCN)₂Cl₂ was inactive even in a noncoordinating solvent such as CHCl₃, although this compound is known to form alkene complexes under these conditions.¹⁴ Second, direct evidence for the formation of a metal-allyl species (species VIII, Scheme II) through the electrophilic cleavage of an allylic C-H bond is provided by eq 4. Finally, the catalysis of C=C bond isomerization by compound 6⁸ cannot possibly involve an oxidative addition step since this would result in the formation of an Eu(V) species, an oxidation state that is unknown for the lanthanide metals.

Electrophilic metal centers are expected to act as initiators for the cationic polymerization of alkenes since carbocations are generated when they interact with alkenes. Indeed, 1 and 4-6 were versatile catalysts for the oligomerization and polymerization of a wide range of alkenic substrates.^{6a-c,7,8} As with other reactions, there was a pronounced solvent effect, with 1 being an effective initiator in both MeCN and MeNO₂, while compounds 4-6 functioned well only in MeNO₂ (Table II). Consistent with a cationic polymerization mechanism were the following observations. Only alkenes bearing substituents capable of stabilizing a carbocation underwent ready polymerization. Simple olefins such as ethylene and propylene were converted to lower molecular weight oligomers only by 1—the strongest electrophile of the group. With styrene derivatives, a head-to-tail arrangement was observed in the polymers and oligomers formed, and this was a consequence of the greater stabilization of the carbocation when located on the α-carbon (eq 5). The mo-



lecular weight of a given polymer was found to increase rapidly with decreasing reaction temperature.²⁴ Finally, 2(10)-pinene underwent ring-opening polymerization through the mechanism shown in eq 6.²⁵



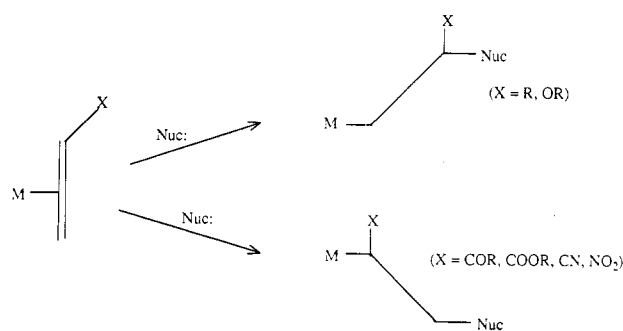
Although we have not carried out a detailed kinetic analysis of our polymerization systems, this has been performed for a related system that involves the electrophile, Fe(NO)₂(solv)₂⁺.²⁶ This species was also found to initiate the cationic polymerization of alkenes, and kinetic experiments indicated a first-order dependence

(24) This is a characteristic feature of cationic polymerizations. See: Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1981; Chapter 4.

(25) 2(10)-Pinene does not undergo anionic or free-radical polymerization. See: Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; Wiley: New York, 1982; Chapter 1.

(26) Ballivet-Tkatchenko, D.; Billard, C.; Revillon, A. *J. Polym. Sci., Polym. Chem. Ed.* 1981, 19, 1697.

Scheme III



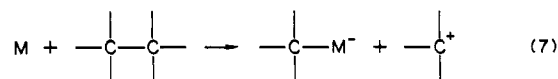
of the initial rate on the alkene monomer and the iron compound. This observation is consistent with the initial formation of a metal-alkene complex.

The formation of incipient carbocations when alkenes interact with electrophilic metal centers has important regiochemical consequences in reactions involving nucleophilic attack on complexed alkenes. In an unsymmetrically substituted alkene, the dominant canonical form would be the one in which the carbocation is located on the carbon bearing the electron-donating substituents. Consequently, the attack by a nucleophile should take place on the carbon with electron-donating substituents and away from the carbon bearing electron-withdrawing substituents. Experimental results are in accord with this prediction (Scheme III). Thus, in the case of terminal alkenes, the nucleophilic attack takes place on the carbon adjacent to the alkyl group. For example, during the oxidation of terminal alkenes with Pd(II) salts, where OH⁻ or H₂O is the nucleophile, the predominant products are the methyl ketones rather than terminal aldehydes.²⁷ Similarly, other electron-donating substituents such as alkoxy groups direct nucleophilic attack on the adjacent carbon atom.²⁸ Conversely, electron-withdrawing substituents such as COR, COOR, NO₂, and CN direct the nucleophilic attack on the remote carbon of the C=C bond.^{27b} Interestingly, the latter observation *contradicts* theoretical prediction²⁰ that nucleophilic attack would occur on the substituted carbon even with electron-withdrawing substituents.

