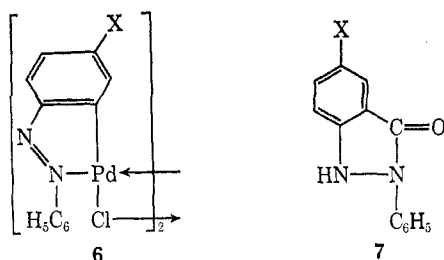


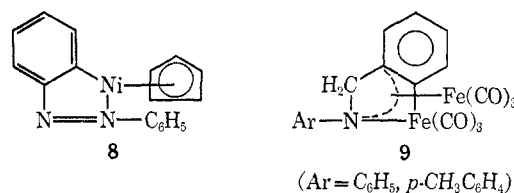
benzenes bearing a *para* substituent on only one of the two aromatic rings.⁶ In this situation, the choice of the ring to be substituted depends on electronic effects and provides some clue to the mechanism of the reaction. The results strongly suggest electrophilic substitution. The preference for attachment of the metal to the substituted ring in the product **6** falls in the order $\text{OCH}_3 > \text{CH}_3 > \text{H} > \text{Cl}$, thus indicating metalation of the more electron-rich ring. With 4-methoxyazobenzene only the substituted ring was attacked to give **6** ($\text{X} = \text{OCH}_3$), but with 4-chloroazobenzene metalation of the unsubstituted ring predominated by a 3:1 margin.



The method of analysis of the isomers⁶ of **6** is interesting because it suggests synthetic applications for this reaction. The crude product, **6**, obtained by reaction of the azobenzene with ethanolic Na_2PdCl_4 , was treated with carbon monoxide (150 atm, 100°) in ethanol to give the indazolone **7**. This product, in turn, was degraded to give aniline and 5-X-2-amino-benzoic acid. The formation of **7** presumably occurs by insertion of CO into the C-Pd bond of **6** followed by displacement of Pd from N to give the indazolone ring. The selectivity of the palladation reaction for *ortho* substitution should make this chemistry useful for synthesis of compounds difficult to obtain by classical methods. It seems likely that an analogous *ortho* metalation of azobenzene by cobalt is a key step in the $\text{Co}_2(\text{CO})_8$ -catalyzed synthesis of indazolone from azobenzene and CO.⁸

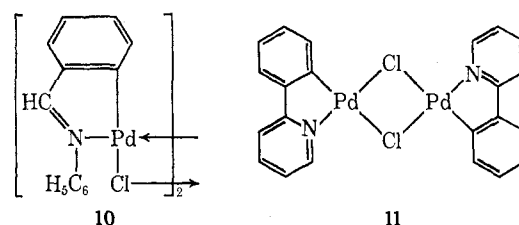
Analogous *o*-metaloazobenzene complexes have been prepared from nickelocene and azobenzene⁹ or substituted azobenzenes.¹⁰ Azobenzene reacts at 135°

to form **8**, presumably with elimination of cyclopentadiene. Compound **8** is soluble, apparently monomeric, and is surprisingly stable to air. This reaction, like that with palladium salts, is accelerated by electron donor substituents on the aromatic rings. The palladium analog of **8** has been prepared by treatment of the chloride-bridged dimer **4** with sodium cyclopentadienide.⁷ Attempts to prepare an iron carbonyl derivative of azobenzene by reaction with $\text{Fe}_2(\text{CO})_9$ ¹¹ gave a rearranged product with no aryl-Fe bonds.¹²



In contrast to azobenzene, the isostructural Schiff bases such as *N*-benzylideneaniline react with $\text{Fe}_2(\text{CO})_9$ to give *ortho*-metalated products.¹³ The crystal structure¹¹ of the *p*-toluidine derivative (**9**, $\text{Ar} = p\text{-CH}_3\text{C}_6\text{H}_4$) displays a nonplanar five-membered ring containing the *ortho*-bonded iron. Another $\text{Fe}(\text{CO})_3$ group bonds to one face of the ring; the CH_2 of the ring is bent away from the second iron. This CH_2 is evidently produced from the azomethine carbon of the Schiff base by transfer of an *ortho* hydrogen from the aromatic ring. When no such hydrogen is present in the starting material as in 2,6-dichlorobenzylideneaniline, complex formation does not occur.

