

and which resists deformation.  $F^-$  is complexed but  $I^-$  does not form a stable complex, nor do other anions like  $NO_3^-$ ,  $SO_4^{2-}$ , etc.<sup>24</sup>

The design of cavities acting as receptors for other anions is feasible; the major requirement is to provide suitable electrostatic interactions and the correct array of hydrogen bonds for the anion while hindering as much as possible the hydration of the hydrogen bond donor sites. A new field of coordination chemistry is thus developing: anion complexes of organic ligands.

### Prospects

Several lines for future developments may be recognized: (1) the design and synthesis of new types of organic molecules; (2) the construction of specific receptors bearing recognition sites for cations, anions, and molecules; (3) the design of molecular catalysts and selective carriers; (4) the synthesis of ligands bearing several cation-complexing sites and thus forming binuclear or polynuclear complexes in which distance and arrangement of the cations may be regulated via ligand

structure; (5) the study of cascade complexes formed by substrate inclusion between metal cations of bi- or polynuclear complexes, which are of interest as bioinorganic models and as catalysts.

As a symbiosis of the architectural power of organic synthesis with the designed manipulation of intermolecular interactions and transformations, the chemistry of macropolycyclic systems may have a broad impact on both fundamental and applied research at the ternary meeting point of three major fields of chemistry: organic chemistry, inorganic chemistry, and biochemistry.

*I wish to express my gratitude to the co-workers whose skill and dedication allowed us to realize the work described above. Their names appear in the references listed. The expenses incurred were borne by grants from the Centre National de la Recherche Scientifique, the Délégation Générale à la Recherche Scientifique et Technique, and the University Louis Pasteur.*

(82) For a recent report see: O. A. Gansow, A. R. Kausar, K. M. Triplett, M. J. Weaver, and E. L. Yee, *J. Am. Chem. Soc.*, **99**, 7087 (1977).

## Reactions of Electrophiles with $\sigma$ -Bonded Organotransition-Metal Complexes

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Mainly because of the need to start with well-characterized substrates, most of the mechanistic studies of the cleavage of carbon-metal  $\sigma$  bonds have utilized isolable, relatively stable, usually diamagnetic, organometallic complexes. Since by their very nature the selected complexes are not very prone to unimolecular decomposition in solution, the overall picture of reaction mechanisms is somewhat distorted, biased in favor of reagent-induced or concerted mechanisms. Nevertheless, such limited studies of mechanism have provided valuable information about ways in which carbon-metal bonds may be cleaved, and much of our present knowledge concerns those reactions promoted by electrophilic reagents. Even within this classification, however, a surprisingly wide range of different mechanisms have been identified and can be ascribed to the versatile character of many organometallic substrates and of electrophilic reagents.

In the field of  $\sigma$ -bonded organotransition-metal complexes, the variety of ligands often required to stabilize the carbon-metal bond ensures that such complexes are frequently polyfunctional molecules

containing groups of widely different character, atoms of significantly different electronegativity and any of a range of possible charges. The highest occupied molecular orbital, which usually plays a vital role in these reactions, may be located on the metal, on one of the ligands, or in metal-ligand bonds. Thus the initial stage of a reaction between an organotransition-metal complex and an electrophile does not necessarily involve cleavage of the carbon-metal bond, though such cleavage frequently occurs in later processes.

Electrophiles are also versatile species, but in a different sense: they are also Lewis acids and oxidizing agents. The term *electrophilicity* should imply a kinetic role,<sup>1</sup> often rather narrowly associated solely with substitution processes, whereas Lewis acidity implies the corresponding thermodynamic role. Electrophilicity and Lewis acidity do not necessarily parallel one another, for each is markedly dependent upon the reacting center on the substrate. There have been a number of theories to account for these variations in electrophilicity and acidity, including the hard/soft<sup>2</sup> or class A/B approach,<sup>3</sup> the Edwards combination of proton acidity and redox potential discussed mainly with the nucleophilic center in mind,<sup>4</sup> and the orbital approach

Michael D. Johnson was born in Newcastle-under-Lyme, England. He studied at Southampton University for his B.Sc. degree, and then went on to graduate work there, receiving the Ph.D. under N. B. Chapman in 1957. After a year of postdoctoral work with E. S. Lewis at Rice University and a year as a chemist at Imperial Oil Ltd., Sarnia, Canada, Dr. Johnson moved to University College London, where he is now Reader in Chemistry. His research is concerned with the mechanisms of reactions of  $\sigma$ -bonded organotransition-metal compounds, with special interest in homolytic displacement reactions, particularly at carbon centers, and their use in organic synthesis.

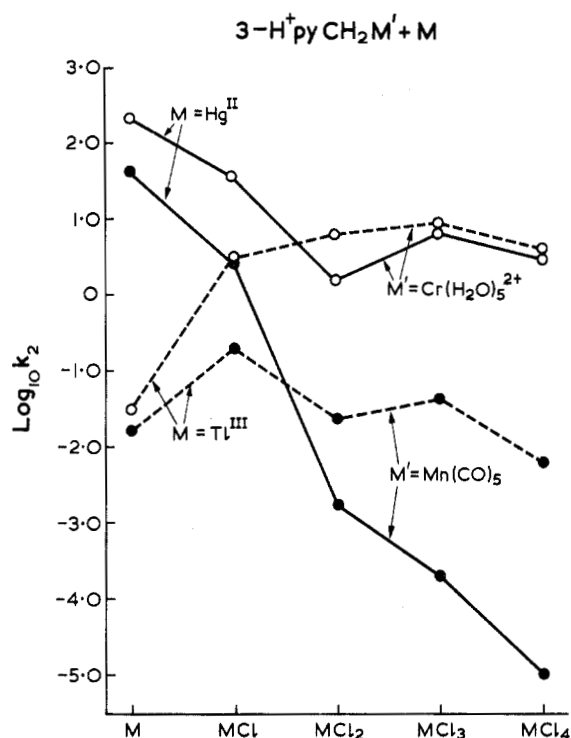
(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967, p 124.

(2) R. G. Pearson, *J. Chem. Educ.*, **45**, 581, 643 (1968).

(3) S. Ahrland, J. Chatt, and N. R. Davies, *Q. Rev., Chem. Soc.*, **12**, 265 (1958).

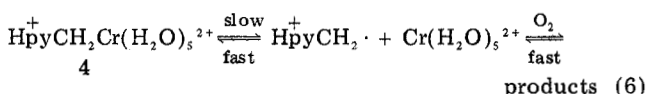
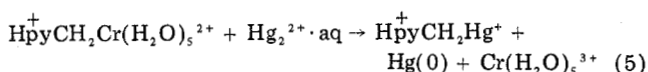
(4) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).





