While electron transfer appears to be the biological function of smaller proteins having sites 1–3, the possibility that these sites or variants thereof may be capable of catalytic transformations should be borne in mind. Hydrogenase is the best current example of an iron–sulfur enzyme containing no other metals or prosthetic groups. Given the numerous precedents in metal complex chemistry,[63] it is entirely probable that dihydrogen activation and heterolytic cleavage, evidenced by H/D exchange in the absence of an electron carrier,[64] occurs at a 4-Fe site. The terminal monooxygenase of the 4-methoxybenzoate O-demethylase system from *Pseudomonas putida* has been described as a nonheme protein whose catalytic site may be similar to the 2-Fe sites of Fd proteins.[65] The catalytic site(s) of the Fe–Mo protein of nitrogenase remains undefined despite massive research attention to this enzyme, rendering it perhaps the next most exhaustively examined metallobiomolecule complex after hemoglobin and cytochrome oxidase. Numerous model studies, which have afforded catalytic systems for the $N_2 \rightarrow NH_3$ conversion[66] involving unidentified intermediates and direct ammonia formation from defined dinitrogen complexes,[67] have focussed heavily on molybdenum as the biocatalytic center. The large complement of Fe–S sites[58,60,62] demands consideration of **2** or **3** or a yet-unrecognized Fe[58,62] or Fe–Mo[68] coordination unit as a binding and activation center. Consequently, the analogues of Table II may be, or may serve as precursors to, complexes useful as test vehicles for stoichiometric or catalytic conversions of biological substrates.

(63) B. R. James, "Homogeneous Hydrogenation", Wiley-Interscience, New York, N.Y., 1973.
(64) L. E. Mortenson and J.-S. Chen, in "Microbial Iron Metabolism", J. B. Neilands, Ed., Academic Press, New York, N.Y., 1974, Chapter 11.
(65) F. H. Bernhardt, H. Packowsky, and H. Staudinger, *Eur. J. Biochem.*, **57**, 241 (1975).
(66) G. N. Schrauzer, *Angew. Chem., Int. Ed. Engl.*, **14**, 514 (1975).
(67) J. Chatt, A. J. Pearman, and R. L. Richards, *Nature (London)*, **253**, 39 (1975); C. R. Brûlet and E. E. van Tamelen, *J. Am. Chem. Soc.*, **97**, 911 (1975).
(68) For one proposal of this type of site, cf. *Scientia Sinica*, **19**, 460 (1976).

Lastly, consideration of a perplexing matter in iron–sulfur protein chemistry is solicited. How does an apoprotein containing at least four cysteinyl residues select, or at least preferentially stabilize, (i) a [Fe(S-Cys)$_4$] (**1**), (ii) a [Fe$_2$S$_2$(S-Cys)$_4$] (**2**), or (iii) a [Fe$_4$S$_4$(S-Cys)$_4$] (**3**) site with the latter capable of physiologically sustaining either the 2–/3– or 1–/2– redox couples.[69] Equivalently, one may ask, as has been done,[70] by what means and at what point in the biosynthesis of a polypeptide is the Fe or Fe–S* constituent introduced? Preference but not specificity for a natural binding site is reflected in the formation of an unstable 1-Fe complex of the adrenodoxin peptide with properties similar to Rd_{ox}. It spontaneously converts to the native Fe$_2$S$_2$* protein upon treatment with sulfide.[71] Possibly a combination of amino acid sequence and protein crystallographic data will ultimately delineate site stabilization factors. In the meantime synthetic elaboration of cysteinyl peptides (guided by sequence results[72]) followed by complexation with Fe(II, III), introduction of *preformed* Fe$_2$S$_2$* and Fe$_4$S$_4$* cores (reactions 16 and 17), and examination of the relative stabilities of these species could prove enlightening. One tetracysteinyl dodecapeptide has been shown to stabilize both 1-Fe[73] and 4-Fe[47,74] sites, but no attempt to convert the former to the latter or to a 2-Fe complex was attempted.

The research described herein was supported by the National Institutes of Health. Special thanks are due to my enthusiastic collaborators whose names are to be found in the text and references.

(69) For interpretations of the potential differences of these couples, cf. ref 17a and E. Adman, K. D. Watenpaugh, and L. H. Jensen, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 4854 (1975).
(70) J. W. Brodrick and J. C. Rabinowitz, *Iron-Sulfur Proteins*, **3**, 101 (1977).
(71) Y. Sugiura, K. Ishizu, and T. Kimura, *Biochem. Biophys. Res. Commun.*, **60**, 334 (1974).
(72) K. T. Yasunobu and M. Tanaka, *Iron-Sulfur Proteins*, **2**, 27 (1973).
(73) J. R. Anglin and A. Davison, *Inorg. Chem.*, **14**, 234 (1975).
(74) Note, however, that this and another cysteinyl peptide may not necessarily act as ligands to a single Fe$_4$S$_4$* core; cf. footnote 30 of ref 47.

Mechanisms of Oxidative Addition of Organic Halides to Group 8 Transition-Metal Complexes

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Received November 8, 1976

Most organic reactions that are catalyzed by transition metals occur by a series of steps, producing reactive intermediates, at least one of which contains a carbon–metal σ bond. One important reaction type by which intermediates containing carbon–metal σ bonds are formed is the oxidative addition of an organic substrate to the transition metal. In this reaction, the increase in the oxidation state of the metal is usually accompanied by an increase in the coordination number.[1] The propensity to undergo oxidative ad-

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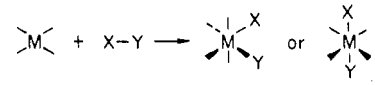
dition is characteristic of group 8 metal complexes of



the d^8 and d^{10} electronic configurations.[1a,e] Compound X–Y may be hydrogen, oxygen, hydrogen halides, hydrogen cyanide, halogens, silanes, sulfonyl halides, epoxides, strained hydrocarbons, or hydrocarbons containing activated hydrogens and organic halides; only the last four classes of compounds form carbon–metal σ bonds. Although hydrocarbon activation is most important in catalytic processes, the most versatile method of carbon–metal σ-bond formation is through the cleavage of carbon–halogen bonds, including alkyl, aryl, and vinyl halides as well as acyl halides.[1b,2]

A number of factors determine the ability of transition metals to undergo oxidative addition. The transition metal must be in a low valent state, behaving either as a nucleophile or a reductant in which electrons are removed from the electron-rich metal center. Unlike the group 1 and 2 metals that readily react in bulk, group 8 metals must be in the atomic state, usually through complexation by ligands. Generally, the reactivity of group 8 metals toward oxidative addition increases in going from right to left in the periodic table, in going down a given group in the table (although there are notable exceptions), and in decreasing the initial oxidation number. The coordination number of the metal and the type of ligand is also important. In order for oxidative addition to take place, prior generation of a vacant site may occur to give a coordinatively unsaturated species (dissociative mechanism).[1b,g] For example, the complexes $M(PPh_3)_4$ ($M = Ni^0, Pd^0, Pt^0$) having the d^{10} configuration are coordinatively saturated and undergo dissociation of phosphine ligands in solution to form three- and two-coordinate compounds which are reactive toward oxidative addition. The phosphine ligands are σ donors (lone-pair donation) which increase the electron density on the metal. This makes the metal a good nucleophile, and, at the same time, increases the tendency for the phosphines to dissociate. Carbon monoxide, on the other hand is a π-acceptor ligand which decreases the electron density on the metal by delocalization into low-lying empty π orbitals of the carbonyl. Dicarbonylbis(triphenylphosphine)nickel, for example, is a relatively unreactive complex since it is coordinatively saturated, and it does not undergo dissociation because of the balancing effect of the σ-donor and π-acceptor ligands. There is good evidence, however, that steric effects are much more important than electronic effects in determining the dissociation of phosphine ligands from transition-metal complexes. The greater the size of the ligand cone, the greater is the tendency for dissociation.[3]

