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Transition-Metal-Mediated Phosphorus–Carbon Bond Cleavage and Its Relevance to Homogeneous Catalyst Deactivation

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I. Introduction

During the past 20 years interest in tertiary phosphine complexes of the transition metals has grown exponentially due, in part, to the observation that many of them are catalysts for such processes as hydrogenation, hydroformylation, and polymerization.

The wide variety of tertiary phosphines that exist have been used extensively in the field of organometallic chemistry to stabilize metal–hydrogen, metal–carbon, and metal–olefin bonds. They appear to be extremely versatile in their ability to stabilize a wide variety of metals in a wide variety of formal oxidation states. Such versatility stems in part from the researchers ability to vary the substituent groups on the phosphorus (R on PR_3) in a synthetic fashion. By so doing, one can alter the tertiary phosphines ability to influence the



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activity, selectivity, and stability of a catalytic system via electronic and/or steric considerations.

Inherent in the attempt to "tailor" tertiary phosphine modified catalysts to meet specific needs has been the belief that the tertiary phosphine ligands have good thermal stability and do not themselves undergo chemical reaction under process conditions.

It was recognized a number of years ago, that a metal atom can react with an aryl or alkyl carbon–hydrogen bond of a phosphorus ligand to form a metal–carbon bond. The term "cyclometalation" was coined by Trofimenko¹ to describe reactions in which a ligand undergoes an intramolecular metalation with concomitant formation of a chelate ring containing a metal–carbon bond. For metalations of phenyl substituted ligands the term "ortho metalation" has been coined and through the years the terms have been used interchangeably. Parshall has likened the "ortho-

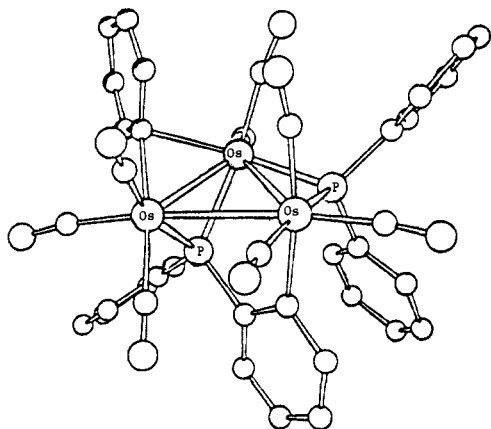
metalation" reaction to classical aromatic electrophilic substitution.² The presence of such reactions has been substantiated via deuteration studies where one observes selective ortho deuteration of ligands such as PPh_3 . Although it has been proposed that such cyclo-metalation reactions are involved in hydrogenation processes, it is important to note that such reactions need not destroy catalytic activity since they are reversible, especially in the presence of hydrogen.²

Only recently has it become apparent that tertiary phosphine-metal complexes are chemically reactive and liable to undergo carbon-phosphorus bond scission depending on the specific reaction conditions that they are exposed to. It is becoming clear that reaction of the phosphorus-carbon bond with the transition metal to which the tertiary phosphine is bound is a general reaction having profound implications on homogeneous catalysis.³ Such observations of phosphorus-carbon reactivity have even stronger ramifications in the area of "heterogenized" or polymer-supported catalysis where phosphorus ligands are usually anchored to a support material through a phosphorus-carbon bond.

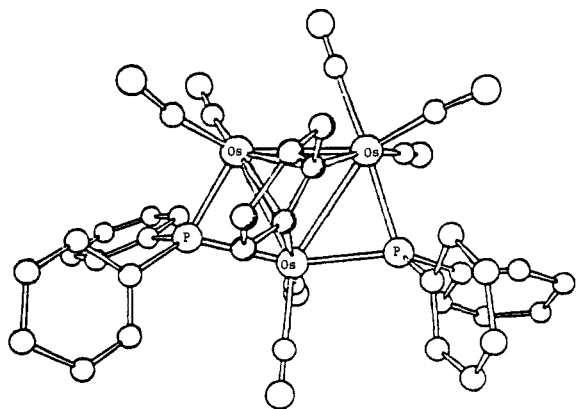
II. Phosphorus-Carbon Bond Cleavage Observed in Model Organometallic Complexes