**Figure 1.** Estimated rate constants for the reaction of mercury(II) and thallium(III) species with 3-pentaaquapyridiniomethylchromium(III) ion and pyridiniomethylpentacarbonylmanganese.

um(III) ions with  $\text{Hg}_2^{2+}\cdot\text{aq}$  in aqueous solution is too fast to involve the low maintained concentration of  $\text{Hg}_2^{2+}\cdot\text{aq}$  (eq 4) and therefore involves the direct attack

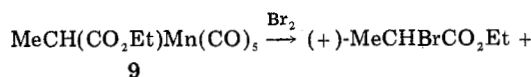
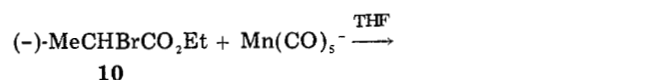
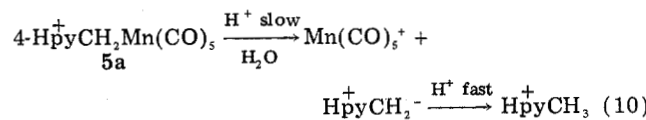
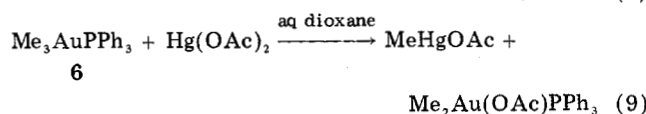
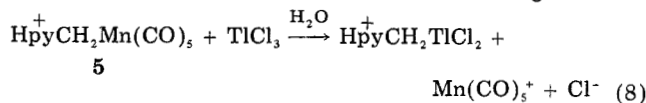
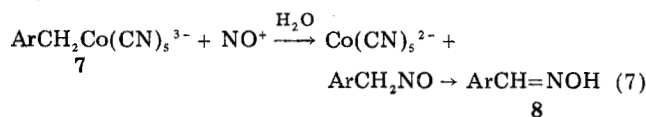


of  $\text{Hg}_2^{2+}\cdot\text{aq}$  on the  $\alpha$  carbon with the formation of three species, the pentaaquachromium(III) ion 2, the new organomercury(II) cation, and mercury(0) (eq 5). The spectrum of the latter is evident in dilute solutions in the early stages of the reaction prior to aggregation. The majority of organometallic substrates react more readily with the low concentrations of  $\text{Hg}_2^{2+}$ .

As aqueous acidic solutions have been used for all of the above studies, the reaction with the proton has special significance. In several cases under aerobic conditions the rates of decomposition of the organochromium ions are independent of the acid concentration (eq 3;  $k_2 = 0$ ) because homolysis of the carbon-chromium bond is rate determining (eq 6).<sup>16</sup> In other cases under anaerobic conditions there is both an acid-dependent and an acid-independent path. Only in the case of the methylpentaaquachromium(III) ion are the clean second-order kinetics and the organic product (methane) consistent with a bimolecular displacement reaction.<sup>17</sup>

The organopentacarbonylmanganese(I), organogold(III), and organopentacyanocobaltate(III) com-

plexes (5, 6, and 7, respectively) are further examples



of substrates that are not prone to oxidation, have nonlabile ligands, and undergo a number of direct displacement reactions. Thus,  $\text{NO}^+$  reacts with 1 ( $\text{R} = \text{Ph}$  or  $\text{Hpy}^+$ ) and 7 by a direct substitution to give, initially, the *C*-nitroso compound 8 which readily dimerizes or rearranges to the oxime.<sup>18</sup> Mercury(II) and thallium(III) species also react with 5,<sup>19</sup> 6,<sup>20</sup> and 7<sup>21</sup> with clean second-order kinetics (eq 8 and 9); rate coefficients estimated for reaction of a range of mercury(II) and thallium(III) species with 5 are shown in the figure.<sup>19</sup> The acidolysis of 6 is also bimolecular and involves a direct displacement of only one of the methyl groups cis to the phosphine,<sup>22</sup> whereas the acidolysis of 5a is independent of acid concentration in up to 4 M perchloric acid; in contrast to the homolysis in eq 6, this reaction involves a unimolecular heterolysis (eq 10).<sup>23</sup>

Kinetic studies have not been carried out on the halogenation of the above complexes, but the bromination of 9 in tetrahydrofuran to give the bromide 10 ( $[\alpha]_D^{1^\circ}$ ) is believed to involve substantial retention of configuration at the  $\alpha$  carbon. This is based on the assumption that its formation from the same bromide ( $[\alpha]_D^{-6^\circ}$ ) and  $\text{Mn}(\text{CO})_5^-$  takes place with inversion of configuration.<sup>24</sup> Retention of configuration has also been observed in the bromination in benzene at  $10^\circ$  and iodination of diastereoisomers of  $d^0$  *t*-BuCHDCHDZr(cp)<sub>2</sub>Cl,<sup>25</sup> which is perhaps the closest analogy to reactions of the main-group alkyls.

The course of these direct displacement reactions is probably dictated by two factors, the coordinative

(18) E. H. Bartlett and M. D. Johnson, *J. Chem. Soc. A*, 523 (1970).

(19) D. Dodd, M. D. Johnson and N. Winterton, *J. Chem. Soc. A*, 910 (1971).

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(21) E. H. Bartlett and M. D. Johnson, *J. Chem. Soc. A*, 517 (1970).

(22) S. Komiya, T. A. Albright, R. Hoffman, and J. K. Kochi, *J. Am. Chem. Soc.*, **98**, 7255 (1976).

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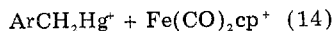
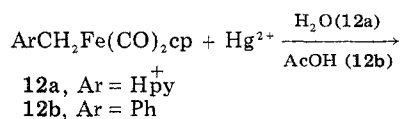
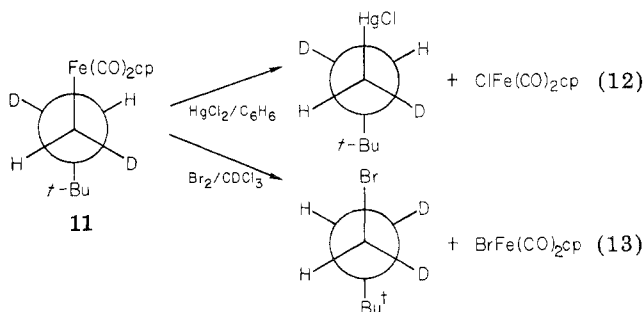
(24) R. W. Johnson and R. G. Pearson, *J. Chem. Soc., Chem. Commun.*, 986 (1970); *Inorg. Chem.*, **10**, 209 (1971).

(25) J. A. Labinger, D. W. Hart, W. E. Seibert, and J. Schwartz, *J. Am. Chem. Soc.*, **97**, 3851 (1975).

(16) R. G. Coombes and M. D. Johnson, *J. Chem. Soc. A*, 177 (1966).