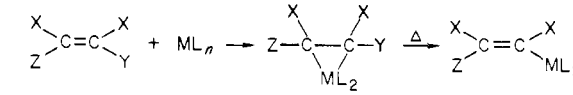
In order that a transformation of an organic reactant to product be effected catalytically, the σ-bonded complex cannot be too stable. The carbon–metal bond must undergo some facile subsequent reaction leading to product, with regeneration of the catalytic species. Consequently, in many cases, the instability of the σ-bonded complex has prevented its isolation, and a systematic study of the reactions of the carbon–metal bond was therefore difficult. As a result, little was known about the mechanisms of these reactions until recently.

There are a number of important similarities and differences between the oxidative addition reaction to transition metals and the Grignard reaction. The Grignard reaction is limited primarily to organic halides and is not a catalytic reaction. Further, there are relatively few insertion reactions that the carbon–magnesium bond will undergo, those being limited mostly to reactions with the carbonyl and nitrile groups. The oxidative addition reaction of transition metals takes place with many kinds of reactants, and there are many more insertion reactions which can be carried out. This is in part because the transition metal is capable of complexing with many substrates, such as carbon monoxide, olefins, hydrogen, etc., and of activating them and bringing them into a reaction which, in the absence of the metal, would occur only with difficulty (highly endothermic). Most importantly, the oxidative addition reaction can be catalytic, and in many examples has been shown to be stereospecific.

This account is concerned with the mechanisms of the oxidative addition reaction of organic halides to group 8 transition metals. The mechanisms of these reactions appear to be different, depending on the type of organic halide; further, the mechanism evidently changes depending on the transition metal, possibly as a result of different oxidation potentials. Because widely different mechanisms have been claimed for the same oxidative addition reaction, in some cases because of contradictory stereochemical results, this account was not arranged on the basis of mechanistic type, but instead by the organic halide and the metal.

Vinyl Halides

Oxidative addition of vinyl halides to transition-metal complexes affords stable σ-vinyl complexes. The reaction is attended with remarkable stereospecificity; the configuration at the trigonal carbon bearing the halogen is retained in the oxidative addition product.[4] Because the oxidative additions of certain perhaloethylenes to platinum(0) afford isoable three-membered platinocycles[5] (1) that rearrange to the σ-vinyl complex, a



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(1) (a) J. P. Collman, *Acc. Chem. Res.*, 1, 136 (1968); (b) J. P. Collman and W. R. Roper, *Adv. Organometal. Chem.*, 7, 53 (1968); (c) R. Cramer, *Acc. Chem. Res.*, 1, 186 (1968); (d) L. Vaska, *ibid.*, 1, 335 (1968); (e) J. Halpern, *ibid.*, 3, 386 (1970); (f) G. W. Parshal, *ibid.*, 3, 139 (1970); (g) J. Tsuji, *Fortsch. Chem. Forsch.*, 28, 41 (1972).

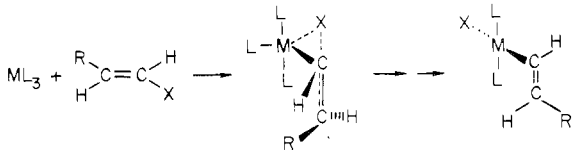
(2) (a) R. Ugo, *Coord. Chem. Rev.*, 3, 319 (1968); (h) L. Malatesta and S. Cenini, "Zero Valent Compounds of Metals", Academic Press, New York, N.Y., 1974, pp 106–111.

(3) C. A. Tolman, *Chem. Rev.*, 77, 313 (1977); L. E. Manzer and C. A. Tolman, *J. Am. Chem. Soc.*, 97, 1955 (1975); C. A. Tolman, W. C. Seidel, and L. W. Gosser, *ibid.*, 96, 53 (1974); C. A. Tolman, *ibid.*, 92, 2956 (1970).

(4) (a) P. Fitton and J. E. McKeon, *Chem. Commun.*, 4 (1968); (b) L. Cassar and A. Giarruso, *Gazz. Chem. Ital.*, 103, 793 (1973); (c) B. E. Mann, B. L. Shaw, and N. I. Tucker, *J. Chem. Soc. A*, 2667 (1971); (d) J. Lewis, B. F. G. Johnson, K. A. Taylor, and J. D. Jones, *J. Organometal. Chem.*, 32, C 62 (1974); (e) B. F. G. Johnson, J. Lewis, J. D. Jones, and K. A. Taylor, *J. Chem. Soc., Dalton Trans.*, 34 (1974); (f) J. Rajaram, R. G. Pearson, and J. A. Ibers, *J. Am. Chem. Soc.*, 96, 2103 (1974).

(5) W. J. Bland and R. D. W. Kemmitt, *Nature (London)*, 221, 963 (1960); W. J. Bland and R. D. W. Kemmit, *J. Chem. Soc. A*, 127 (1968); A. J. Mukhedkar, M. Green, and F. G. A. Stone, *ibid.*, 947 (1970); M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *ibid.*, 2525 (1968); J. Asbley-Smith, M. Green, and D. C. Wood, *ibid.*, 1847 (1970).

similar mechanism has been proposed for the oxidative addition of vinyl halides to palladium(0) and nickel(0) complexes.[4f,6] An alternative mechanism requires a five-coordinate transition state from the nucleophilic attack of the metal on the carbon–halogen bond of the vinyl halide. The observed stereospecific retention of

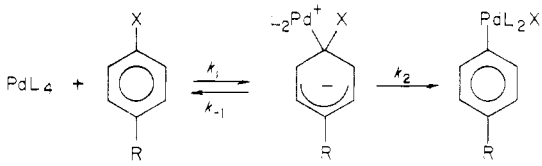


L = PPh_3

configuration at the carbon center discounts the intervention of vinyl radical which, if formed, would undergo facile configurational inversion.[7,8]

Aryl Halides

A comparative reactivity study of the substituent effects in the oxidative addition of aryl halides to



L = PPh_3

palladium(0) reveals the following orders of reactivity: PhI > PhBr > PhCl; p-$NO_2C_6H_4Cl$ > p-NCC_6H_4Cl > p-$PhCOC_6H_4Cl$ > C_6H_5Cl.[8] A mechanism analogous to nucleophilic aromatic substitution has been proposed in which the observed effect of the halide dictates that bond breaking (k_2) must be rate determining.