Compared to alkenes, examples of nucleophilic attack on coordinated alkynes are less common. However, in the few cases reported, a regioselectivity analogous to that found for alkenes has been observed; i.e., the attack by the nucleophile takes place preferentially at the carbon bearing the electron-donating substituent and away from the carbon with an electron-attracting substituent.²⁹

Reactions Involving C-C Bonds

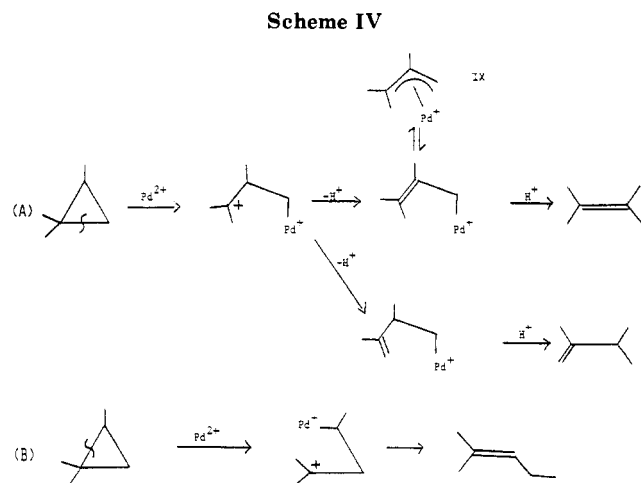
The heterolytic cleavage of C-C bonds by electrophilic metal ions (eq 7) was first studied in detail by



(27) (a) Reference 5c, Chapter II. (b) Jira, R.; Freiesleben, W. *Organomet. React.* 1972, 3, 1.

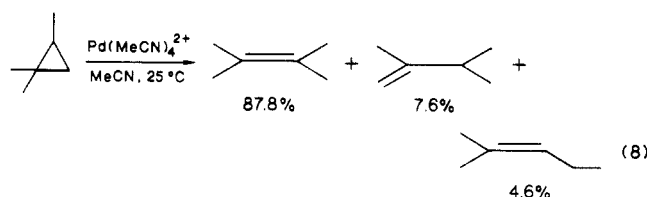
(28) Chang, T. C. T.; Rosenblum, M.; Samuels, S. B. *J. Am. Chem. Soc.* 1980, 102, 5930.

(29) Specific examples: (a) Reger, D. L.; Klaeren, S. A.; Lebioda, L. *Organometallics* 1986, 5, 1072. (b) Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligott, P. J. *Organometallics* 1984, 3, 134. (c) Rosenblum, M.; Scheck, D. *Organometallics* 1982, 1, 397. (d) Chisholm, M. H.; Clark, H. C.; Manzer, L. E. *Inorg. Chem.* 1972, 11, 1269.

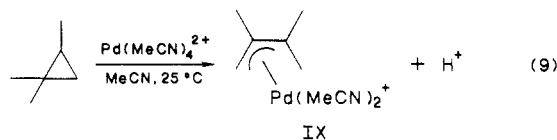


Halpern et al. using Ag^+ as the electrophile.³⁰ More recently, results from theoretical studies of cyclopropane ring opening by Pd(II) complexes indicate³¹ that, as expected, this reaction pathway was favored by the species PdCl^+ , while high activation barriers were found for the less electrophilic species PdCl_2 and PdCl_4^{2-} . With Pd(0) compounds, the favored pathway involved the oxidative addition of a C–C bond of the cyclopropane ring.

Consistent with the above conclusions, we had earlier observed the catalytic ring opening of small-ring compounds by 1.^{6d} A plausible mechanism for the rearrangement of 1,1,3-trimethylcyclopropane (eq 8) is



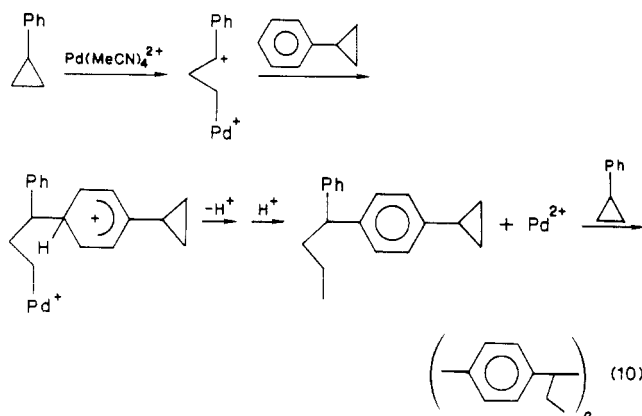
shown in Scheme IV. Paths A and B are the only cleavage modes that lead to the formation of the stable tertiary carbocation. Path A was presumably favored over path B due to steric reasons. The organometallic species observed in the course of the reaction is the cationic η^3 -allyl complex (eq 9).