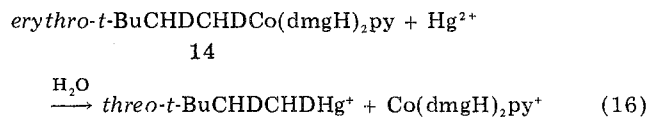
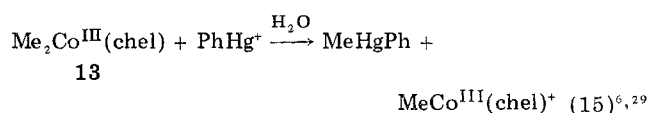
(17) W. Schmidt, J. H. Swinehart and H. Taube, *J. Am. Chem. Soc.*, **93**, 1117 (1971).

saturation of the metal and the fact that the HOMO is the carbon-metal bond orbital.<sup>26</sup> Where other orbitals are close in energy to the carbon-metal bond orbital and the metal is not coordinatively saturated, other pathways may intrude and polarizability effects may dominate. In such circumstances consideration of the ground-state orbital energies alone may not be sufficient to determine the reaction course, which will be strongly influenced by the nature of the electrophile. For example, several organoiron complexes (e.g., 11 and 12a) react cleanly with metallic electrophiles such as HgCl<sub>2</sub>,<sup>27,28</sup> but the course of reaction with halogens is solvent dependent. Thus, diastereoisomeric 11 reacts with HgCl<sub>2</sub> in benzene with retention of configuration (eq 12) and the rate profile for the reaction of 12a with



Hg(II) and Tl(III) species in aqueous solution almost exactly parallels that shown in Figure 1 for 5. On the other hand 11<sup>27a</sup> and other organoiron complexes<sup>27b</sup> react with iodine and bromine in aprotic solvent to give the corresponding alkyl halide with inversion of configuration (eq 13) and react with chlorine and bromine in protic solvents to give products characteristic of an initial oxidation process. It seems likely that the halogenation in aprotic solvents also involves oxidation as outlined in a later section.

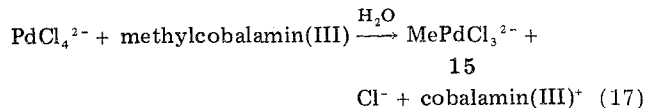
Similar mechanistic borderlines are even more apparent with alkylcobalt(III) complexes. The reactions of several such complexes with mercury(II) species have been studied in detail<sup>29-34</sup> because of their relation to the role of methylcobalamin in the biological methylation of mercury. In almost all cases primary alkylcobalt(III) complexes, e.g., 13, react with aqueous Hg<sup>2+</sup>



and Tl<sup>3+</sup> with clean second-order kinetics, in some cases acid dependent because of a rate-retarding protonation of equatorial ligands, consistent with the direct substitution mechanism. Studies of the influence of anionic ligands on the reactivity of the mercury(II) species have not been in sufficient detail to allow precise conclusions about the reactivity of individual electrophiles.<sup>32</sup> The influence of micelles has also been studied.<sup>35</sup> The observation that diastereoisomeric 14 reacts with Hg<sup>2+</sup> with inversion of configuration is not necessarily at variance with the substitution mechanism because the leaving group is so large that the electrophile can only interact with the rear lobe of the carbon-metal bond orbital. The use of such diastereoisomeric primary alkyl complexes is now common because of the low reactivity and/or difficulties in preparation of chiral secondary alkyl complexes and the problem of assigning their configuration.

Secondary alkylcobalt(III) complexes do not usually undergo clean substitution reactions with metallic electrophiles and, though primary and secondary organocobaloximes react under some conditions with halogens to give alkyl halides<sup>36,37</sup> with inversion of configuration, these reactions have characteristics of oxidation processes.

Besides the biological methylation of mercury, methylcobalamin has also been implicated in a number of other reactions in which alkyl groups are transferred to other metals.<sup>38</sup> Several preliminary studies have been made on the reactions with tin(IV),<sup>39</sup> lead(IV),<sup>40</sup> arsenic,<sup>41</sup> palladium(II),<sup>42</sup> platinum(II) and platinum(IV), and gold(I) and gold(III).<sup>43</sup> The most unexpected of these results concerns the postulate that low-valent d<sup>8</sup> PdCl<sub>4</sub><sup>2-</sup> is the active electrophile in the formation of the unstable methylpalladium(II) complex 15 from



$$-d[\text{methylcobalamin}]/dt = k[\text{methylcobalamin}][\text{Pt}^{\text{IV}}][\text{Pt}^{\text{II}}] \quad (18)$$

methylcobalamin.<sup>42</sup> In contrast, neither platinum(II)

(26) W. A. Nugent and J. K. Kochi, *J. Am. Chem. Soc.*, **98**, 5979 (1976).  
(27) (a) P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 2814 (1974); (b) K. M. Nicholas and A. M. Rosin, *J. Organomet. Chem.*, **84**, 351 (1975).  
(28) D. Dodd and M. D. Johnson, *J. Chem. Soc. B*, 662 (1971).  
(29) J. H. Espenson, W. R. Bushey and M. E. Chmielewski, *Inorg. Chem.*, **14**, 1302 (1975); J. H. Espenson, H. L. Fritz, R. A. Heckman, and C. Nicolini, *ibid.*, **15**, 906 (1976).  
(30) P. Abley, E. R. Dockal, and J. Halpern, *J. Am. Chem. Soc.*, **95**, 3166 (1973).  
(31) R. E. DeSimone, M. W. Penley, L. Charbonneau, S. G. Smith, J. M. Wood, H. A. O. Hill, J. M. Pratt, S. Ridsdale, and R. J. P. Williams, *Biochim. Biophys. Acta*, **304**, 851 (1973).  
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(34) H. L. Fritz, J. H. Espenson, D. A. Williams, and G. A. Molander, *J. Am. Chem. Soc.*, **96**, 2378 (1974).

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(36) F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Am. Chem. Soc.*, **93**, 5283 (1971); R. Dreos, G. Tauzher, N. Marsich, and G. Costa, *J. Organomet. Chem.*, **92**, 227 (1975); S. N. Anderson, D. H. Ballard, and M. D. Johnson, *J. Chem. Soc., Perkin Trans. 2*, 311 (1972); *J. Chem. Soc., Chem. Commun.*, 685 (1972).  
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(38) J. M. Wood, *Naturwissenschaften*, **62**, 357 (1975).  
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(42) W. M. Scovell, *J. Am. Chem. Soc.*, **96**, 3451 (1974).  
(43) G. Agnes, S. Bendle, H. A. O. Hill, F. R. Williams, and R. J. P. Williams, *J. Chem. Soc., Chem. Commun.*, 850 (1971).

nor platinum(IV) reacts with methylcobalamin on their own; each requires the presence of the other in at least catalytic quantity, according to eq 18. A likely mechanism involves electrophilic attack on the  $\alpha$  carbon by platinum(IV) with reductive catalysis through interaction of platinum(II) with either cobalt or platinum. An identical situation arises with gold(I) and gold(III).<sup>43</sup>

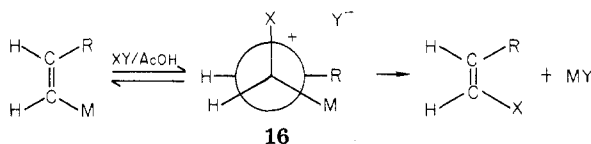
Radical displacements are sometimes disguised as electrophilic reactions; thus, the displacement of cobalt(III) from some alkylcobalt(III) complexes by other electrophilic cobalt(III) complexes (eq 19)<sup>44</sup> is catalyzed

$$\text{RCo}^{\text{III}}(\text{dmgH})_2\text{B} + \text{Co}^{\text{III}}(\text{salen})\text{B}^+ \rightleftharpoons \text{RCo}^{\text{III}}(\text{salen})\text{B} + \text{Co}^{\text{III}}(\text{dmgH})_2\text{B}^+ \quad (19)$$

by traces of cobalt(II) complexes, probably through a direct *homolytic* displacement at the  $\alpha$  carbon of the alkyl group.<sup>45</sup> Similarly, in the acidolysis of alkylcobaloximes in the presence of thiols,<sup>41</sup> the kinetic form is inconsistent with the proposed attack of a proton on an alkyl(thiolato)cobaloxime; radical pathways are also competitive in the reactions of alkylgold complexes with thiols.<sup>46</sup>