Schiff bases and other structural analogs of azobenzene react with PdCl_2 complexes to give products strictly analogous to the *o*-palladioazobenzene complexes (**4**). A considerable series of *N*-benzylideneanilines have been treated with $(\text{C}_6\text{H}_5\text{CN})_2\text{PdCl}_2$ to give compounds such as **10**, in which the palladium is bound to the benzylidene ring.¹⁴ Similarly, 2-phenylpyridine with Na_2PdCl_4 gives **11** and 2-phenylquinoline gives a benzo derivative of **11**.¹⁵



Phosphorus Donor Ligands

Triarylphosphine and phosphite complexes of many group VIII metals undergo intramolecular aromatic

(6) H. Takahashi and J. Tsuji, *J. Organometal. Chem.*, **10**, 511 (1967).

(7) R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 313 (1968).

(8) S. Horie and S. Murahashi, *Bull. Chem. Soc. Jap.*, **33**, 247 (1960).

(9) J. P. Kleiman and M. Dubeck, *J. Amer. Chem. Soc.*, **85**, 1544 (1963).

(10) Yu. A. Ustynyuk, I. V. Barinov, T. I. Voevodskaya, and N. A. Rodionova, Abstracts, 4th International Conference on Organometallic Chemistry, Bristol, 1969, p J16.

(11) M. M. Bagga, W. T. Flannigan, G. R. Knox, and P. L. Pauson, *J. Chem. Soc., C*, 1534 (1969).

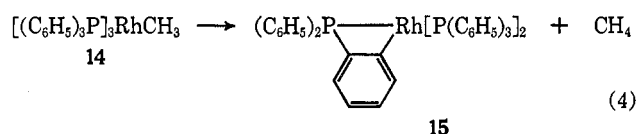
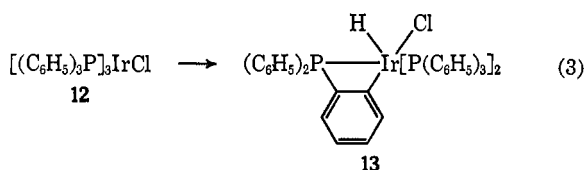
(12) P. E. Baikie and O. S. Mills, *Chem. Commun.*, 707 (1966).

(13) M. M. Bagga, W. T. Flannigan, G. R. Knox, P. L. Pauson, F. J. Preston, and R. I. Reed, *J. Chem. Soc., C*, 36 (1968).

(14) S. P. Molnar and M. Orchin, *J. Organometal. Chem.*, **16**, 196 (1969).

(15) A. Kasahara, *Bull. Chem. Soc. Jap.*, **41**, 1272 (1968).

substitution. As with the N-donor ligands, *ortho* substitution occurs, but the role of the metal atom is more complex. For example, the substitution may involve a formal oxidation of the metal as in eq 3.¹⁶ More commonly the initial and final oxidation states of the metal are the same since, as in eq 4,^{17,18} substitution is accompanied by elimination. However, in contrast to the N-donor ligand complexes studied to date, the elimination involves H₂ or alkane, rather than HCl.