A remarkable step-growth polymerization that is based on the electrophilic opening of cyclopropanes is the polymerization of cyclopropylbenzene that is catalyzed by 1 and 6.⁸ The polymerization is initiated by the heterolytic C–C bond cleavage of the cyclopropane ring followed by the alkylation of the phenyl group of a second monomer by the resultant cation, the whole process then being repeated (eq 10). Although the mechanism, as outlined, indicates a para substitution pattern for the phenyl groups, both ortho and para substitutions are expected and were observed.

(30) Reviews: (a) Halpern, J. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. II, p 705. (b) Bishop, K. C. *Chem. Rev.* 1976, 76, 461.

(31) Blomberg, M. R. A.; Siegbahn, P. E. M.; Blackvall, J. E. *J. Am. Chem. Soc.* 1987, 109, 4450.



Reactions Involving C–H Bonds

The activation of C–H bonds by transition metals that leads to the *selective functionalization* of hydrocarbons, especially alkanes, is one of the most challenging problems in organometallic chemistry.³² The two common modes for the nonradical activation of C–H bonds are the oxidative addition³³ and electrophilic displacement³⁴ pathways (cf. eq 1 and 2, where X = hydrocarbyl and Y = H).

The electrophilic displacement (heterolytic cleavage) pathway (eq 2) is generally more favorable than the corresponding oxidative addition reaction for two reasons.^{32a} First, the low reactivity of alkanes vis-à-vis most metal compounds is due, at least in part, to the absence of low-lying unoccupied orbitals. Hence, reactions involving such molecules often require the promotion of electrons into antibonding orbitals. Accordingly, the reactivity of alkanes is expected to be highest toward species having low-lying unoccupied orbitals, i.e., electrophiles. Second, the driving force for processes such as eq 2 can be favorably influenced by the stabilization of the leaving group, H^+ . For example, it has been shown that the analogous heterolytic cleavage of H_2 by metal ions such as Cu^{2+} , Ag^+ , and Hg^{2+} is favored by the presence of bases that serve to stabilize the released H^+ ion.³⁵

(32) Reviews: (a) Halpern, J. In *Fundamental Research in Homogeneous Catalysis*; Shilov, A. E., Ed.; Gordon and Breach: New York, 1986; Vol. 1, p 393. (b) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Dordrecht, 1984. (c) Ephritikhine, M. *Nouv. J. Chim.* 1986, 10, 9. (d) Crabtree, R. H. *Chem. Rev.* 1985, 85, 245. (e) Bergman, R. G. *Science (Washington, D.C.)* 1984, 223, 902.

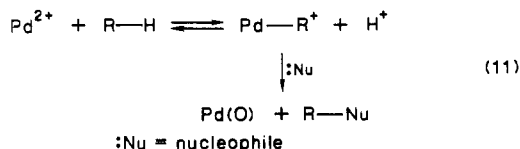
(33) Leading references: (a) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* 1986, 108, 7332. (b) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* 1987, 109, 4726. (c) Jones, W. D.; Maguire, J. A. *Organometallics* 1987, 6, 1301. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* 1986, 108, 4814. (e) Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* 1987, 6, 696. (f) Felkin, H.; Fillebeen-Khan, T.; Gault, Y.; Holmes-Smith, R.; Zakrzewski, J. *Tetrahedron Lett.* 1984, 1279. (g) Nemeth, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* 1983, 2, 1442. (h) Chetcuti, P. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* 1987, 109, 942. (i) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 1449. (j) Fisher, B. J.; Eisenberg, R. *Organometallics* 1983, 2, 764. (k) Sakakura, T.; Sodeyama, T.; Tokunaga, Y.; Tanaka, M. *Chem. Lett.* 1988, 263. (l) Sakakura, T.; Sasaki, K.; Tokunaga, Y.; Wada, K.; Tanaka, M. *Chem. Lett.* 1988, 155. (m) Gustavson, W. A.; Epstein, P. S.; Curtis, M. D. *Organometallics* 1982, 1, 884.