A. Iron Subgroup

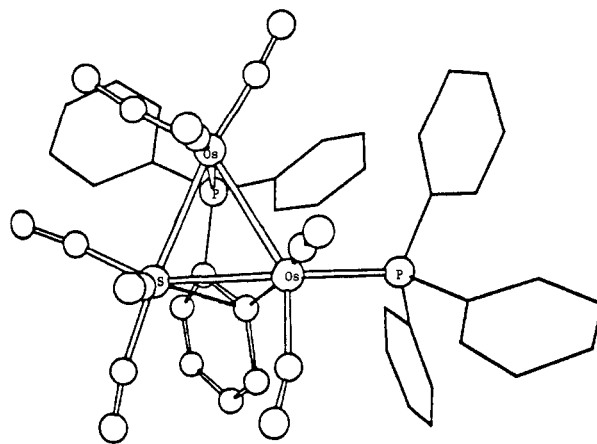
Extensive studies were carried out by Nyholm⁴⁻⁶ and later Deeming^{7,8} on the reaction of $\text{Os}_3(\text{CO})_{12}$ with PPh_3 . Reaction of $\text{Os}_3(\text{CO})_{12}$ with PPh_3 in a 1:2 molar ratio in refluxing xylene gave nine products that were separated by fractional crystallization and chromatography. Complexes 1-6 were subjected to crystallographic



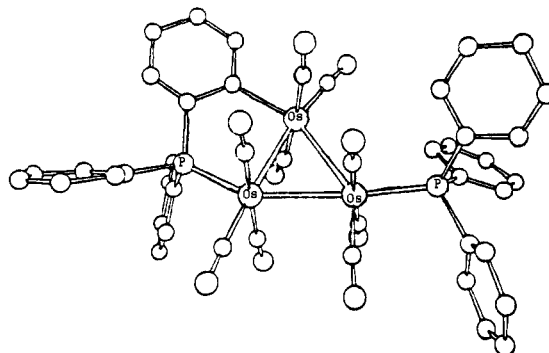
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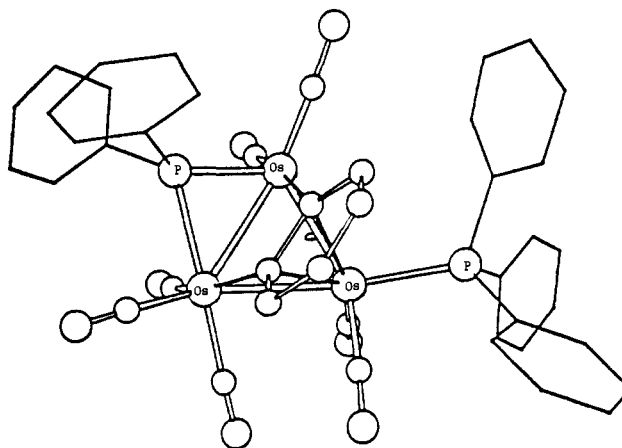
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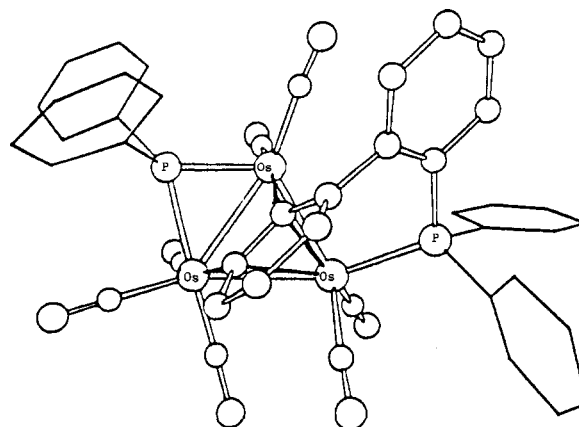
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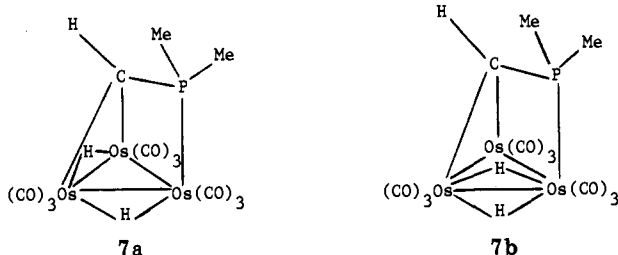