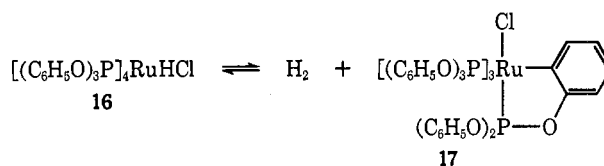
The oxidative substitutions such as those of eq 3 are typical examples of the "oxidative addition" reactions recently recognized in transition metal chemistry¹⁹ since the metal undergoes an increase in both formal oxidation state and coordination number. For example, in eq 3, a four-coordinate, d⁸ iridium (1+) complex (12) is converted to a six-coordinate, d⁶ iridium (3+) compound (13) by addition of an *ortho* C-H bond to the metal.¹ Although the gross reaction is simply an isomerization, the product is easily detected by the presence of characteristic Ir-H absorptions in the infrared and nmr spectra. Bennett and Milner¹⁶ have shown that the *ortho* substitution is promoted by electron-donating substituents on the aromatic ring. For the *para*-substituted phosphine complexes [(XC₆H₄)₃P]₃IrCl, the rate of the reaction decreases in the series CH₃ > OCH₃ > H >> F. A single *ortho* deuterium on each ring brings about a slight slowing of the reaction, corresponding to *k*_H/*k*_D of about 1.4, but experimental problems prevent an accurate determination of this ratio. The acceleration of the reaction by electron-donor substituents could be due to either or both of two effects: (1) an enhancement of the electron density in the ring should promote electrophilic substitution as was noted for the N-donor complexes; or (2) enhanced electron density on the metal atom should promote "oxidative addition"¹⁹ to the metal.

The more common type of *ortho* substitution exemplified by reaction 4^{17,18} may also involve oxidative addition. In the thermolysis of 14, which occurs even at 0°, the first step may be addition of an *ortho* C-H bond to the metal atom to give a six-coordinate rhodium (3+) species very similar in structure to 13. This

intermediate may then undergo "reductive elimination"¹⁹ of CH₄ to give the observed product, 15. Such an elimination of H and alkyl attached to the same metal atom is commonly accepted as a key step in the hydrogenation of olefins.^{20,21} Consistent with this postulated reaction sequence, pyrolysis of [(C₆D₅)₃P]₃-RhCH₃ produces CH₃D.

The C-Rh bond in 15 undergoes many normal reactions of an organometallic compound,²⁰ including cleavage and insertion. Carbon monoxide "inserts" into the C-Rh bond to give an acyl function, C-C(=O)-Rh,¹⁸ as diagnosed by the appearance of infrared absorption at 1620 cm⁻¹. Phenol and H₂ cleave the bond to give C₆H₅ORh[P(C₆H₅)₃]₃ and HRh[P(C₆H₅)₃]₃, respectively.¹⁷ The latter cleavage is apparently reversible, since use of D₂ leads to extensive incorporation of deuterium into the triphenylphosphine ligand.¹⁸

Transition metal hydride complexes containing aromatic phosphorus ligands readily eliminate H₂ on *ortho* substitution. This tendency is illustrated in the equilibrium between the triphenyl phosphite complexes 16 and 17. Although either H₂ or HCl could be formed by *ortho* substitution of a phenoxy group, hydrogen is cleanly evolved when 16 is heated in an inert solvent.²² The *ortho*-bonded compound (17) is stable, but readily reverts to the hydride (16) on treatment with hydrogen. If 17 is treated with D₂ rather than H₂, the corresponding metal deuteride is formed and deuterium appears in the *ortho* positions of the phenoxy groups. The equilibrium between 16 and 17 is evidently facile because equilibrium is readily attained in the deuteration of the 24 *ortho* positions of 16 at room temperature. Phenol added to solutions of 16 under D₂ is also *ortho* deuterated, apparently by exchange with the phenoxy groups of triphenyl phosphite. In contrast to the rhodium complex 15, the *ortho*-bonded ruthenium species 17 does not readily undergo CO insertion.



The exchange of aromatic hydrogens with D₂ is a useful tool for detecting a reversible reaction analogous to 16 ⇌ 17 when the equilibrium concentration of the *ortho*-bonded species is very small.²² The appearance of hydrogen in the gas phase indicates the rate and extent of exchange. Nmr analysis of the aromatic ligand shows the position at which deuterium is introduced. The exchange of *ortho* hydrogens with D₂ is rapid, even at room temperature with the hydrogenation catalyst [(C₆H₅)₃P]₃RuHCl. This compound cata-

(16) M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, **91**, 6983 (1969).