(34) Leading references: (a) Gretz, E.; Oliver, T. F.; Sen, A. *J. Am. Chem. Soc.* 1987, 109, 8109. (b) Aoyama, Y.; Yamagishi, A.; Tanaka, Y.; Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.* 1987, 109, 4735. (c) Aoyama, Y.; Yoshida, T.; Sakurai, K.; Ogoshi, H. *Organometallics* 1986, 5, 168. (d) Shul'pin, G. B.; Nizova, G. V.; Nikitav, A. T. *J. Organomet. Chem.* 1984, 276, 115. (e) Kushch, L. A.; Lavrushko, V. V.; Misharin, Yu. S.; Moravsky, A. P.; Shilov, A. E. *Nouv. J. Chim.* 1983, 7, 729. (f) Geletii, Yu. V.; Shilov, A. E. *Kinet. Katal.* 1983, 24, 486. (g) See also ref 3.

(35) (a) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1977. (b) Halpern, J. *Annu. Rev. Phys. Chem.* 1965, 16, 103.

In principle, it is possible to design a metal-mediated procedure for the oxidation of arenes and alkanes that is based on eq 2. The oxidant could be the metal itself or a separate reagent. With respect to the former, the Pd(II) ion is a particularly attractive choice for three reasons. First, as we have demonstrated, Pd(II) is a powerful electrophile. Second, it is a good two-electron oxidant,^{5c} thus avoiding the formation of radicals. Finally, Pd metal is readily oxidized back to Pd(II) using several different cooxidants, and this forms the basis for a number of Pd(II) catalyzed oxidation processes (e.g., the Wacker process).³⁶

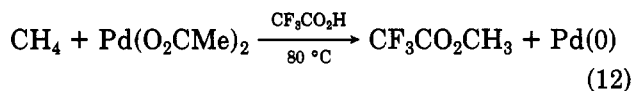
Equation 11 summarizes our approach to the functionalization of arenes and alkanes using the Pd(II) ion as both an electrophile and an oxidant.^{34a} The steps



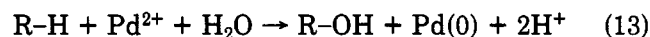
involved in eq 11 are not totally unprecedented since Shilov et al. have postulated a similar mechanistic pathway for the oxidation of hydrocarbons by a combination of Pt(II) and Pt(IV) reagents.^{34e} In addition, the alkylation of arenes by electrophilic Pd(II)-benzyl complexes that we had reported earlier presumably proceeds through an analogous mechanism.³⁷

The initial problem involved the proper choice of the Pd(II) compound and the solvent, and for our preliminary studies we have employed Pd(O₂CCF₃)₂ in CF₃-CO₂H for the following reasons. The CF₃CO₂⁻ ion is a relatively poor base and M-O₂CCF₃ bonds are known to be quite labile.³⁸ Therefore, the Pd(II) species present in the above system is expected to be labile and highly electrophilic. In this context, we note that the electrophilic metalation of arenes by Tl(O₂CCF₃)₃ occurs readily under mild conditions while the corresponding acetate derivative is unreactive.³⁹ Finally, CF₃CO₂H lacks C-H bonds and is a good solvent for a wide spectrum of organic substrates.

Heating adamantane with Pd(O₂CMe)₂ in CF₃CO₂H (i.e., effectively Pd(O₂CCF₃)₂⁴⁰) at 80 °C resulted in the precipitation of Pd metal and the formation of 1-adamantyl trifluoroacetate in >50% yield. Perhaps more significantly, CH₄ (at 800 psi) was oxidized to CF₃CO₂Me in >60% yield (relative to Pd(II)) under the same conditions (eq 12).^{34a}



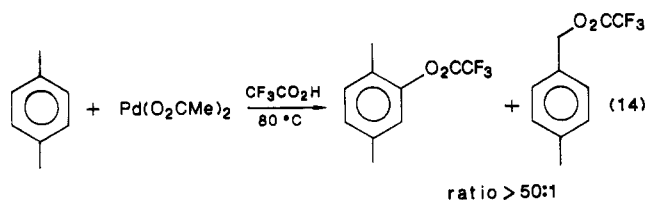
Since the ester can be hydrolyzed to the corresponding alcohol, the overall reaction can be written as follows (eq 13).