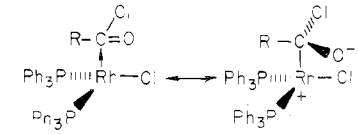
A comparison of the order of reactivity of the aryl halides with the order of their reduction potentials (PhCl > PhBr > PhI) suggests that an electron-transfer mechanism[9] may be important. The facilitating effect of the electron-withdrawing group possibly is a result of a lowering of the energy of the π^* orbitals. This energy lowering also manifests itself in lowering the reduction potential of the aryl halide. A mechanism involving electron transfer as the initial step in the oxidative addition is supported by the observation that one-electron acceptors such as tetracyanoethylene, 2,3-dichloro-5,6-dicyano-1,4-quinone, and chloranil are rapidly reduced by a variety of zerovalent nickel and platinum complexes in solution, with simultaneous generation of the corresponding radical anions.[10]

A third proposal,[11] a three-center mechanism involving direct attack of the metal at the aryl–halogen bond, also can accommodate the available data. It is noteworthy that the *nucleophilic* nature of low-valent metals is emphasized in all three mechanisms proposed.

Acyl Halides

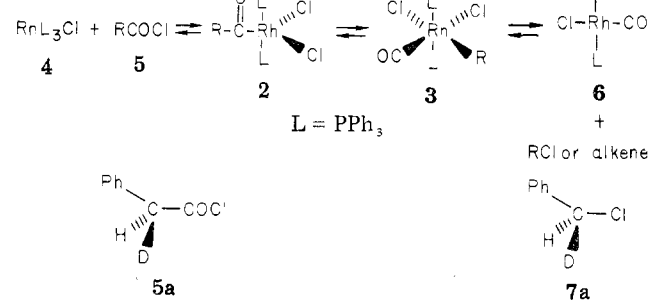
The oxidative addition of carboxylic acid chlorides to Rh(I), Ir(I), Pd(0), and Pt(0) complexes yields the corresponding acylmetal complexes, the stability of which depends on the metal, the ligands, and the acyl halide.[12] The acylpalladium(II) and acylplatinum(II) products are the trans isomers, but the oxidative addition of acyl halides to Rh(I) affords the five-coordinate acyl (**2**) or six-coordinate carbonyl (**3**) complex, depending on the migratory aptitude of the alkyl group (**2** → **3**).[13]

The rapid rates in the oxidative addition of acyl halides has been attributed to the longer, weaker carbon–halogen bond.[13] The higher electrophilicity of



the carbonyl carbon and the initial formation of the acid chloride complex also could account, in part, for the greater reactivity.

The decarbonylation of acid chlorides with chlorotris(triphenylphosphine)rhodium(I) yields alkyl chlorides or alkenes and hydrogen chloride, depending on the presence of a β-hydrogen in the acid chloride and thus on the substituents on the carbon β to the carbon–rhodium σ bond in the reductive elimination step.[14] The reaction proceeds through a series of intermediate complexes, **2** and **3**, each of which can be isolated. (*S*)-α-Deuteriophenylacetyl chloride (**5a**) undergoes



L = PPh_3

decarbonylation to (*S*)-benzyl-α-*d* chloride (**7a**) with 20–27% net *retention* of configuration at carbon. If the acyl–alkyl rearrangement step (**2** → **3**) proceeds with retention of configuration at carbon,[15] then the *reductive elimination step* (**3** → **7**) *also takes place with retention of configuration at carbon.*[16] This same stereochemistry has been observed in the decarbon-

(6) J. Browning, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 453 (1971); A. J. Mukhedkar, M. Green, and F. G. A. Stone, *ibid.*, 3023 (1969); J. Ashley-Smith, M. Green, and F. G. A. Stone, *ibid.*, 3019 (1969); H. D. Empsall, M. Green, S. K. Shakshooki, and F. G. A. Stone, *ibid.*, 3472 (1971).

(7) O. Simamura, K. Tokumaru, and H. Yui, *Tetrahedron Lett.*, 5141 (1966); J. A. Kampmeier and R. M. Fantazier, *J. Am. Chem. Soc.*, **88**, 1959 (1965); G. M. Whitesides, C. P. Casey, and J. K. Krieger, *ibid.*, **93**, 1379 (1971).

(8) P. Fitton and E. A. Rick, *J. Organometal. Chem.*, **28**, 287 (1971).

(9) J. K. Kochi, *Acc. Chem. Res.*, **7**, 351 (1974); M. L. Poutsma, *Free Radicals*, **2**, 169 (1973).

(10) I. H. Elson, D. G. Morrell, and J. K. Kochi, *J. Organometal. Chem.*, **84**, C7 (1975).

(11) M. F. Semmelhack and L. Ryono, *Tetrahedron Lett.*, 2967 (1973).

(12) S. P. Dent, C. Eaborn, and A. Pidcock, *J. Organometal. Chem.*, **97**, 307 (1975); A. J. Cheney and B. L. Shaw, *J. Chem. Soc. A*, 3545 (1971); A. J. Cheney and B. L. Shaw, *ibid.*, 3549 (1971); A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, **9**, 243 (1970); I. C. Douek and G. Wilkinson, *J. Chem. Soc. A*, 2604 (1969); M. Kubota and D. M. Blake, *J. Am. Chem. Soc.*, **93**, 1368 (1971).

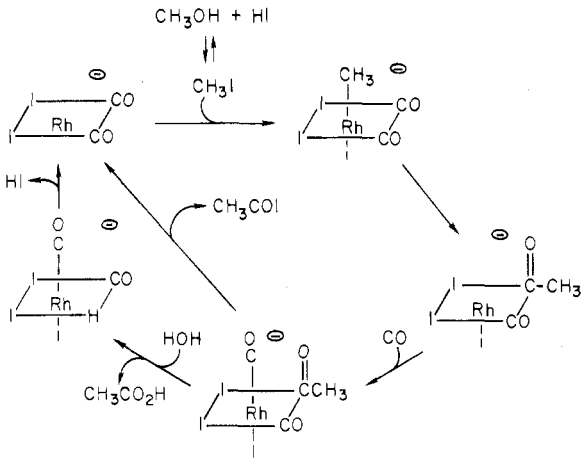
(13) M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1347 (1967).

(14) J. K. Stille, M. T. Regan, R. W. Fries, F. Huang, and T. McCarley, *Adv. Chem. Ser.*, **No. 132**, 181 (1974); J. K. Stille and M. T. Regan, *J. Am. Chem. Soc.*, **96**, 1508 (1974); J. K. Stille and R. W. Fries, *ibid.*, **96**, 1514 (1974); J. K. Stille, F. Huang, and M. T. Regan, *ibid.*, **96**, 1518 (1974).

(15) In every case of acyl–alkyl rearrangement examined in transition-metal complexes, retention of configuration at carbon has been observed.

(16) K. S. Y. Lau, Y. Becker, F. Huang, N. C. Baenziger, and J. K. Stille, *J. Am. Chem. Soc.*, in press.

Scheme I



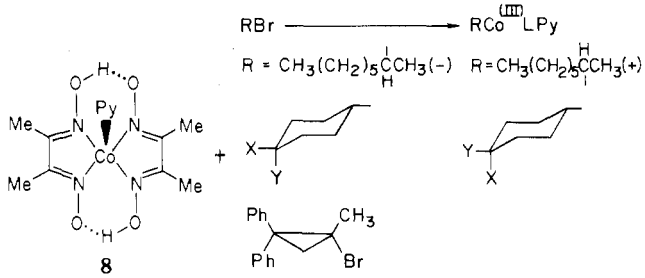
ylation of aldehydes with chlorotris(triphenylphosphine)rhodium(I).[17] The reverse reaction, oxidative addition, should also proceed (microscopic reversibility) with retention of configuration at carbon, although this is difficult to confirm since benzyl chloride will not oxidatively add to **6**. These results are somewhat surprising since the oxidative addition of **7a** to palladium(0) complexes takes place with a high net *inversion* of configuration at carbon (vide infra).