(17) W. Keim, *J. Organometal. Chem.*, **14**, 179 (1968).

(18) W. Keim, *ibid.*, **19**, 161 (1969).

(19) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

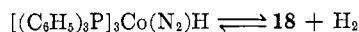
(20) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, **7**, 157 (1968).

(21) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

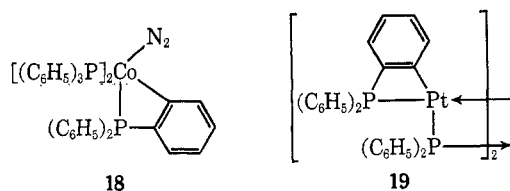
(22) G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, **91**, 4990 (1969).

lyzes specific *ortho* deuteration of $(C_6H_5)_3P$ since the coordinated phosphines are in rapid equilibrium with free ligand in solution.²² The triphenyl phosphite complexes $[(C_6H_5O)_3P]_4CoH$ and $[(C_6H_5O)_3P]_3RhH$ undergo statistical *ortho* exchange with D_2 at 100° , but with the cobalt compound the exchange is inhibited by excess $(C_6H_5O)_3P$. This inhibition suggests that dissociation of a ligand to give a "coordinatively unsaturated" complex is essential.²² The osmium complexes $[(C_6H_5)_3P]_3(CO)OsH_2$ and $[(C_6H_5)_3P]_3(CO)OsHCl$ exchange *ortho* hydrogen with D_2 at 100 – 120° .²³ The latter compound also exchanges aromatic hydrogens with D_2O at high temperatures.²⁴ The exchange of H_2 with a deuterated ligand as in $[(C_6D_5)_3P]_3CoH_3$ ²⁵ is also a useful way to determine the extent and position of exchange.

The molecular nitrogen complex $[(C_6H_5)_3P]_3Ru(N_2)H_2$ readily exchanges *ortho* hydrogens with D_2 at 65° , but the *ortho*-substituted product is not isolable.²² The related iron compound, $[(C_6H_5)_2PC_2H_5]_3Fe(N_2)H_2$, evolves hydrogen in sunlight to give a stable *ortho*-bonded compound.²⁶ It has been suggested²⁷ that earlier confusion as to whether the cobalt complex of N_2 is $[(C_6H_5)_3P]_3Co(N_2)H$ or simply $[(C_6H_5)_3P]_3Co(N_2)$ is due to an equilibrium between the hydride and an *ortho*-bonded complex

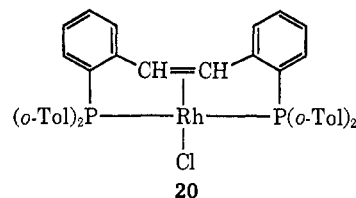


The hydride form of the compound has been conclusively identified by crystallography²⁵ and does indeed exchange *o*-H with D_2 .²² The cobalt complex decomposes thermally with formation of benzene²⁹ and, by inference and odor,²³ diphenylphosphine. This cleavage may occur by way of an *ortho*-substituted triphenylphosphine complex (**18**) like that (**19**) reported in the decomposition of $[(C_6H_5)_3P]_2Pt(C_2O_4)$.³⁰



In a few instances, aliphatic hydrogens from phosphine ligands interact with coordinatively unsaturated metal atoms. The zerovalent complex $[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2Ru$ is reported to exist in equilibrium with a Ru(II) hydride which forms by transfer of a hydrogen from one of the methyl groups of the ligand.³¹ The source of the hydride H was determined by syn-