If the electrophilic displacement step in eq 11 is reversible, the incorporation of deuterium into the

starting alkane may be expected in the presence of CF₃CO₂D. However, no deuterium incorporation into adamantane was observed during its oxidation, thus indicating that the subsequent nucleophilic attack was fast.

Further information concerning the mechanism of the Pd(II) oxidation of hydrocarbons was obtained through the study of arene oxidations which were also performed at 80 °C using Pd(O₂CMe)₂ in CF₃CO₂H.^{34a} Using these conditions, the monotrifluoroacetoxylation of 1 equiv of *p*-dimethoxybenzene proceeded to completion in 1 h.⁴¹ Under identical conditions, monotrifluoroacetate esters of *p*-xylene were obtained in 35% yield. Furthermore, competition experiments indicated the following relative oxidation rates: *p*-dimethoxybenzene (1), *p*-xylene (0.1), toluene (0.02), benzene (0).⁴² For *p*-xylene and toluene, attack on the ring rather than the benzylic position accounted for >97% and >90%, respectively, of the monotrifluoroacetate esters obtained (eq 14). *This result is in sharp contrast to that re-*



ported for the PtCl₄²⁻-mediated H-D exchange reactions where *para*-disubstituted benzenes do not exchange ring hydrogens at all.⁴³ For example, only the benzylic positions undergo H-D exchange in *p*-xylene. The two conclusions that can be drawn from our own observations on Pd(II) oxidations are that (a) radical pathways are *not* involved since the weak benzylic C-H bonds were not attacked to any significant extent and (b) the enhanced rate of oxidation with electron-rich arenes is consistent with an electrophilic displacement pathway as shown in eq 11.

Using toluene-*d*₀ and toluene-*d*₈, a primary isotope effect (*k*_H/*k*_D) of 5.0 (5) was observed for the oxidation reaction. The magnitude of the isotope effect clearly indicates that the rate-determining step involves C-H bond breaking rather than a simple π-coordination of the arene or the formation of a Wheland intermediate.⁴⁴ The formation of the latter species has been proposed as the slow step in the electrophilic metalation of arenes by Pt(IV).^{34d} We note, however, that the electrophilic mercuriation of arenes is usually accompanied by similar large isotope effects.⁴⁵

Finally, preliminary results indicate that the Pd(II)-mediated monotrifluoroacetoxylation of *p*-dimethoxybenzene can be made catalytic in Pd(II) by using K₂S₂O₈ as the cooxidant. For example, quantitative conversion of *p*-dimethoxybenzene was observed in 1 h at 80 °C in CF₃CO₂H, starting with the following

(41) Pd(II)-mediated ring acetoxylation of arenes is well-known. (a) Review: ref 5c, Chapter VI. (b) Mechanism: Ebersson, L.; Jönsson, L. *Liebigs Ann. Chem.* 1977, 233.

(42) Significant quantities of biaryls, formed by a mechanistically independent pathway (ref 5c, Chapter VI), were also observed for toluene and benzene.

(43) Reference 32b, Chapter V.

(44) Reviews on isotope effects in aromatic electrophilic substitutions: (a) Zollinger, H. *Adv. Phys. Org. Chem.* 1964, 2, 163. (b) Berliner, E. *Prog. Phys. Org. Chem.* 1964, 2, 253.

(45) Lau, W.; Kochi, J. K. *J. Am. Chem. Soc.* 1986, 108, 6720. See also: Shue, R. S. *J. Am. Chem. Soc.* 1971, 93, 7116.

(36) Reference 5c, Chapter II.

(37) Gretz, E.; Sen, A. *J. Am. Chem. Soc.* 1986, 108, 6038.

(38) Review: Garner, C. D.; Hughes, B. *Adv. Inorg. Chem. Radiochem.* 1975, 17, 1.

(39) McKillop, A.; Taylor, E. C. In ref 4, p 499.

(40) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffere, J. P.; Wilkinson, G. *J. Chem. Soc.* 1965, 3632.

concentrations: *p*-dimethoxybenzene (0.43 M), Pd(O₂CMe)₂ (0.09 M), K₂S₂O₈ (1.1 M).