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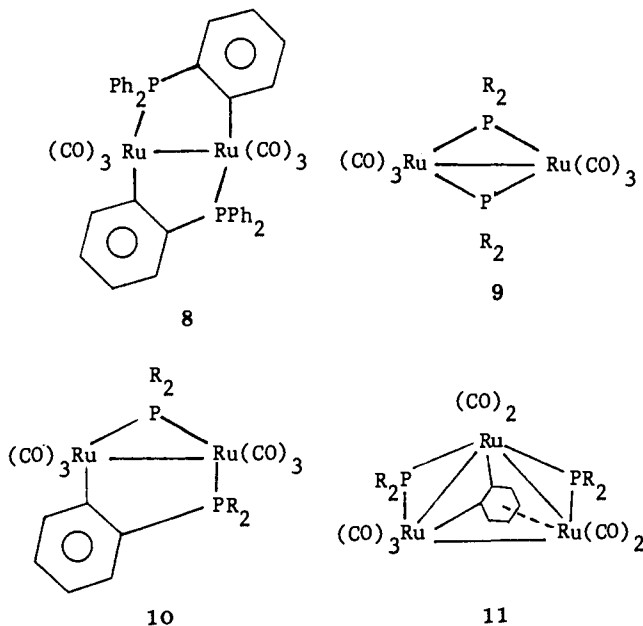
studies. Complexes 3, 4, and 5 were shown to be monohydrides by ^1H high-field NMR although the hy-

drides were not located crystallographically. It was shown that these species resulted from the decomposition of $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2$ and that the yield of the hydrides **3** and **4** decreased with reaction time suggesting that the reactions proceeded via hydride intermediates. Support for this proposal came from heating **3** under similar conditions and observing **2** and **6**. They concluded that **4** was first formed by ortho metalation of a PPh_3 ligand by an osmium atom not coordinated to the PPh_3 . **4** then lost a CO ligand and formed **3**, which in turn decomposed to **1**, **2**, and **5**. The authors proposed that these isolated Os species represented intermediates involved in cluster-mediated ortho metalation and phosphorus-carbon bond-cleavage reactions.

Similar studies were conducted with PPhMe_2 .⁷ Reaction of $\text{Os}_3(\text{CO})_{12-x}(\text{PPhMe}_2)_x$ in refluxing octane resulted in the isolation of analogues to **2**, **5**, and **6**. When PMe_3 was reacted with $\text{Os}_3(\text{CO})_{12}$ in refluxing nonane only **7** could be isolated, which on the basis of NMR data, could be assigned either structure **7a** or **7b**. Thus, while C-H activation was observed for $\text{P}(\text{alkyl})_3$, phosphorus-alkyl bond cleavage was not.

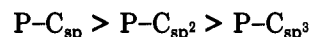


The reaction of $\text{Ru}_3(\text{CO})_{12}$ with PR_3 ($\text{R} = \text{Ph}$, *p*- MeC_6H_4 , *m*- MeC_6H_4 , MePh_2) in refluxing decalin produced **8**, **9**, **10**, and **11**.⁹ The structures were assigned

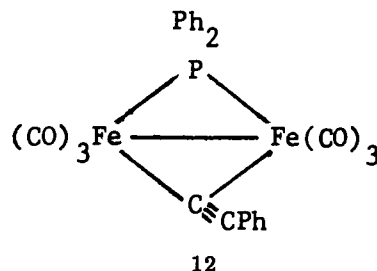


based on IR and NMR data and by analogy to their Os analogues. In contrast to the Os work one observes a preponderance of binuclear ruthenium complexes and no isolable ruthenium hydride species. In similar fashion, C-H activation by a metal not bound to the phosphorus and the bridging phenyl group, achieved via P-Ph cleavage (**2** vs. **11**) appear to be stable structures attained by both systems.