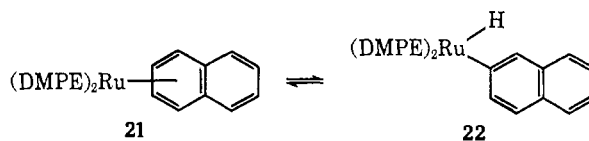
thesis of the complex from selectively deuterated ligands. Metal-carbon bond formation has also been postulated in platinum complexes of $(C_2H_5)_3P$ ³² and $(C_6H_5)_2PCH_3$.³³ A metal-aliphatic hydrogen interaction is also implicated in the reaction of tri-*o*-tolylphosphine with $RhCl_3$ to produce coupling of methyl groups to give the complex **20**.³⁴



Mechanism

The preceding examples of intramolecular substitution in aromatic N- and P-donor ligands illustrate both the broad scope of this reaction and the dearth of information about its mechanism. The observed substituent effects in the azobenzene complexes suggest electrophilic attack of the aromatic ring by the metal nucleus. However, the corresponding information is generally lacking for triaryl phosphite and phosphine complexes. Despite the many gaps in our knowledge, enough is known to permit reasonable guesses about some possible intermediates in *ortho* substitution. Figure 1 shows some plausible sequences for the *ortho* bonding of the ruthenium complex **16** and for the *ortho* substitution of azobenzene. The two sequences indicate some of the similarities and differences expected.

In both sequences, the first significant interaction between the metal atom and the aromatic ring is in the π -arene complex that results from step B. No direct evidence for a π -arene complex has been found in the systems described above, but many are known in transition metal chemistry. The closest parallel is the naphthalene complex **21** formed by reduction of the $(CH_3)_2PCH_2CH_2P(CH_3)_2$ (DMPE) complex of $RuCl_2$ with sodium naphthalide. The reduction product displays chemical properties corresponding to the π -



arene formulation **21**, but its spectroscopic properties indicate hydride structure **22**.^{31,35} This system is particularly pertinent to the Ru complex of Figure 1 because the equilibrium $\mathbf{21} \rightleftharpoons \mathbf{22}$ is exactly analogous

(23) G. W. Parshall, unpublished results.

(24) L. Vaska, *J. Amer. Chem. Soc.*, **86**, 1943 (1964).

(25) A. Sacco and M. Rossi, *Inorg. Chim. Acta*, **2**, 127 (1968).

(26) A. Sacco and M. Aresta, *Chem. Commun.*, 1223 (1968).

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(30) D. M. Blake and C. J. Nyman, *Chem. Commun.*, 483 (1969).

(31) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

(32) S. Bresadola, P. Rigo, and R. Turco, *Chem. Commun.*, 1205 (1968).

(33) M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.*, A, 3083 (1968).

(34) M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, **91**, 6266 (1969).

(35) S. D. Ibekwe, B. T. Kilbourn, U. A. Raeburn, and D. R. Russell, *Chem. Commun.*, 433 (1969). A crystal structure determination showed that, in the solid state, this compound exists as the 2-naphthylruthenium hydride (**22**).