Conclusion

It is clear from the preceding discussions that the reaction pathways favored by electrophilic metal complexes differ significantly from those involved in reactions of electron-rich metal compounds. However, more detailed mechanistic studies are required to fully understand the reactivity profile of electrophilic metal species and how it can be influenced by the proper choice of the metal and the ligands attached to it. Apart from their fundamental scientific importance, such studies are also useful from a practical standpoint. As the rich organic chemistry of Pd(II)⁴⁶ and Ln(III)⁴⁷ (to pick two very different metals as examples) clearly indicates, electrophilic metal ions are employed in many different facets of organic synthesis. In addition, since electrophilic metal ions are less sensitive to oxidizing agents than electron-rich metal centers, it should be easier to design catalytic systems employing the former

(46) Review: ref 5. Few specific recent examples: (a) Trost, B. M. *J. Organomet. Chem.* 1986, 300, 263. (b) Hegedus, L. S.; Mulhern, T. A.; Asada, H. *J. Am. Chem. Soc.* 1986, 108, 6224.

(47) Review: Natale, N. R. *Org. Prep. Proced. Int.* 1983, 15, 387. Few specific recent examples: Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* 1986, 108, 7060.

species to convert hydrocarbon raw materials to valuable oxidatively functionalized organic products. This is particularly relevant to the problem of catalytic oxidative functionalization of alkanes.

Finally, while we have restricted our discussions to one class of electrophilic metal complexes, work on other types of electrophilic early transition, lanthanide, and actinide compounds has shown that they play a critical role in such important reactions as C-H³ and C-C⁴⁸ activation and polymerization of simple olefins.⁴⁹

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(48) Leading reference: (a) Reference 3a. (b) Vol'pin, M. E.; Akhrem, I. S.; Reznichenko, S. V.; Grushin, V. V. *J. Organomet. Chem.* 1987, 334, 109. See also: Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* 1984, 1260.

(49) Leading references: (a) Lin, Z.; Le Marechal, J.-F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* 1987, 109, 4127. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Sweptson, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* 1985, 107, 8091. (c) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* 1986, 108, 7410. (d) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* 1985, 107, 7219. (e) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* 1985, 18, 51. (f) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* 1984, 56, 1.

Aspects of Intermediacy of Carbalkoxymetal Complexes in CO Reactions

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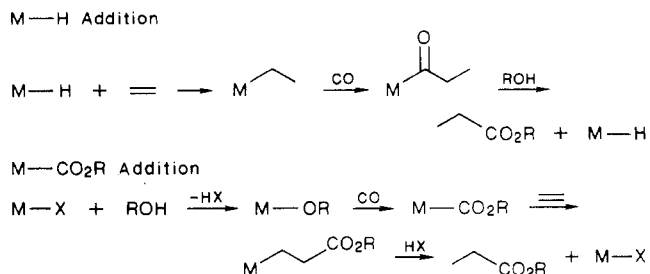
Carbonylation reactions rank among the most useful transformations homogeneously catalyzed by transition-metal complexes, forming the basis for industrial and laboratory processes currently in practice. Among these are a considerable number of reactions that lead to formation of carbalkoxy-containing organic molecules. These diverse reactions, some of which are summarized in Table I, may have as a unifying mechanistic theme the generation and controlled decomposition of a carbalkoxymetal intermediate, M-CO₂R.¹

In this Account, we describe mechanistic aspects of olefin carbalkoxylation, alkyl halide carbalkoxylation, carbalkoxylation of π -alkyl complexes, and CO hydrogenation. By utilizing model carbalkoxy complexes, the

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process	proposed key reaction
olefin carbalkoxylation	$M-CO_2R + \text{olefin} \rightarrow M-\text{CH}_2\text{CH}_2\text{CO}_2R$
RX carbonylation	$R'-M-CO_2R \rightarrow R'/CO_2R$
oxalates from alcohols	$RO_2C-M-CO_2R \rightarrow RO_2C-CO_2R$
carbonates from alcohols	$M-CO_2R + R'OH \rightarrow RO_2C-M-CO_2R$
carbamates from amines	$M-CO_2R + R'NH_2 \rightarrow R'NHCO_2R$
methyl formate from CO/H ₂	$M-CO_2CH_3 + H_2 \rightarrow HCO_2CH_3$

Scheme I



question of intermediacy of such species in those reactions is being addressed, emphasizing recent work from our laboratory.