Alkyl Halides

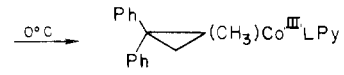
Oxidative addition of alkyl halides to low-valent group 8 transition-metal complexes has proven to be a convenient and practical way to form alkylmetal complexes which are of widespread use both as reagents and as isolable intermediates in organic synthesis.[18] The catalytic carbonylation of methanol to acetic acid is an industrial process the key step of which is an oxidative addition reaction of methyl iodide to Rh(I).[19] The kinetics of the catalytic process (Scheme I) have been shown to be zero order with respect to methanol and carbon monoxide and first order with respect to the rhodium catalyst and the promoter (some form of iodine, e.g., HI).[20] The thermodynamic data obtained from the kinetic study are in agreement with the assumption that the oxidative addition of methyl iodide to rhodium(I) is the rate-determining step in the catalytic cycle. The presence of the intermediate alkylrhodium, alkylcarbonylrhodium, and acylrhodium complexes in the sequential transformation has been established by an infrared study.[21]

The stability of alkylmetal complexes depends on the nature of the metal atom, the ancillary ligands, and the structural characteristics of the alkyl group. Metal alkyls possessing a β-hydrogen tend to undergo β elimination (Rh > Ir; Pd > Pt) to afford olefins and metal hydrides. Different mechanisms for the oxidative addition appear to be taking place depending on the metal and the substrate. Indeed, for some reactions involving the same metal complex and the same organic halide, several different mechanisms have been proposed.

The oxidative addition reactions of alkyl halides to pyridine(bis(dimethylgloximato))cobalt(I) show the characteristics of nucleophilic displacement by cobalt.[22]



8 9



10

Inversion of configuration at carbon has been demonstrated in the oxidative addition of secondary cyclohexyl bromides to the nucleophilic cobalt(I) anion **8**.[23] Although a stereospecific oxidative addition of optically active 2-bromooctane to **8** was observed, the stereochemistry of the reaction could not be determined.[24] The reaction of **8** with the optically active tertiary bromide **9** gave an oxidative addition product **10**.[25] The stereochemistry of this reaction could not be ascertained, however, since optical rotations on the highly colored complex could not be observed, and cleavage of **10** gave a racemic product, raising the question of the racemization step.

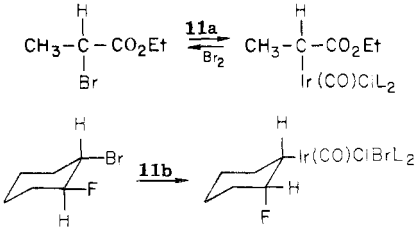
Two different mechanisms have been proposed from kinetic results obtained in the oxidative addition of hydrogen, oxygen, methyl iodide, and benzyl halides to iridium(I).[26] The homonuclear molecules give cis addition products. A cyclic three-centered transition state has been proposed, in accord with the large entropies and enthalpies of activation, suggestive of a highly ordered transition state. By contrast, trans addition of benzyl halides and methyl iodide to iridium has been observed. The activation parameters are larger for the alkyl halides than for those of the homonuclear molecules, and the rate of reaction showed a marked solvent dependence. An S_N2-type mechanism involving nucleophilic attack from the low-valent metal at carbon was postulated. It is possible, however, that a cyclic three-center transition state may also be applied to the oxidative addition of heteronuclear bonds to transition-metal complexes. The observed solvent dependence of the rates of reaction can be explained not only by a large dipolar interaction between the addend and the metal (S_N2 type) but also by a large deformation in the three-center transition state.[26b]

The oxidative addition reaction of alkyl halides to chlorocarbonylbis(triphosphine)iridium(I) complexes

(17) H. M. Walborsky and L. E. Allen, *J. Am. Chem. Soc.*, **93**, 5465 (1971).
(18) S. J. Lapporte and V. P. Kurkov, in "Organotransition Metal Chemistry", Y. Ishii and M. Tsutsui, Ed., Plenum Press, New York, N.Y., 1975, p 199.
(19) F. E. Paulik and J. F. Roth, *Chem. Commun.*, 1578 (1968); J. F. Roth, J. H. Craddock, A. Hershman, and F. E. Paulik, *Chem. Technol.*, 600 (1971); J. F. Roth, *Platinum Met. Rev.*, **19**, 12 (1975).
(20) J. Hjortkjaer and V. W. Jensen, *Ind. Eng. Chem., Prod. Res. Dev.*, **15**, 46 (1976).
(21) D. Forster, *J. Am. Chem. Soc.*, **98**, 846 (1976).
(22) C. J. Cooksey, D. Dodd, C. Gatford, M. D. Johnson, G. J. Lewis, and D. M. Titchmarsh, *J. Chem. Soc., Perkin Trans. 2*, 655 (1972).
(23) F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Am. Chem. Soc.*, **92**, 1414 (1970).
(24) D. Dodd and M. D. Johnson, *J. Chem. Soc. D*, 571 (1971).
(25) F. R. Jensen and D. H. Buchanan, *J. Chem. Soc., Chem. Commun.*, 153 (1973).
(26) (a) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966); (b) R. Ugo, A. Pasini, A. Fusi, and S. Cenine, *ibid.*, **94**, 7364 (1972).

(11) initially was reported to proceed with retention of

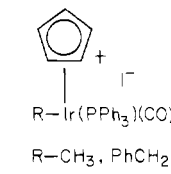
11a, L = PPh_2Me
b, L = PMe_3



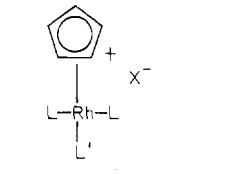
configuration at carbon[27] (**11a** with ethyl α-bromopropionate) and with inversion[28] (*trans*-2-fluorocyclohexyl bromide). The stereochemistry of the oxidative addition of optically active ethyl α-bromopropionate to **11a** was assigned on the assumption that bromine cleavage of the oxidative addition product occurs with retention of configuration at carbon. Since bromine cleavage of iron–carbon bonds has been reported to occur with inversion of configuration at carbon[29a] and since the stereochemistry of cleavage of palladium–carbon bonds can be altered by the presence (inversion) or absence (retention) of halide ion,[29b] the interpretation of these results is open to question. A reinvestigation[30] of the reported[28] reaction of **11b** with *trans*-2-fluorocyclohexyl bromide revealed that, with the careful exclusion of oxygen and purification of reagents, the reaction does not take place.[30] Subsequently, it was reported[31] that the oxidative addition could proceed by free-radical pathways provided a radical source was present. Loss of stereochemistry at carbon in the oxidative addition product, rate retardation by radical scavengers, and rate enhancement by radical initiators provided the basis for a radical chain mechanism.[31c]

In the absence of a radical source, however, nucleophilic displacement by iridium complexes is consistent with second-order kinetics,[26,32] the large negative entropies of activation, marked solvent dependence, the steric retardation of rates by bulky phosphine ligands, and the increase in rate observed on increasing the donor power of L (increasing the electron density on iridium).[32,33] Additional support for the S_N2 displacement has been obtained from the isolation of ionic intermediates such as **12**.[34]