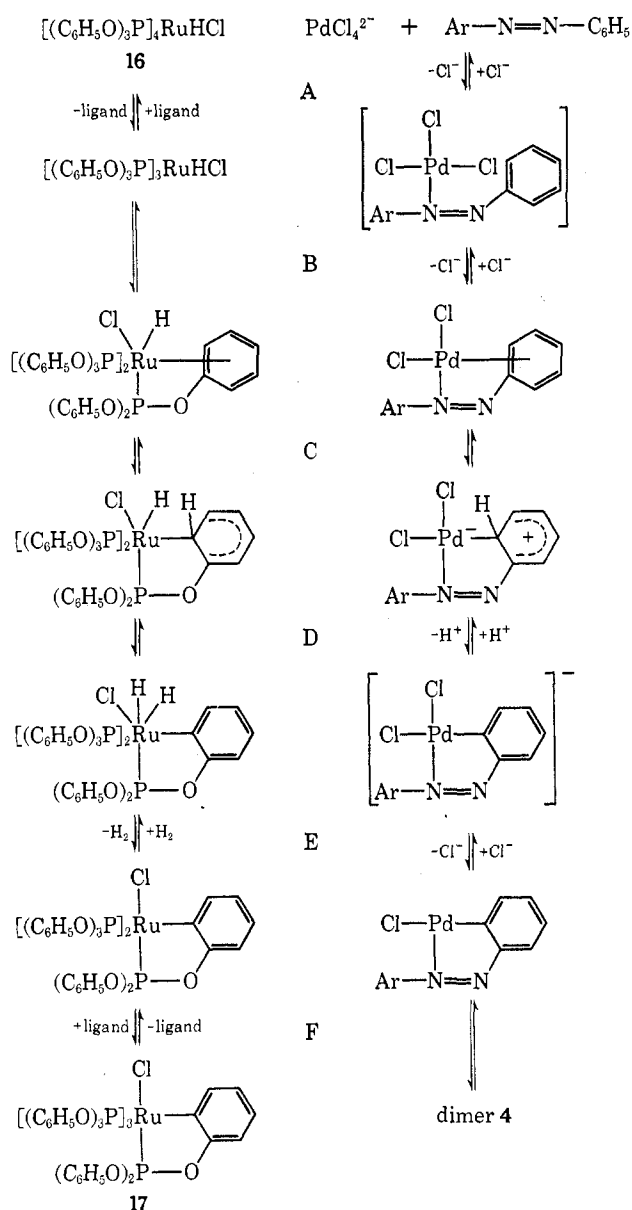


Figure 1.

to the transformation effected by steps C and D. The mechanism of these steps is unknown, but the very small deuterium isotope effect noted in substitution of *o*-deuteriotriphenylphosphine suggests a three-center intermediate such as¹⁶

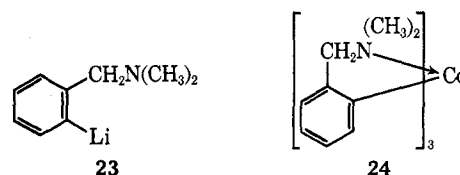


This type of carbon-to-metal hydrogen transfer should be facilitated by π -arene complex formation, but is not absolutely required. In complexes such as $[(C_6H_5)_3P]_3RuCl_2$, one aryl hydrogen approaches the metal atom very closely (2.59 Å) in the solid state.³⁶

The postulated ruthenium and palladium reaction sequences differ in many respects. Steps A and B in the Ru series correspond to an S_N1 replacement of phosphite by arene.³⁷ In contrast, ligand displace-

ments in the Pd sequence may occur by either S_N1 or S_N2 mechanisms. A simple azobenzene complex of palladium analogous to that formed in step A has been isolated recently.³⁸ It is readily converted to the *ortho*-bonded complex 4 by heating in solution. Steps C-E in the Pd complex more closely resemble those established in classical electrophilic aromatic substitutions than that proposed for the Ru complex. The reversible loss of H_2 (step E) from the ruthenium compound is a common reaction of transition metal dihydride complexes.²¹ In both sequences, step F restores the metal atom to its normal coordination number, six for divalent Ru, four for divalent Pd.

The palladation reaction of dialkylbenzylamines is formally analogous to a lithiation reaction discovered by Hauser.³⁹ *n*-Butyllithium reacts with benzyldimethylamine to give the *o*-lithium compound 23.



This derivative, in turn, has been used to prepare transition metal complexes such as 24.⁴⁰ The formal analogy between palladation and lithiation, however, may not be valid mechanistically because there is evidence that contradicts an electrophilic substitution of aromatics by lithium.⁴¹ In addition, the analogy does not extend to the metalation of triphenylphosphine which, as we have seen, readily undergoes *ortho* substitution in several transition metal complexes. The reaction with *n*-butyllithium proceeds very slowly and gives *m*-lithiophenyldiphenylphosphine.⁴² This failure to promote *ortho* lithiation could be ascribed to poor complexing of Li by the phosphine or to the unfavorable ring size involved in an intramolecular transition state. At any event, the lithiation is slow, comparable to that of benzene,⁴¹ and gives a different isomer from that predicted by our analogy.