#### Electrophilic Attack at $\alpha$ (Unsaturated) Carbon.

The electrophilic displacement of cobalt(III) from *cis*- and *trans*- $\beta$ -styrylcobaloximes by  $\text{Hg}(\text{OAc})_2$  and halogens in acetic acid proceeds with complete retention of configuration (e.g., eq 20; R = Ph, M = Co-

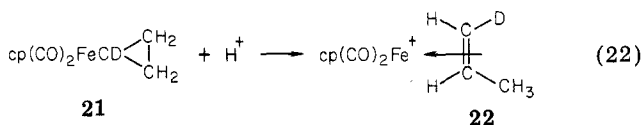
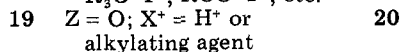
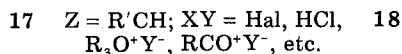
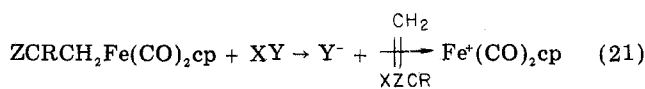


( $\text{dmgH}$ )<sub>2</sub>py; X-Y =  $\text{AcOHg-OAc}$  or  $\text{Hal}_2$ ).<sup>47</sup> Many other substituted vinylcobaloximes do not react stereospecifically, either because cationic intermediates such as **16** (e.g., R = EtOCO, XY = Br<sub>2</sub>) have sufficient lifetime for rotation to occur about the carbon-carbon bond or because radical pathways intrude.

#### Reactions Involving Substantial Modification of the Carbon-Metal Bond

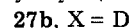
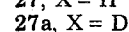
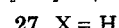
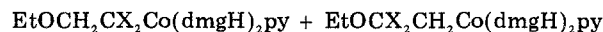
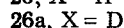
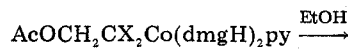
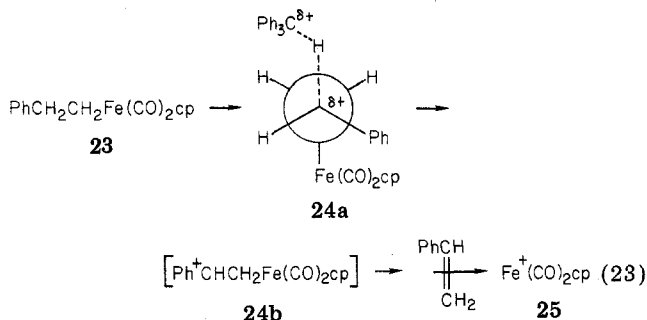
Though in principle synchronous cleavage of the carbon-metal bond may also occur when electrophiles attack at other than the  $\alpha$  carbon, there is an appreciable tendency in such cases for the carbon-metal bond merely to be modified.

**Rearrangement to Stable  $\pi$  Complexes through Electrophilic Attack at the  $\gamma$  Carbon of Allyl Complexes, and Related Reactions.** Protonation, acylation, bromination, and alkylation of several  $\sigma$ -allyliron complexes **17** in aprotic solvents lead directly to the corresponding terminal  $\pi$ -complex **18**.<sup>48,49</sup> Related  $\sigma$ - $\pi$  rearrangements include: stannylation<sup>50</sup> or protonation<sup>51</sup> of propargyliron complexes to give  $\pi$ -



allene complexes; protonation or alkylation of a  $\beta$ -carbonyl group as in **19** to give the  $\pi$ -complex **20**;<sup>52</sup> and  $\alpha$  protonation of the deuterated cyclopropyliron complex **21** with subsequent prototropic shift to give the single  $\pi$ -complex **22**.<sup>53</sup> The role of these complexes in organic synthesis, including further reactions of the  $\pi$  complexes in nucleophilic solvents, has been very well reviewed.<sup>48</sup>

**Formation of  $\pi$  Complexes by Hydride Abstraction from  $\sigma$  Complexes.** The trityl cation and related species readily abstract hydride ion from primary and secondary alkyl complexes to give  $\pi$  complexes.<sup>54</sup> For example, the  $\beta$ -phenylethyl complex **23**



(24)

reacts with the trityl cation to give the  $\pi$ -complex **25**; deuterium labeling indicates that the hydride abstraction takes place predominantly by a trans-anti-periplanar process through the gauche conformation **24a**,<sup>55</sup> though a further intermediate **24b**, configurationally stabilized by hyperconjugation,<sup>56</sup> cannot be ruled out.

**Transient  $\pi$  Complexes in  $\sigma$ - $\pi$ - $\sigma$  Rearrangements.** The reaction of  $\beta$ -acetoxyethylcobaloxime **26** in absolute ethanol gives the corresponding  $\beta$ -ethoxyethylcobaloxime **27** at a rate ( $k = 4.37 \times 10^{-6} \text{ s}^{-1}$  at 25 °C) that is far higher than expected for a normal ethanolysis of a primary alkyl acetate.<sup>57</sup> That this and

(44) G. Mestroni, C. Cocevar, and G. Costa, *Gazz. Chim. Ital.*, **103**, 273 (1973).

(45) D. Dodd, M. D. Johnson, and B. L. Lockman, *J. Am. Chem. Soc.*, **99**, 3664 (1977).

(46) N. G. Hargreaves, A. Johnson, R. J. Puddephat, and L. H. Sutcliffe, *J. Organomet. Chem.*, **69**, C21 (1974).

(47) D. Dodd, M. D. Johnson, B. S. Meeks, D. M. Titchmarsh, K. N. V. Duong, and A. Gaudemer, *J. Chem. Soc., Perkin Trans. 2*, 1262 (1976).

(48) M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974).

(49) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

(50) C. V. Magatti and W. P. Giering, *J. Organomet. Chem.*, **73**, 85 (1974).

(51) S. Raghu and M. Rosenblum, *J. Am. Chem. Soc.*, **95**, 3060 (1973).

(52) M. L. H. Green and C. R. Hurley, *J. Organomet. Chem.*, **10**, 188 (1967); S. Raghu and M. Rosenblum, *ibid.*, **77**, 381 (1970).

(53) A. Cutler, R. W. Fish, W. P. Giering, and M. Rosenblum, *J. Am. Chem. Soc.*, **94**, 4354 (1972).

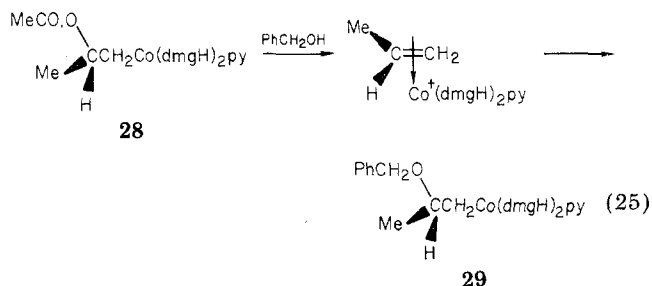
(54) M. L. H. Green and P. L. I. Nagy, *J. Organomet. Chem.*, **1**, 58 (1963).