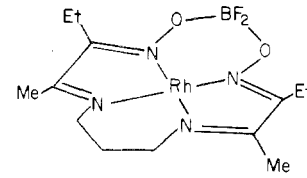
A systematic study on the structure–reactivity relationship in rhodium complex **13** showing orders of



12



15, L,L′ = CO, phosphines



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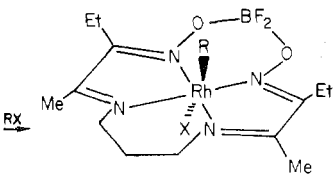
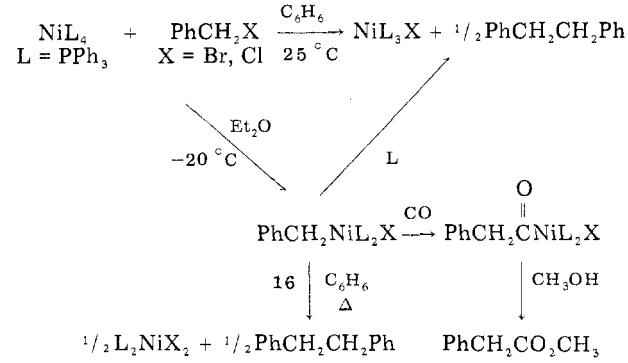


14

reactivity, R = CH_3 > CH_3CH_2 > secondary > cyclohexyl > adamantyl, and X = I > tosylate ~ Br > Cl, imply S_N2 attack at carbon by rhodium.[35] Unfortunately, the rapid rhodium–rhodium nucleophilic exchange between **13** and **14** has prevented the demonstration of stereochemical inversion of configuration at carbon which would provide the most convincing evidence for the S_N2 displacement mechanism. Second-order kinetics for the oxidative addition of methyl and ethyl iodide to Rh(I) complexes[32a,36a] and the isolation of cationic complexes such as **15**[34a,36] as a result of the addition also are consistent with an S_N2 reaction.

Benzyl halides undergo oxidative addition to nickel(0)

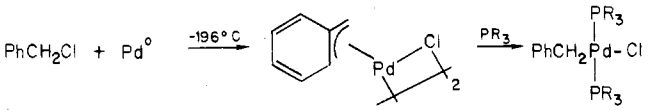


in benzene at 25 °C to give bibenzyl and a Ni(I) complex.[32b,37] At −20 °C in ether, the same reactions yield the expected alkylnickel(II) complexes **16** which upon warming in benzene reverted to bibenzyl, metallic nickel, and nickel(II).[38] The decomposition of **16** in the presence of added phosphine ligand in benzene, however, gives the Ni(I) complex and bibenzyl.

The alkylnickel(II) complexes undergo carbonylation to give the corresponding acyl complexes which can be directly converted to the carboxylic acid ester.[39] In an effort to determine the stereochemistry of the oxidative addition of benzyl halides to nickel(0), an oxidative addition–carbonylation–methanolysis sequence was applied to optically active benzyl-α-*d* halides. The resulting methyl α-deuteriophenylacetate was racemic.[39]

(27) R. G. Pearson and W. R. Muir, *J. Am. Chem. Soc.*, **92**, 5519 (1970).
(28) J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *J. Chem. Soc. D*, 612 (1970).
(29) (a) G. M. Whitesides and D. J. Boschetto, *J. Am. Chem. Soc.*, **93**, 1529 (1971); (b) P. K. Wong and J. K. Stille, *J. Organometal. Chem.*, **70**, 121 (1974).
(30) F. R. Jensen and B. Knickel, *J. Am. Chem. Soc.*, **93**, 6339 (1971).
(31) (a) J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Am. Chem. Soc.*, **94**, 4043 (1972); (b) J. A. Labinger, A. V. Kramer, and J. A. Osborn, *ibid.*, **95**, 7908 (1973); (c) J. A. Osborn, "Organotransition Metal Chemistry", Y. Ishii and M. Tsutsui, Ed., Plenum Press, New York, N.Y., 1975, p 65.
(32) (a) A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, **9**, 2658 (1970); (b) B. L. Shaw, *J. Organometal. Chem.*, **94**, 251 (1975).
(33) B. L. Shaw and R. E. Stainbank, *J. Chem. Soc., Dalton Trans.*, 223 (1972); E. M. Miller and B. L. Shaw, *ibid.*, 480 (1974).
(34) (a) J. W. Kang and P. M. Maitlis, *J. Organometal. Chem.*, **26**, 393 (1971); (b) A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, **9**, 2653 (1970).
(35) J. P. Collman and M. R. MacLaury, *J. Am. Chem. Soc.*, **96**, 3019 (1974); J. P. Collman, D. W. Murphy, and G. Dolcetti, *ibid.*, **95**, 2687 (1973).
(36) (a) A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, **10**, 1653 (1971); (b) Y. Wakatsuki and H. Yamazaki, *J. Organometal. Chem.*, **64**, 393 (1974); (c) A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, **10**, 1165 (1971); (d) F. Faraone, C. Ferrara, and E. Rotondo, *J. Organometal. Chem.*, **33**, 221 (1971).
(37) (a) K. Jacob, I. Wiswedel, T. Zeine, and K. H. Thiele, *Z. Anorg. Allg. Chem.*, **402**, 193 (1973); (b) P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, **3**, 648 (1964); (c) C. S. Cundy, *J. Organometal. Chem.*, **69**, 305 (1974).
(38) K. Jacob and R. Niebuhr, *Z. Chem.*, **15**, 32 (1975); E. Bartsch, E. Dinjus, and E. Uhlig, *ibid.*, **15**, 317 (1975).
(39) A. Cowell and J. K. Stille, *J. Organometal. Chem.*, **124**, 253 (1977).

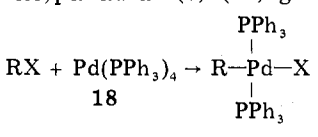
The oxidative addition of alkyl halides to atomic palladium obtained by the high-temperature vaporization of palladium onto a cold surface provides a novel entry to alkylpalladium complexes.[40] The addition of benzyl chloride to atomic palladium at −196 °C leads to the formation of the π-complex dimer **17** which



17

undergoes bridge cleavage in the presence of phosphine ligands to give the same benzylpalladium complexes obtainable from the oxidative addition of benzyl chloride to tetrakis(phosphine)palladium(0) complexes.

Phosphine complexes of Pd(0) and Pt(0) also undergo oxidative addition reactions with alkyl halides. For example, the addition of alkyl halides to tetrakis(triphenylphosphine)palladium(0) (**18**) gives the *trans*-



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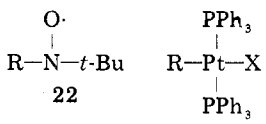
alkyl-palladium(II) complex **19**.[41] Complex **18** is coordinatively saturated, yet it undergoes dissociation in solution to the tris- and bis(triphenylphosphine) complexes, thereby allowing oxidative addition to take place. The mechanism of the oxidative addition reaction to a coordinatively unsaturated species is controversial, and indeed different mechanisms may be operating depending on the alkyl group, the halogen, the phosphine ligands, and the metal, Pd or Pt. Both radical and concerted nucleophilic mechanisms have been proposed on the basis of a variety of experimental results, some of which are conflicting.