Carty and co-workers¹⁰ have carried out extensive investigations on the reactions of metal clusters with the phosphinoacetylene $\text{PPh}_2\text{C}\equiv\text{CR}$. The cleavage of the P-C bond of the phosphinoacetylene is very facile and in certain circumstances occurs under ambient conditions. It appears that the ease of P-C cleavage in such systems follows the order

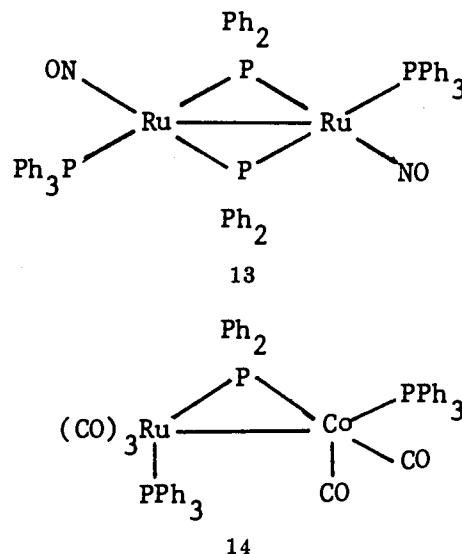


The conditions observed for P-C cleavage during the reaction of such iron-subgroup clusters are shown in Table I. All of the complexes have been structurally characterized by X-ray diffraction. $\text{Fe}_2(\text{CO})_6(\text{PPh}_2)(\text{C}\equiv\text{CPh})$, **12**, revealed the molecular geometry shown.

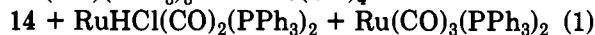


The two $\text{Fe}(\text{CO})_3$ fragments are joined by a metal-metal bond, a bridging diphenylphosphido group and a unique acetylide ligand which is σ bonded to one Fe and π bonded to the other.

The reaction of $\text{RuH}(\text{NO})(\text{PPh}_3)_3$ in refluxing decalin resulted in the formation of **13** in 25% yield.¹¹

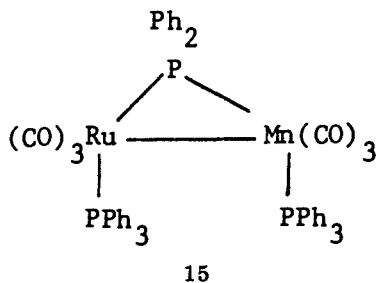


Geoffroy and co-workers¹² examined the reaction of $\text{NaCo}(\text{CO})_4$ with $\text{RuHCl}(\text{PPh}_3)_3(\text{CO})$ at 40 °C (eq 1) and isolated 28% of **14**. **14** was characterized by



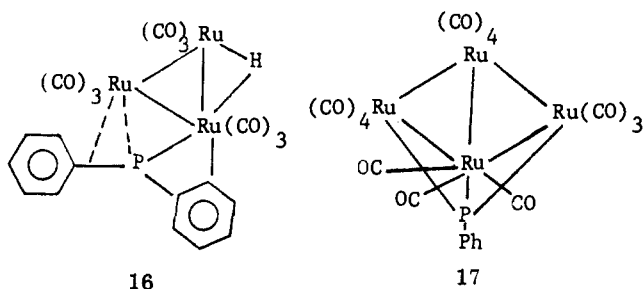
spectroscopic methods and a complete X-ray diffraction study. Benzene was detected in the THF solvent after the reaction implying that the phosphido bridge formed via the reaction of a PPh_3 phenyl group with a hydride initially on Ru.

In a similar fashion reaction of $\text{NaMn}(\text{CO})_5$ with $\text{RuCl}_2(\text{PPh}_3)_3$ produced $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ and **15**.¹³ Again benzene was detected in the GLC of the filtrate and the formation of the phosphido group was explained by the intermediate formation of a hydrido complex.



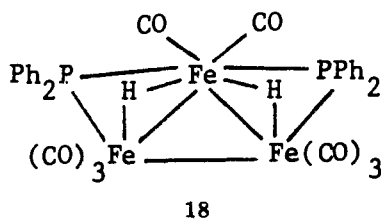
The interaction of $\text{RuHCl}(\text{PPh}_3)_3$ with KOH in THF led to a red tetranuclear complex of stoichiometry $\text{Rh}_4\text{H}_4(\text{OH})_2(\text{PPh}_2)_2(\text{CO})_2(\text{PPh}_3)_6$.¹⁴ Spectroscopic data did not allow for stereochemical assignment.