(55) D. Slack and M. C. Baird, *J. Chem. Soc., Chem. Commun.*, 701 (1974).

(56) C. W. Fong and M. D. Johnson, unpublished work.

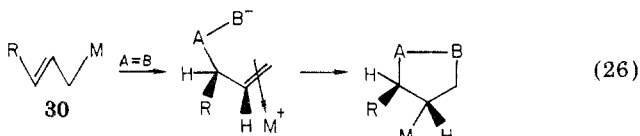
related reactions involve the formation of a cobalt(III)  $\pi$  complex has been demonstrated by the formation of equal amounts of **27a** and **27b** from **26a**;<sup>58</sup> this rearrangement has been confirmed by carbon-13 labeling.<sup>59</sup>

The formation of [(+)-S]-2-(benzyloxy)propylcobaloxime **29** from [(+)-S]-2-acetoxypropylcobaloxime



**28** and benzyl alcohol indicates that formation of the  $\pi$  complex takes place with a stereospecific antarafacial migration of the metal.<sup>58</sup> Transient  $\pi$  complexes are also formed in a number of other acid-catalyzed reactions of cobaloximes, including the rearrangement of  $\beta$ -hydroxyisopropyl- to  $\beta$ -hydroxy-*n*-propylcobaloxime catalyzed by acidic ion-exchange resins<sup>59</sup> and the hydrolysis of acetals of formylmethylcobaloxime.<sup>60,61</sup>

**$\sigma$ - $\pi$ - $\sigma$  Rearrangements with Cyclization.** The earliest example of cyclization via  $\pi$ -complex formation was in the reaction of  $\sigma$ -propargyl complexes with sulfur dioxide.<sup>62</sup> A wide range of related cyclizations have since been observed with allenyl, allyl, and cyclopropylcarbinyl complexes of a variety of metals with a variety of unsaturated electrophiles,<sup>63-65</sup> and these have been well reviewed.<sup>48</sup> In the case of allyl complexes **30**



M = (from)  $\text{Co}(\text{dmgH})_2\text{py}$ ,  $\text{Mn}(\text{CO})_5$ ,  $\text{Fe}(\text{CO})_2\text{cp}$ ,  $\text{Re}(\text{CO})_5$ ,  $\text{W}(\text{CO})_3\text{cp}$ , etc.

A = B = (from) TCNE,  $(\text{CF}_3)_2\text{CO}$ ,  $\text{ClSO}_2\text{NCO}$ , etc.

the rearrangements involve an antarafacial migration of the metal induced by attack of the dipolar or potentially dipolar electrophile.<sup>63,65</sup> However, a number of these reactions are complicated by competing processes involving electron transfer and insertion reactions.

**Insertion Reactions.** Insertion, particularly of  $\text{SO}_2$ <sup>64</sup> and TCNE,<sup>66</sup> between the organic ligand and the metal of allyl- and alkyl-metal complexes, though far from

(57) B. T. Golding, H. L. Holland, U. Horn, and S. Sakrikar, *Angew. Chem.*, **9**, 959 (1970).

(58) B. T. Golding and S. Sakrikar, *J. Chem. Soc., Chem. Commun.*, 1183 (1972).

(59) K. L. Brown and L. L. Ingraham, *J. Am. Chem. Soc.*, **96**, 7681 (1976).

(60) R. B. Silverman and D. Dolphin, *J. Am. Chem. Soc.*, **98**, 4626 (1976).

(61) T. M. Vickerey, R. N. Katz, and G. N. Schrauzer, *J. Am. Chem. Soc.*, **97**, 7248 (1975).

(62) J. E. Thomasson, P. W. Robinson, D. A. Ross, and A. Wojcicki, *Inorg. Chem.*, **10**, 2130 (1971).

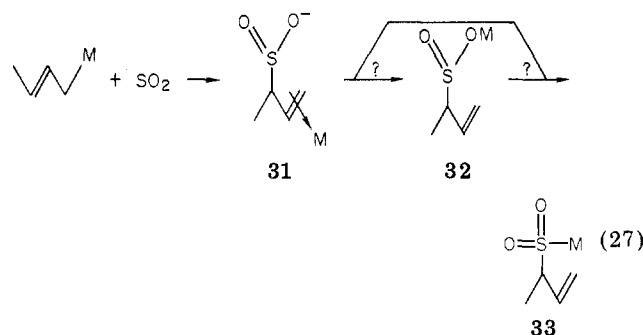
(63) A. Cutler, D. Entholt, W. P. Giering, P. Lennon, S. Raghu, A. Rosan, M. Rosenblum, J. Tancredi, and D. Wells, *J. Am. Chem. Soc.*, **98**, 3495 (1976).

(64) S. R. Su and A. Wojcicki, *Inorg. Chem.*, **14**, 89 (1975); W. P. Giering and M. Rosenblum, *J. Am. Chem. Soc.*, **93**, 5299 (1971).

(65) D. Dodd, M. D. Johnson, and E. D. McKenzie, *J. Am. Chem. Soc.*, **98**, 6399 (1976).

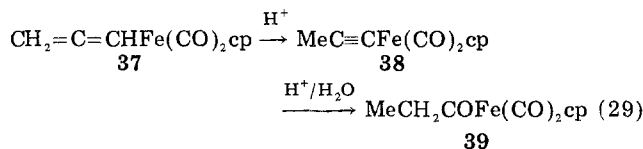
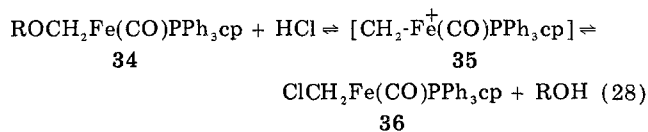
(66) A. Wojcicki, *Acc. Chem. Res.*, **4**, 344 (1971); *Adv. Organometal. Chem.*, **12**, 31 (1974).

fully understood, has frequently been assumed to involve an electrophilic attack of the inserting species. The situation is often complicated by the formation of several isomeric products such as **32** and **33** and also by the fact that some reactions (e.g., where M =  $\text{Co}(\text{dmgH})_2\text{py}$ ) are not true insertions, but probably involve chain reactions including homolytic displacement by  $\text{MSO}_2$  radicals.<sup>67</sup>



### Formation of Transient Carbene Complexes.

Attack of an electrophile, especially of a proton, at a nucleophilic  $\beta$  atom can lead to the formation of carbene-like complexes. Thus, **34** (R = alkyl) is readily



converted into the chloroalkyl complex **36** (optically active in the case of the resolved diastereoisomeric complex **34**, R = menthyl),<sup>68b</sup> probably via the transient carbene complex **35**;<sup>68</sup> similarly, the  $\sigma$ -allenyl complex **37**<sup>69</sup> is hydrolyzed to the alkynyl complex **38** and thence to the acyl complex **39**, probably via first a  $\pi$ -acetylene and then a carbene complex.<sup>49,70</sup>

### Oxidative Processes

**Electrophilic Attack on the Metal.** Attack of the electrophile on the metal is most likely to occur with coordinatively unsaturated low-valent complexes such as the  $d^8$  and  $d^{10}$  organoplatinum(II), -iridium(I), and -gold(I) complexes. For example, the *cis*-platinum(II) complex **40a** reacts with chlorine or iodine in aprotic solvents to give the platinum(IV) adduct, whereas **40b** reacts with iodine to give the platinum(II) complex **42** and the alkyl iodide.<sup>71</sup> Alkyl halides react in a similar manner, but the formation of the alkane  $\text{R}_2$  and *trans*- $\text{Pt}(\text{PEt}_3)_2\text{I}_2$  from **40**<sup>71</sup> and alkyl iodides is strongly indicative of free radical processes.