The rate of oxidative addition of alkyl halides to palladium(0) and platinum(0) has been shown to be retarded by radical scavengers.[31c,42] Complete loss of stereochemistry at carbon took place when optically active ethyl α-bromopropionate was used. Furthermore, the reaction of 6-bromo-1-hexene with the zerovalent metal afforded both cyclized and linear alkylmetal complexes, indicative of participation of free-radical intermediates. The observation of CIDNP during the oxidative addition of isopropyl iodide and benzyl bromide to either **20** or **21** has been cited as definitive evidence that free-radical processes are involved in the oxidative addition of alkyl halides to d^{10} metal complexes.[31c,42b] In addition, reaction products typical of radical disproportionation and recombination were obtained. Since the oxidative addition of benzyl chloride to complex **20** afforded only the expected alkylplatinum chloride and no CIDNP was observed

$M(PEt_3)_3$
20, M = Pt
21, M = Pd

during the reaction, it was suggested that certain alkyl halides undergo oxidative addition to palladium or platinum via an S_N2 mechanism while others take place via free-radical processes. The choice of a particular reaction pathway depends on the nature of the carbon–halogen bond, the nucleophilicity of the metal complex, the ability of the metal complex to undergo one-electron processes, steric effects, and ligand exchange processes.[31c,42]

A nonchain radical mechanism has been postulated for the oxidative addition of methyl iodide, ethyl iodide, and benzyl bromide to platinum(0) on the basis of the observed lack of retarding effect of radical scavengers on the rates of reaction and on the basis of the generation of the nitroxide radical **22** when *tert*-nitroso-

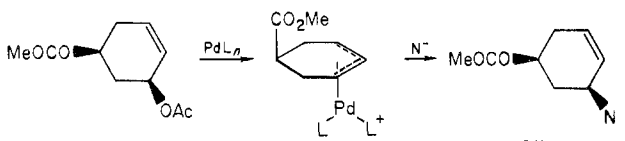


22 **23**

R = CH_3, CH_2CH_3, CH_2Ph

butane was added to the reaction mixture.[43] The formation of **22**, however, can be a consequence of *tert*-nitrosobutane-induced decomposition of the preformed alkylplatinum complex **23**. Indeed, it has been demonstrated (vide infra) that the palladium analogue (R = $PhCH_2$) of **23** undergoes a reaction with *tert*-nitrosobutane to give **22**. Thus, the validity of *tert*-nitrosobutane as a probe for the mechanism of oxidative addition is questionable.

On the other hand, convincing evidence has been obtained for nonradical oxidative addition reactions of phosphine-ligated palladium(0) complexes. The reaction of *cis*-3-acetoxy-5-carbomethoxycyclohexene with **18** and the sodium salt of methyl phenylsulfonylacetate gave the alkylation product **25**.[44] Formation of the cis isomer is the net result of two consecutive inversions, since the conversion of the intermediate π-allylpalladium complex **24** to **25** has been shown to occur



24 **25**

N = $PhSO_2CHCO_2Me$

with displacement of palladium by nucleophilic attack on the side opposite to the attachment of palladium. The initial displacement of acetate therefore takes place with inversion of configuration at the carbon bearing the acetate group. Control of the stereochemistry at the C-20 center of steroids also has been realized by the same double-inversion sequence.[45]

The first unambiguous demonstration of stereochemical inversion at carbon in the oxidative addition of benzyl halides to palladium was provided by two sequential reactions, in which the stereochemistry of only the oxidative addition reaction was unknown[46] (Scheme II). The remaining steps in the sequence

(40) K. J. Klabunde, *Acc. Chem. Res.*, **8**, 393 (1975).
(41) P. Fitton, M. P. Johnson, and J. E. McKeon, *Chem. Commun.*, 6 (1968); P. Fitton, J. E. McKeon, and B. C. Ream, *ibid.*, 370 (1969).
(42) (a) A. V. Kramer, J. A. Labinger, J. S. Bradley, and J. A. Osborn, *J. Am. Chem. Soc.*, **96**, 7145 (1974); (b) A. V. Kramer and J. A. Osborn, *ibid.*, **96**, 7832 (1974).
(43) M. F. Lappert and P. W. Ledner, *J. Chem. Soc., Chem. Commun.*, 948 (1973).
(44) B. M. Trost and P. E. Strege, *J. Am. Chem. Soc.*, **99**, 1649 (1977).
(45) B. M. Trost and T. R. Verhoeven, *J. Am. Chem. Soc.*, **98**, 630 (1976).
(46) (a) K. S. Y. Lau, R. W. Fries, and J. K. Stille, *J. Am. Chem. Soc.*, **96**, 4983 (1974); (b) P. K. Wong, K. S. Y. Lau, and J. K. Stille, *ibid.*, **96**, 5956 (1974); (c) K. S. Y. Lau, P. K. Wong, and J. K. Stille, *ibid.*, **98**, 5832 (1976); (d) J. K. Stille and K. S. Y. Lau, *ibid.*, **98**, 5841 (1976).

Scheme II

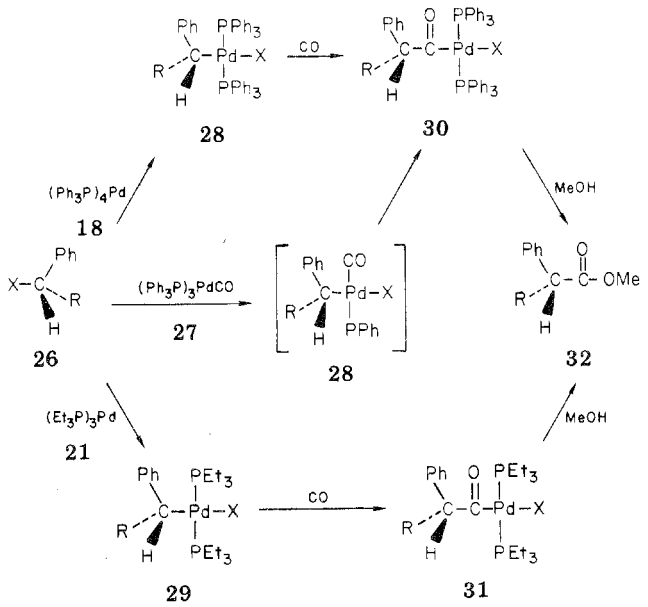


Table I
Oxidative Addition of Benzyl Halides to Palladium(0)

Pd(0) Complex	26 R	26 X	Net inversion	Relative rate
$(Et_3P)_3Pd$ (21)	D	Br	30[b]	10^3
	D	Cl	72	5×10^2
$(Ph_3P)_4Pd$ (18)	D	Cl	74	3
$(Ph_3P)_4Pd$ (18)[a]	D	Cl	100	
$(Ph_3P)_3PdCO$ (27)	D	Cl	100	2
$(Ph_3P)_4Pd$ (18)[a]	CH_3	Br	90	1.5
$(Ph_3P)_3PdCO$ (27)	CH_3	Br	90	1
$(Ph_3P)_4Pd$ (18)	CF_3	Cl	<10	Very slow

[a] Carbon monoxide present during the oxidative addition reaction. [b] Racemic coupling product, PhCHDCHDPh, also formed.

either did not affect the active center or had a known stereochemistry. Thus, the oxidative addition reaction was followed by carbonylation in which the carbon monoxide "insertion" into the carbon–palladium σ bond is known to proceed with *retention* of configuration at carbon, and the decomposition to ester was completed by the solvent, a reaction which does not affect the asymmetric center. Since the absolute configuration and purity of the alkyl halides and the ester products could be determined from their optical rotations, the stereochemistry of the oxidative addition reaction could be assessed.