Intermolecular Substitution

The still unresolved mechanistic question as to whether *ortho* metalation is promoted by a kinetic effect such as stabilization of a transition state or by a thermodynamic stabilization of the product has importance beyond the understanding of the mechanism. If

(37) The postulated dissociation of 16 is supported by the observation that excess triphenyl phosphite inhibits exchange with D_2 . A similar inhibition was also noted in D_2 exchange with $[(C_6H_5O)_3P]_4CoH$ for which there is more direct evidence for ligand dissociation. Dr. R. A. Schunn has found that the apparent molecular weight of the cobalt hydride in aromatic solvents falls from 1261 at 37° to 1174 at 80°, and to 1090 at 110°.

(38) A. L. Balch and D. Petridis, *Inorg. Chem.*, **8**, 2247 (1969).

(39) R. L. Gay and C. R. Hauser, *J. Amer. Chem. Soc.*, **89**, 2297 (1967), and references cited therein.

(40) A. C. Cope and R. N. Gourley, *J. Organometal. Chem.*, **8**, 527 (1967).

(41) H. Gilman and J. W. Morton, *Org. React.*, **8**, 258 (1954).

(42) H. Gilman and G. E. Brown, *J. Amer. Chem. Soc.*, **67**, 824 (1945).

(36) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

the effect of the donor substituent is simply to lower the activation energy for metalation, one might expect metalation of benzene itself to occur, although at a much lower rate. If metalation of nonactivated aromatics does occur and can be promoted by catalysts, new patterns of substitution may become available.

Indeed, some reactions of benzene do suggest the formation of metal-carbon bonds under mild conditions. When $[(\text{CO})_2\text{RhCl}]_2$ and tetraphenylporphine (tpp) are boiled in benzene, $\text{C}_6\text{H}_5\text{RhCl}(\text{tpp})$ is formed,⁴³ apparently by substitution of rhodium on benzene. Exchange between aromatic C-H and D_2O is catalyzed by PtCl_4^{2-} in CH_3COOD solution, possibly by a mechanism⁴⁴ closely analogous to that proposed for the palladation of azobenzene in Figure 1. Similar exchanges with Au^{3+} , Hg^{2+} , Tl^{3+} , Pd^{2+} , and Pt^{2+} have been taken as evidence for the formation of aryl-metal bonds with these ions.⁴⁵

The expectation of new aromatic substitution chemistry has been realized in the reactions of palladium carboxylates with benzene derivatives. Palladium acetate and benzene,^{45,46} depending on reaction conditions, give either phenyl acetate or biphenyl. With toluene, the isomer distribution in the bitolyl that is formed suggests an electrophilic reaction to form a tolylpalladium complex (at 50° , *ortho:meta:para* is 8.7:26.3:65.0) which decomposes to give the observed products. In contrast to these reactions of the acetate, palladium propionate reacts with benzene to give cinnamic acid.⁴⁷

Catalysis

Many of the triarylphosphine complexes that undergo *o*-H exchange with D_2 are active catalysts for the hydrogenation of olefins. It now seems likely that the aryl hydrogens sometimes become involved in the hydrogenation process.

In a study of catalytic reactions of olefins⁴⁸ a series of transition metal hydrides were allowed to react with $\text{D}_2\text{C}=\text{CD}_2$. Hydride complexes that showed activity in the isomerization of olefins usually produced substantial amounts of $\text{C}_2\text{D}_3\text{H}$, $\text{C}_2\text{D}_2\text{H}_2$, and C_2DH_3 . However, some hydrides such as $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RuHCl}$ and $[(\text{C}_6\text{H}_5\text{O})_3\text{P}]_4\text{CoH}$ gave partially deuterated ethanes in addition to the ethylenes. The total amount of hydrogen introduced into the gases exceeded that available from the M-H function. Since both complexes undergo exchange of their *ortho* hydrogens with D_2 ,²² it seems reasonable to propose that the "excess" hydrogen in the C_2 products originated in the aryl groups.