Alkyl groups are readily cleaved by acids from monoalkylbis(phosphine)palladium(II) complexes,<sup>72</sup> but

(67) A. E. Crease, A. Gaudemer, and M. D. Johnson, unpublished work.

(68) (a) M. L. H. Green, M. Ishaq, and R. Whiteley, *J. Chem. Soc. A*, 1508 (1967); (b) T. C. Flood, F. G. DiSanti, and D. L. Miles, *Inorg. Chem.*, **15**, 1910 (1976).

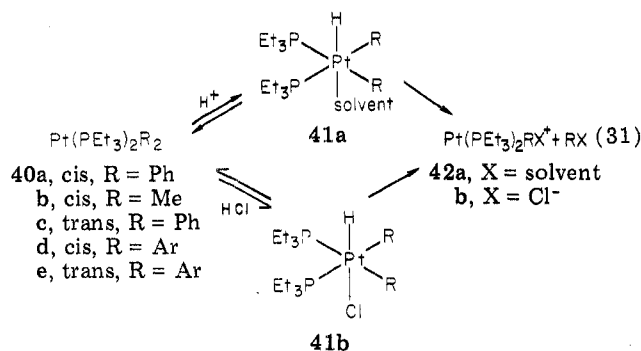
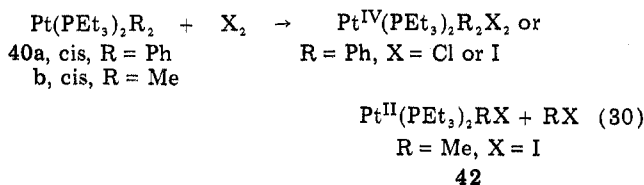
(69) Complex **51** has twice been wrongly characterized,<sup>48,70</sup> the incorrect structures being quoted in most reviews. Cf. M. D. Johnson and C. Mayle, *J. Chem. Soc., Chem. Commun.*, 192 (1969).

(70) P. W. Jolly and R. W. Pettit, *J. Organomet. Chem.*, **12**, 491 (1968).

(71) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959); 4020 (1959).

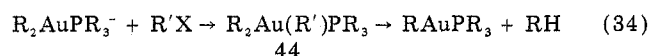
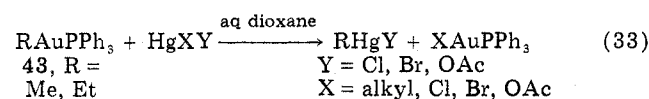
(72) J. K. Stille and K. S. Y. Lau, *J. Am. Chem. Soc.*, **98**, 5841 (1976).

the reaction of dialkyl- and diarylplatinum(II) complexes with acid is a convenient route to monoalkyl or aryl complexes. Thus, the diphenyl complexes **40a** and **40c** react with anhydrous HCl in aprotic solvents to give



the corresponding cis or trans monophenyl complexes, respectively. The kinetics of reaction of several *cis*-PtAr<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub> complexes **40d** in methanol are clearly second order<sup>73,74</sup> and are accelerated by electron-donating groups in the aromatic rings (the Hammett reaction constant  $\rho$  is -4.6).<sup>74</sup> Added chloride ion causes no change in the rate of acidolysis, but ensures that the product **42b** has the same stereochemistry as the substrate. In the absence of a nucleophilic anion like chloride ion, the more stable *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>Ar(solvent) **42a** is formed. These reactions have been interpreted as involving an initial attack of the proton on the metal in a rapid preequilibrium step to give a low concentration of an intermediate platinum(IV) complex **41**<sup>75</sup> which slowly extrudes the aromatic hydrocarbon.<sup>73,74</sup> However, the observed kinetics are equally in accord with a direct displacement by attack of the proton at the  $\alpha$  carbon, and there is no evidence for the complex **41**. While it is semantic to consider that the attack of the proton commences at one or other center, especially if the carbon-platinum bonding orbital is involved, it is important to establish if an intermediate is formed or not.

In the acidolysis of the dimethyl complex **40b**, there is an additional kinetic term involving chloride ion (eq 32) which has been interpreted as chloride ion en-

$$-d[\text{40b}]/dt = k_2[\text{40b}][\text{H}^+] + k_3[\text{40b}][\text{H}^+][\text{Cl}^-] \quad (32)$$


hancement of the formation of the platinum(IV) intermediate as **41b**.<sup>76</sup> Similar ambiguities arise in the

(73) U. Belluco, U. Croatto, P. Uguagliati, and R. Pietropaolo, *Inorg. Chem.*, **6**, 718 (1967).

(74) R. Romeo, D. Minniti, S. Lanza, P. Uguagliati, and U. Belluco, *Inorg. Chim. Acta*, **19**, L55 (1976).

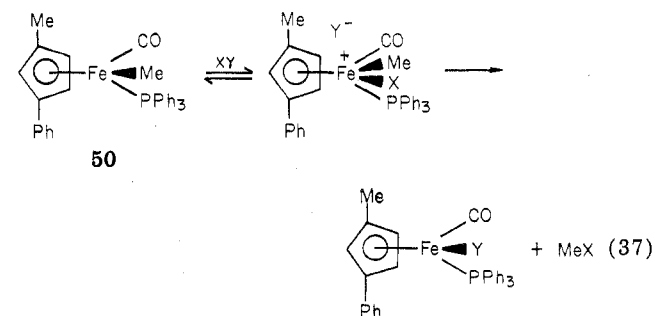
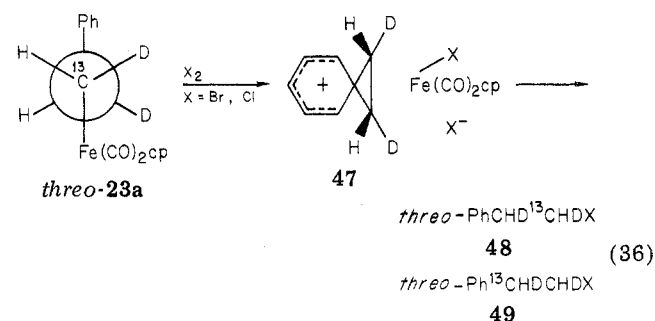
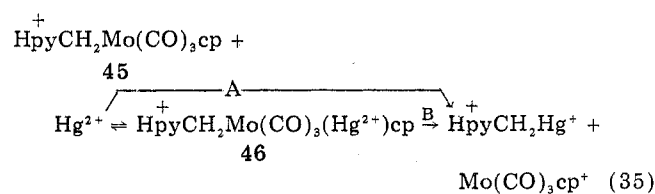
(75) Shown here only for the reaction of the *cis* complexes.