The reaction proceeds with predominate *inversion* of configuration at carbon.[46,47] In some examples, 100% net inversion of configuration occurs while in one instance only 30% enantiomeric excess of one oxidative addition product was obtained (Table I).

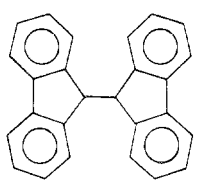
Complexes **28** and **29** (R = D) could be isolated as stable complexes since they do not contain hydrogen β to palladium, and optical rotations of the more soluble complexes **29** and **31** (X = Cl, Br) could be observed. Because of the tendency for **28** ($R = CH_3$) to undergo β elimination, it could not be isolated from the reaction, but was converted directly to **30**, either by using carbonyl complex **27** or by the presence of carbon monoxide during the oxidative addition.

(47) Y. Becker and J. K. Stille, submitted for publication.

It is apparent that tetrakis(triphenylphosphine)-palladium(0) (**18**) and carbonyltris(triphenylphosphine)palladium(0) (**27**) behave differently than tris-(triethylphosphine)palladium(0) (**21**). Although the net inversion of configuration in oxidative addition could be improved either by the use of the carbonyl complex **27** or by completing the reaction in the presence of carbon monoxide, the optical yields could not be similarly improved in the additions to **21**, since it reacts rapidly with carbon monoxide to give inert carbonyltris(triethylphosphine)palladium(0) and other carbonylated palladium(0) complexes.

The loss of stereochemistry in the oxidative addition of **26** (R = D) to **18** can be accounted for, in part, by the partial racemization of **26** (R = D) under the reaction conditions, since **26** (R = D) recovered from an oxidative addition reaction suffered a 10% loss of its optical activity. Over longer periods of time, the reaction of excess **26** with **18** led to complete racemization of **26**. However, the optical activity of **29** was unchanged under the reaction conditions. In all these reactions no CIDNP could be observed, and in the reactions of **18** and **26**, the presence of radicals could not be detected by chemical means. Thus, a nucleophilic exchange process involving **28** (R = D) and **18** is a plausible explanation for racemization. Rapid transformation of the alkyl complex **28** to the acyl complex **30** would supress racemization.

In the absence of carbon monoxide, complex **28** ($R = CH_3$) decomposes to styrene, ethylbenzene, and bis(triphenylphosphine)palladium bromide. The reaction of 9-bromofluorene or ethyl α-bromophenylacetate with **18** at 0 °C affords the coupled products **33** and **34**, respectively, and bis(triphenylphosphine)pal-



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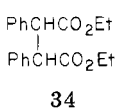
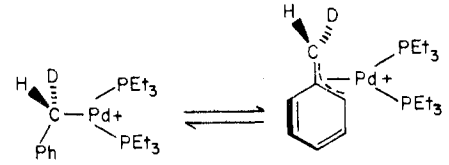


34

ladium bromide. In the latter case a mixture of *erythro*- and *threo*-2,3-diphenylsuccinate is obtained. Although higher temperatures are usually required for the coupling reaction, the greater reactivity of 9-bromofluorene and ethyl α-bromophenylacetate accounts for the lower reaction temperatures. For example, **28** (R = H, X = Cl) undergoes a reaction with benzyl chloride at 80 °C to give bibenzyl.[46d] In these coupling reactions, no CIDNP could be observed, but chemical tests indicated the presence of radicals.

The oxidative addition product (**29**) is configurationally stable in solution over long periods of time, and its optical activity is unaffected by the presence of **26**, **18**, or triethylbenzylphosphonium chloride, another product present when **26** (R = D, X = Cl) reacts with **18**. Thus, racemization in this reaction cannot be attributed to a nucleophilic exchange between **21** and **29**. In addition, the π-benzyl complex **36** maintains its configurational integrity in solution. Even though CIDNP could not be observed from the reaction of **26** (R = H, X = Cl or Br), the possibility that racemization is taking place either by an oxidative addition reaction involving a benzyl radical or by the dissociation of the

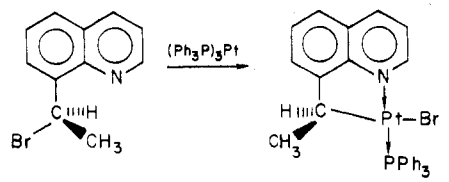


35 36

oxidative addition product **29** into a radical pair followed by rotation of the benzyl group cannot be excluded. Only in the reaction of **29** (R = D, X = Br) with **21** is any coupling product, racemic dideuteriobibenzyl, obtained.

The inversion of configuration at carbon, the order of reactivity [$PhCH_2Br > PhCH_2Cl > PhCHCH_3Br > PhCHCH_3Cl > PhCHCF_3Cl$ and $(Et_3P)_3Pd > (Ph_3P)_4Pd > (Ph_3P)_3PdCO$], and the inability to detect free radicals during the oxidative addition reaction of the optically active benzyl halides clearly are in favor of a nucleophilic displacement mechanism. Radical species probably participate only during the decomposition of the oxidative addition product, and, depending on the characteristics of the alkyl group of the organic halide, alternative pathways for the decomposition of the oxidative adduct are possible.

One recent example of a stereochemical experiment involving an oxidative addition to Pt(0) supports a heterolytic mechanism.[48] The addition of optically active 8-(α-bromoethyl)quinoline to tris(triphenyl-



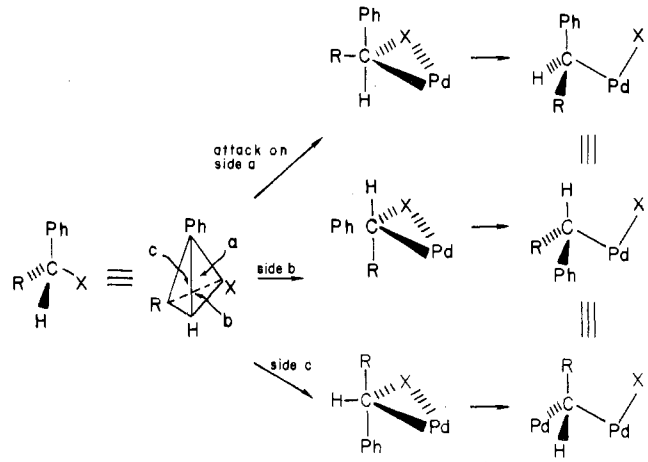
phosphine)platinum(0) gives a stable optically active oxidative addition product, the configuration of which was deduced from Brewster's rules to have been formed with inversion of configuration at carbon. The stereochemistry of this reaction could be greatly influenced by coordinated nitrogen guidance, however.

Conclusions

There is ample evidence for both radical and nucleophilic displacement mechanisms in the oxidative additions of organic halides to group 8 transition metals. The demonstration of stereochemical inversion of configuration at carbon is convincing evidence for an S_N2-type mechanism in which the low-valent metal serves as a nucleophile.

In a classical S_N2 reaction involving palladium(0), for example, a cationic palladium complex and the displaced halide ion would be the intermediates that would collapse to the oxidative addition product after migration of the halide to the other side of the cation or to a different cation. However, we have observed that a cationic palladium complex such as **35** $\rightleftharpoons$ **36** reacts rapidly with the starting palladium(0) complex (**21**) to form a new complex. Since the formation of this new complex is not observed under the conditions of the oxidative addition reaction, free cationic complex (**35** $\rightleftharpoons$ **36**) either is not generated or is too short-lived. Thus, the conventional S_N2 mechanism may not be suitable to describe the reaction.