Carty and coworkers¹⁵ observed the facile reduction of $\mu\text{-PPh}_2$ groups in $\text{Ru}_3(\text{CO})_9(\mu_3\text{-PPh})(\mu_2\text{-H})_2$ via an intermediate electron-deficient hydride, 16, which contains a weak P-Ph interaction to a Ru atom. 16



offers a unique view of an intermediate stage in P-C bond activation and cleavage. Reaction of 16 with H_2 at 80°C resulted in 17 in which a molecule of benzene has been lost and cluster rearrangement has occurred. Carty accurately pointed out that this reactivity of phosphido ligands under reducing conditions would limit their utility in cluster catalysis.

Reaction of the carbonyl anion $\text{Fe}_4(\text{CO})_{13}^{2-}$ with strong acids in the presence of diphenylphosphine affords the trinuclear phosphido-bridged cluster $\text{Fe}_3(\mu\text{-H})_2(\mu\text{-PPh}_2)_2(\text{CO})_8$, 18, which was characterized by X-ray diffraction.¹⁶ Reaction of 18 with CO at room temperature yields the complex $\text{Fe}_3(\mu\text{-PPh}_2)(\text{CO})_9$ via elimination of benzene.



B. Cobalt Subgroup

Two groups^{17,18} simultaneously discovered that refluxing $\text{IrHCO}(\text{PPh}_3)_3$ in a high-boiling solvent resulted in the separation of purple, diamagnetic crystals of 19.

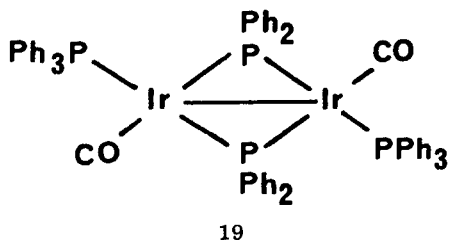
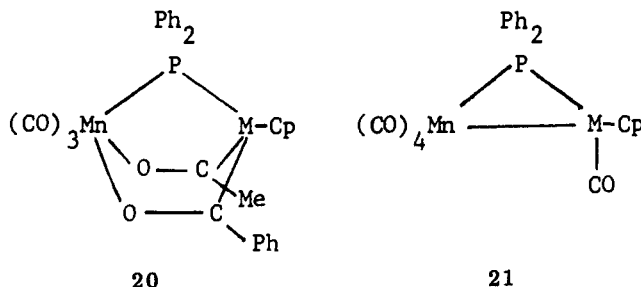


TABLE I. P-C Bond Cleavage during the Reaction of $\text{PPh}_2(\text{C}\equiv\text{CR})$ with Iron-Subgroup Clusters

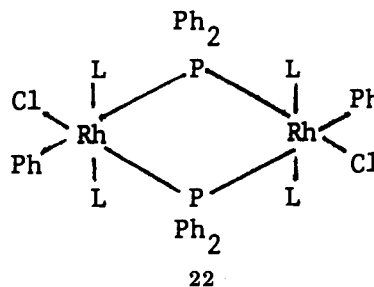
cluster	temp, °C	time, h	product	ref
$\text{Fe}_3(\text{CO})_{11}(\text{PPh}_2\text{C}\equiv\text{CR})$	60	2	$\text{Fe}_2(\text{CO})_8(\text{PPh}_2\text{-C}\equiv\text{CR})$	16a
$\text{Ru}_3(\text{CO})_{11}(\text{PPh}_2\text{C}\equiv\text{CR})$	80	8	$\text{Ru}_2(\text{CO})_8(\text{PPh}_2\text{-C}\equiv\text{CR})$	16a
$\text{Os}_3(\text{CO})_{11}(\text{PPh}_2\text{C}\equiv\text{CR})$	203	0.33	$\text{Os}_2(\text{CO})_8(\text{PPh}_2\text{-C}\equiv\text{CR})$	16a
$\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{C}\equiv\text{CR})_3$	80	1	$\text{Ru}_3(\text{CO})_8(\text{PPh}_2)_2\text{-C}\equiv\text{CR})$ ($\text{PPh}_2\text{C}\equiv\text{CR}$)	16b