(76) U. Belluco, M. Giustiniani, and M. Graziani, *J. Am. Chem. Soc.*, **89**, 6494 (1967).

cleavage of alkylgold(I) complexes **43** by mercury(II) electrophiles; these reactions are clearly second order and there is no evidence for the formation of any intermediate alkylgold(III) complexes.<sup>20</sup> Similarly, the postulate that gold(III) intermediates (**44**, R = H) are formed in the acidolysis of several dialkylaurate(I) complexes is based solely on the formation of gold(III) species (**44**, R = alkyl) in the reaction with other electrophiles.<sup>77</sup>

There are probably many cases of attack of the electrophile on the metal, though it is clear that they are often difficult to verify. The reaction of Hg<sup>2+</sup> with **45** in aqueous solution involves a very fast but reversibly bimolecular formation of an intermediate **46** accompanied by a much slower appearance of an organomercury complex.<sup>78</sup> It is proposed that the latter is formed by a reaction between Hg<sup>2+</sup> and small amounts of free **45** (eq 35, path A) rather than the kinetically indistinguishable unimolecular reaction in path B.<sup>78</sup>

This inability to decide from kinetic evidence alone whether an observed intermediate is on the reaction path or in a cul-de-sac is a major problem which also arises in the reaction between HgCl<sub>2</sub> and several organoiron complexes in THF. These reactions are complicated by the formation of a variety of products and by mixed orders in [HgCl<sub>2</sub>], but the observation of ClHgFe(CO)cp among the products is indicative of attack of Hg(II) on the metal at an early stage of the reaction.<sup>79</sup> Attack at iron is also proposed for the reaction of bromine and chlorine with diastereoisomeric **23a** which gives two halides, **48** and **49**, with substantial



(77) A. Tamaki and J. K. Kochi, *J. Chem. Soc., Dalton Trans.*, 2620 (1973).

(78) J. Z. Chrzastowski and M. D. Johnson, *J. Chem. Soc., Dalton Trans.*, 2456 (1976).

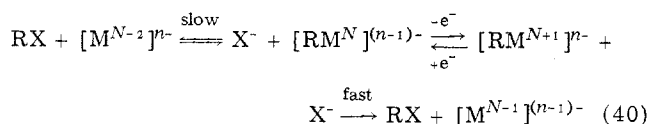
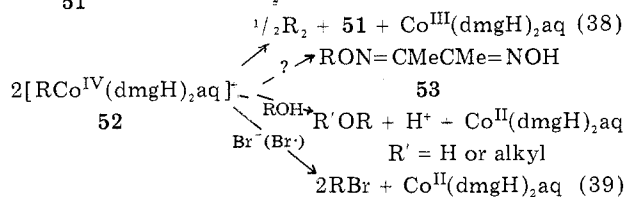
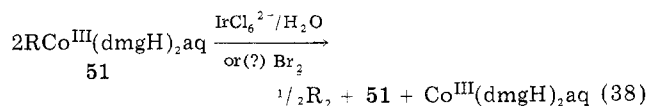
(79) L. J. Dizikes and A. Wojcicki, *J. Am. Chem. Soc.*, **97**, 2540 (1975).



retention of configuration;<sup>80</sup> a phenonium ion **47** is proposed as the key intermediate. A comparable rearrangement has been demonstrated using the 1,1-deuterio derivative of **23**.<sup>81</sup> It is most important in such reactions to take adequate note of the role of solvent. The partial epimerization of diastereoisomeric **50** during its reaction with a deficiency of I<sub>2</sub>, HI, or HgI<sub>2</sub> is also indicative of an attack on iron.<sup>82</sup>

Electrophilic attack on the metal is thus formally a two-electron oxidation process liable to induce subsequent free-radical reactions and difficult to distinguish from other oxidative processes involving electron transfer. For example, the bromination of benzylaquacobaloxime **51** (R = PhCH<sub>2</sub>) in aqueous acidic solution is rapid, and the products are benzyl alcohol, the *O*-benzyl derivative of dimethylglyoxime **53** and their 4-brominated derivatives.<sup>83</sup> No benzyl bromide is formed and the extent of ring bromination is ca. 75%. Using more concentrated solutions in acetic acid, benzyl bromide is formed without ring bromination, possibly through attack of bromide ion or bromine atoms on an oxidized intermediate such as **52**.

Similar results may be achieved using outer sphere oxidants such as IrCl<sub>6</sub><sup>2-</sup>. Thus, several organocobaloximes **51** are oxidized to organocobalt(IV) species **52** which are sufficiently stable at low temperatures to allow characterization.<sup>84</sup> They decompose by a variety of routes; a bimolecular disproportionation regenerates the cobalt(III) substrate **51** and gives fission products (eq 38), but in the presence of nucleophilic solvents or



added nucleophiles such as bromide ion, nucleophilic attack may occur at the  $\alpha$  carbon (eq 39). Such attack occurs with inversion of configuration and may be confused with a direct electrophilic substitution.<sup>86,87</sup> It is an interesting example of how organometallic complexes in the *N*th oxidation state and normally inert to nucleophilic substitution may be activated by a preliminary oxidation to the (*N* + 1)th oxidation state (eq 40).

Oxidation of alkylmetalcarbonyl complexes may also lead to interesting products. For example, the first stage in the oxidation of **54** and **55** by IrCl<sub>6</sub><sup>2-</sup> is bimolecular and rapid ( $k_2 \gg 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$  at 25 °C in aqueous solution);<sup>78</sup> subsequent rapid stages lead to the

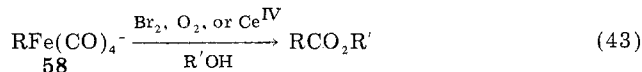
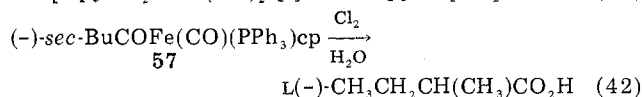
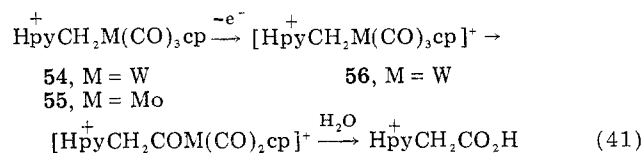
(80) D. A. Slack and M. C. Baird, *J. Am. Chem. Soc.*, **98**, 5539 (1976).

(81) T. C. Flood and F. J. DiSanti, *J. Chem. Soc., Chem. Commun.*, **18** (1975).

(82) T. G. Attig and A. Wojcicki, *J. Am. Chem. Soc.*, **96**, 262 (1974).

(83) S. N. Anderson, D. H. Ballard, J. H. Espenson, and M. D. Johnson, unpublished work.