Scheme III



An alternative mechanism (Scheme III) that does not require an ion-pair intermediate is conceivable however. A concerted attack of palladium at the carbon–halogen bond from any one of three of the tetrahedral faces common to the carbon–halogen bond results in a trigonal-bipyramidal transition state. Attack at face b would be preferred for steric reasons, whether R = D or CH_3. If carbon–halogen bond scission occurs always with least motion of the equatorial group in one preferred direction (i.e., toward palladium), then the same enantiomer is always obtained, having the net effect of a configurational inversion at carbon. Since the palladium–carbon distance is greater than the carbon–halogen bond distance, motion of the equatorial group toward palladium would be the least hindered pathway, at least in a transition state where Pd–C bond making and C–X bond breaking were progressing equally.

This mechanism could possibly accommodate the loss of optical purity in the product and the racemization of starting material. Motion of the equatorial group in the opposite direction, or away from palladium, would produce the other enantiomer, resulting in a loss of optical purity. The extent of this loss, as a result of the competitive motions, could be expected to be dependent on steric factors. Both the size of the alkyl group and the different ligands[26b] on palladium could influence the direction of motion. More important, the extent of bond making (Pd–C) and breaking (C–X) in the transition state would influence the enantiomer distribution. If the transition state resembled products (i.e., well-formed Pd–C and Pd–X bonds and a long C–X bond) motion of the equatorial group toward X would become important. Thus, greater racemization would be expected in the reactions of benzyl halides ($PhCHCH_3 > PhCH_2$; Br > Cl) with **21** than with **18**.

A pseudorotation of the trigonal bipyramid followed either by collapse to product or reversion to starting material (reductive elimination) would account not only for a reduction in optical yield of the product but also for the observation that recovered starting halide is partially racemized.

If carbon–halogen bond breaking precedes carbon–palladium bond making, and occurs by a one-electron transfer process,[49] then a radical pair is formed. Rotation of the alkyl radical followed by collapse to product or reversion to starting material would account

(48) V. I. Sokolov, *Inorg. Chim. Acta*, 18, L9 (1976).

(49) T. Takabe and K. Yamaguchi, *Chem. Phys. Lett.*, 40, 347 (1976).

for the loss of stereospecificity in the product or racemization of the starting material, respectively.

Although the concerted mechanism of Scheme III is somewhat attractive, it is highly speculative, and must await further experimental tests. This type of three-centered mechanism involving *nucleophilic* attack by the metal at the carbon–halogen bond has been advocated, however, both for the oxidative addition of vinyl halides and aryl halides to the platinum group metals.

Alkene Synthesis via β-Functionalized Organosilicon Compounds

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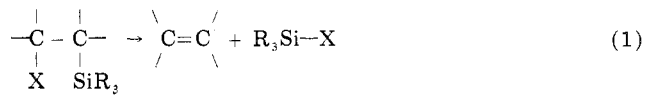
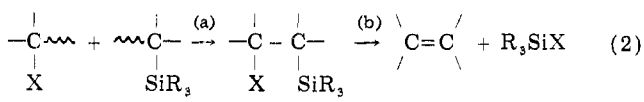
Reactions leading to the formation of carbon–carbon double bonds are of great importance to organic chemistry. Numerous named reactions (Hofmann, Saytzeff, Cope, Wittig, etc.) have been developed for that purpose. A new alkene synthesis, based on the propensity of β-functional alkylsilanes to undergo elimination,[1] has recently been introduced. In the late forties, a series of papers by Sommer, Whitmore, and their co-workers[2-5] established clearly that the general reaction with all these compounds is the formation of alkenes and the elimination of functionalized silyl compounds (reaction 1). Notwithstanding such important early observations and subsequent work on the β elimination of silicon compounds,[1] the recognition that reaction 1 can serve as a general method of alkene synthesis is a recent one. Much work in several laboratories, including our own, has demonstrated the usefulness of β-functionalized organosilicon compounds in alkene synthesis. This method, besides being generally competitive with other similar reactions such as the Wittig reaction, is particularly useful in the synthesis of heterosubstituted alkenes, α,β-unsaturated esters, aldehydes, and nitriles. The silicon method also enables the generation of strained alkenes such as allene oxides, cyclopropenes, and bridgehead alkenes which would have been difficult to prepare otherwise.



(1)

The generality of the alkene synthesis can be expressed by eq 2. Simply stated, any formation of a

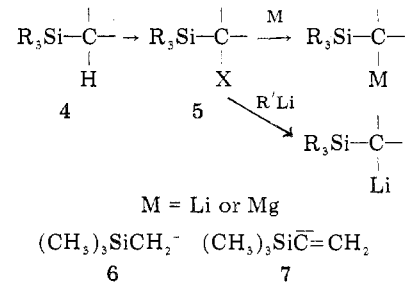


(2)

carbon–carbon single bond which brings together the β relationship of the silyl group and the leaving group

T. H. Chan was born in China in 1941. He obtained his Ph.D. degree from Princeton University, with R. K. Hill, and then joined R. B. Woodward's research group as one of the 100 postdoctoral fellows who worked on the synthesis of vitamin B_{12}. He joined the faculty at McGill University, where he is associate professor of chemistry, in 1966. Dr. Chan's research interests concern the chemistry of organosilicon, phosphorus, and sulfur compounds and their application to organic synthesis; mechanistic studies; and the structural determination and chemical synthesis of natural products.

Scheme I



M = Li or Mg

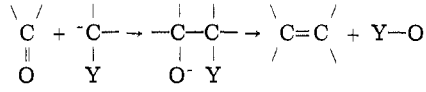
$(CH_3)_3SiCH_2^-$ $(CH_3)_3Si\overline{C}=CH_2$

6 7

X can be considered as an alkene synthesis. The reactions which have been brought to bear to execute step a include the reaction of carbonyl compounds with α-silyl carbanions, carbene insertion into vinylsilanes, and the Diels–Alder reaction of vinylsilanes. So far, our experience has been that it is always possible to execute step b, even when the alkene to be generated is highly strained. There are, of course, problems still associated with this alkene synthesis, and these will be touched upon in the course of this Account.

The Synthesis of Alkenes from Carbonyl Compounds and Carbanions α to Silicon

The most useful version of eq 2 involves the reaction of carbonyl compounds with carbanions α to silicon (eq 3, Y = SiR_3). This version bears obvious similarity to



(3)

the Wittig reaction[6] (Y = PR_3^+) and its many modifications.[7] Indeed, in 1962, Gilman and Tomasi[8]

(1) For review, see A. W. P. Jarvie, *Organometal. Chem. Rev., Sect. A*, **6**, 153 (1970).
(2) L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 485 (1946).
(3) L. H. Sommer, D. L. Bailey, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2869 (1948).
(4) L. H. Sommer, E. Dorfman, G. M. Goldberg, and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 488 (1946).
(5) L. H. Sommer, G. M. Goldberg, E. Dorfman, and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 1083 (1946).
(6) G. Wittig and U. Schollkopf, *Ber.*, **87**, 1318 (1954).
(7) For review, see S. Trippett, *Q. Rev., Chem. Soc.*, **17**, 406 (1963).