This donation of hydrogen from an aryl C-H bond

(43) E. B. Fleischer and D. Lavalley, *J. Amer. Chem. Soc.*, **89**, 7132 (1967).

(44) R. J. Hodges and J. L. Garnett, *J. Phys. Chem.*, **73**, 1525 (1969), and references therein.

(45) J. M. Davidson and C. Triggs, *J. Chem. Soc., A*, 1324 (1968).

(46) J. M. Davidson and C. Triggs, *ibid.*, **A**, 1331 (1968).

(47) S. Nishimura, T. Sakakibara, and Y. Odaira, *Chem. Commun.*, 313 (1969).

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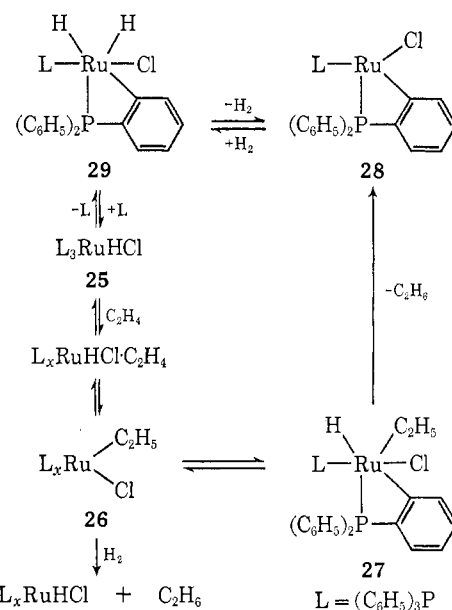
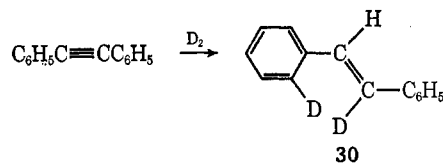


Figure 2.

may explain the rather puzzling hydrogenation of olefins in the absence of H_2 by catalysts such as $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{NiBr}_2$.⁴⁹ A plausible mechanism that has been proposed⁴⁸ for this stoichiometric reduction process is illustrated in Figure 2. The illustration deals with $[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RuHCl}$ (**25**) since the mechanisms of hydrogenation⁵⁰ and of H-D exchange²² are better defined for this catalyst than for most others. The conventional hydrogenation path involves conversion of the hydride to the alkylruthenium compound (**26**, $x = 2$ or 3) which then reacts with H_2 to give alkane and regenerates a ruthenium hydride. However, complex **26** may also undergo *ortho* substitution to form **27**. This species may, in turn, evolve alkane and produce **28**. Thus, hydrogenation of the olefin may occur in absence of added hydrogen. If H_2 is present in the system, **28** may be reconverted to the starting hydride (**25**) via **29**.

The involvement of *ortho* C-H bonds in hydrogenation is also apparent in the reaction of D_2 with diphenylacetylene reported recently.⁵¹ This reaction, which is catalyzed by a $(\text{py})_3\text{RhCl}_3-(\text{CH}_3)_2\text{NCHO}-\text{NaBH}_4$ combination, leads to the formation of *o*-deuterio-*trans*-stilbene (**30**). *ortho* substitution of the aromatic ring by rhodium provides a mechanism for hydrogen transfer from the ring to the α carbon.



(49) H. Itatani and J. C. Bailar, *J. Amer. Chem. Soc.*, **89**, 1600 (1967).

(50) P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc., A*, 3143 (1968).

(51) P. Abley and F. J. McQuillin, *Chem. Commun.*, 1503 (1969).