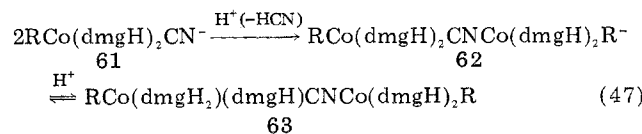
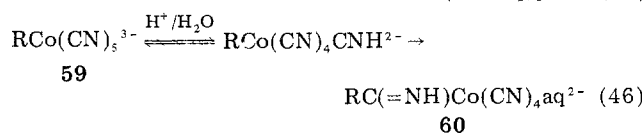
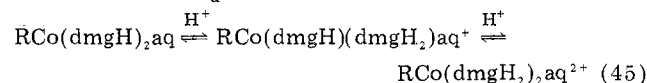
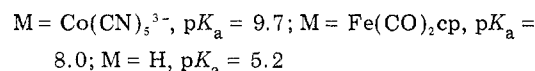
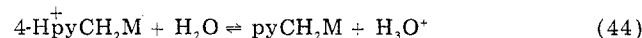
(84) J. Halpern, M. S. Chan, J. Hanson, T. S. Roche, and J. A. Topich, *J. Am. Chem. Soc.*, **97**, 1606 (1975).



carboxylic acid via a carbonyl insertion reaction. The same rate of unimolecular insertion of the intermediate **56** has been observed following oxidation by both IrCl<sub>6</sub><sup>2-</sup> and NO<sup>+</sup>.<sup>85</sup> Similar oxidative formation of carboxylic acids and esters has been observed with complexes **11** and **57** oxidized by chlorine in aqueous solution,<sup>24,86</sup> with **57** or other organoiron complexes oxidized by cerium(IV) in methanol,<sup>86</sup> and especially with alkyltetra-carbonylferrates **58** oxidized by a variety of electrophilic reagents. These latter reactions have considerable preparative value and have been well reviewed.<sup>87</sup>

### Reactions Involving Minimal Changes in the Carbon-Metal Bond

There are a great many reactions of electrophiles with organometallic complexes which do not involve substantial changes in the character of the carbon-metal bond. It is beyond the scope of this review to describe these in detail, but it is useful to distinguish between two types: reactions of ligands at positions remote from, and barely influenced by, the metal and reactions which cause sufficient change in the electronic character of the metal to influence the rates of further, more substantial, reactions at the carbon-metal bond. The latter include preequilibria of particular relevance to the reactions discussed earlier: (i) prototropic equilibria of the pyridine derivatives such as **4**, **5**, **7**, and **54** (eq 44) which



are themselves influenced by the nature of the metal substituent,<sup>88</sup> (ii) reversible protonation of dioximate ligands (eq 45)<sup>85</sup> of relevance to the reactions of alkylcobaloximes in acidic solution;<sup>29-31,34,84</sup> (iii) protonation and mercuriation of the 5,8-dimethylbenz-

(85) J. Z. Chrzastowski and M. D. Johnson, unpublished work.

(86) S. N. Anderson, C. W. Fong, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, **163** (1973).

(87) J. P. Collman, *Acc. Chem. Res.*, **8**, 342 (1975).

(88) M. D. Johnson and N. Winterton, *J. Chem. Soc. A*, **507** (1970).



imidazole ligand of methylcobalamin,<sup>32</sup> which has a significant influence on the rate of displacement of cobalt by mercury(II); (iv) protonation of a cyanide ligand of alkylpentacyanocobaltates **59** which induces a unimolecular rearrangement to an insertion product **60**,<sup>89,90</sup> and (v) protonation of cyanide ligands of organo(cyano)cobaloximes **61** which leads to bridged complexes **62** and **63**.<sup>91,92</sup>

(89) M. D. Johnson, M. L. Tobe, and L. Y. Wong, *J. Chem. Soc. A*, 923 (1968); 929 (1968).

(90) J. Kwiatek, *Catal. Rev.*, 1, 37 (1967).

These reactions, and those of the former class, serve one particularly useful purpose: they illustrate that the reactivity of carbon-metal bonds toward electrophiles is not inherently greater than that of other organic molecules but depends much upon the exact nature of the molecules concerned.

*I acknowledge with gratitude my debt to the co-workers named in the references and to many friends for stimulating discussions!*

(91) A. L. Crumbliss and P. L. Gauss, *Inorg. Chem.*, 14, 486 (1975).

(92) D. Dodd and M. D. Johnson, *J. Chem. Soc., Dalton Trans.*, 1218 (1973).

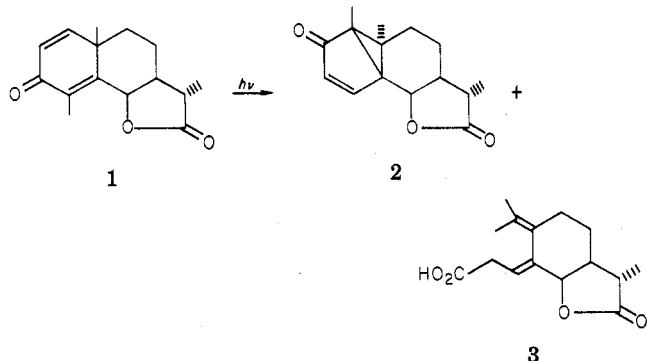
## Mechanisms of Photochemical Transformations of Cross-Conjugated Cyclohexadienones

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Received January 10, 1977

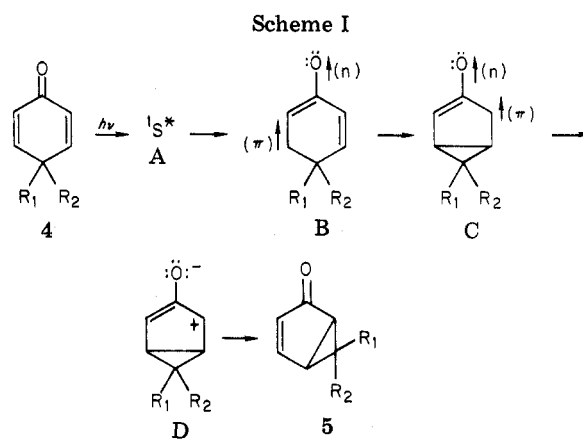
Cross-conjugated cyclohexadienones have been subjected to intensive photochemical studies for many years. Originally, these compounds fascinated organic chemists because of the deep-seated rearrangements which occurred when irradiated with ultraviolet light in the 250–370 nm region, typified by the conversion of santonin (**1**) to lumisantonin (**2**) and to photosantonin



acid (**3**).<sup>1</sup> The extensive studies which elucidated the sequence of thermal and photochemical events involved in these and other complex transformations have been summarized in several reviews.<sup>2</sup>

Following the pioneering studies by Barton, Jeger, van Tamelen, and their groups which established the structures of the photoproducts of santonin and related steroid dienones, a unifying mechanistic concept was proposed in 1961 and 1962 by Zimmerman and this author<sup>3</sup> which satisfactorily rationalized the nature of the primary processes occurring on irradiation of such

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dienones (Scheme I). Thus, the formation of bicyclo[3.1.0]hexenone (**5**) from a model 2,5-cyclohexadienone (**4**) was postulated to occur in a series of events involving (a) formation of the  $n,\pi^*$  singlet excited state, symbolized as A, (b) intersystem crossing to the triplet  $n,\pi^*$  state B, (c) bridging ("rebonding") to give C, which is still an electronically excited molecule of the  $n,\pi^*$  type, (d) electron demotion to give the ground-state zwitterion D, and finally (e) rearrangement of D to lumiketone **5**, a process subsequently designated a sigmatropic shift of order [1,4]. Precedent and theory were cited for all of these steps. Furthermore, this approach was successful in rationalizing the formation of rearranged products (phenols and ketones) involving

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