Interaction of $\text{MCp}(\text{CO})\text{PPh}_3$ ($\text{M} = \text{Rh}$ or Ir) and $\text{MnMe}(\text{CO})_5$ in refluxing toluene resulted in the isolation of a species for which the accumulated spectroscopic and analytical data "did not lead to any familiar structural formulations ..." so single crystal X-ray was undertaken to elucidate the Ir structure, 20.^{19,20} For-



mation of the acetyl and benzoyl groups must involve migration of methyl and phenyl groups from metal to coordinated carbonyls. The presence of a phenyl group on the Rh or Ir was thought to arise from cleavage of coordinated PPh_3 on $\text{MCp}(\text{CO})\text{PPh}_3$ to give $\text{MCp}(\text{Ph})(\text{PPh}_2)(\text{CO})$. The diphenylphosphido group could then bridge the $\text{MnMe}(\text{CO})_5$ fragment causing Me migration to form acyl and phenyl migration to the other coordinated CO group. Thermolysis of 20 was shown to form 21 and $\text{MeC}(\text{O})\text{Ph}$. This sequence of reactions is indeed complex. The major point is that the P-aryl bond was cleaved in refluxing toluene.

$\text{RhCl}(\text{PPh}_3)_3$ undergoes thermal decomposition above 140°C in solution or in the solid state to yield biphenyl.²¹ It was shown that rhodium complexes of para-substituted tertiary phosphine ligands form exclusively 4,4'-disubstituted biphenyls. Mixtures of $\text{RhCl}(\text{PAR}'_3)_3$ and $\text{RhCl}(\text{PAR}'_3)_3$ result in cross-coupling products. The mechanism was once again thought to involve oxidative addition of dissociated phosphine to $\text{RhCl}(\text{PPh}_3)_2$ to give an intermediate such as 22. Al-



though no phenyl-rhodium complex was isolated, its participation was confirmed by an experiment in which styrene was added as solvent and 1,1-diphenylethylene and *trans*-stilbene were formed along with biphenyl. No mechanisms were proposed for the biaryl formation;

TABLE II. Benzene Formation vs. Hydrogen-Donating Ability in the Transfer Hydrogenolysis of the PPh_3 Ligands of $\text{RhCl}(\text{PPh}_3)_3$

H donor	mol of C_6H_6 /mol of $\text{RhCl}(\text{PPh}_3)_3$
pyrrolidine	8.0
piperidine	6.9
piperazine	6.2
2-propanol	5.8
<i>n</i> -propylamine	3.9
dioxane	1.2
1-propanol	0.8
tetralin	0.5

TABLE III. Effect of Reaction Solvents on the Transfer Hydrogenolysis of the PPh_3 Ligands of $\text{RhCl}(\text{PPh}_3)_3$ ^a

solvent	H donor	yield of C_6H_6 , mol
phenetole	indoline	0.24
	pyrrolidine	0.26
xylene	indoline	0.20
	pyrrolidine	0.15
cumene	indoline	0.15
	pyrrolidine	0.15
benzonitrile	indoline	0.13
	pyrrolidine	0.05

^a $\text{RhCl}(\text{PPh}_3)_3$ (0.05 M) and H donor (0.45 M) at 140 °C for 3 h in the designated solvent.

however, one could envision redistribution sequences similar to those observed for Ni.^{34, 37}

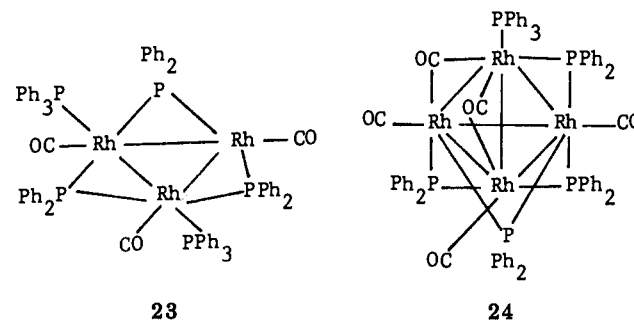
$\text{CoMe}(\text{PR}_3)_3$ ($\text{R} = \text{Ph}, 4\text{-MePh}, 3\text{-MePh}$) decomposes in solutions of THF, benzene, or chlorobenzene to yield biaryls at -20 to 25 °C.²² About 0.8 mol of biaryl is obtained per mole of cobalt in 24 h. Although excess PR_3 seems neither to suppress nor to increase the yield of biphenyl, free PR_3 must be involved in the reaction since addition of $(4\text{-MePh})_3\text{P}$ to $\text{CoMe}(\text{PPh}_3)_3$ resulted in the formation of biphenyl, 4-methylbiphenyl, and 4,4'-dimethylbiphenyl in the ratio of 16:10:2. Crossover experiments of $\text{CoMe}(\text{PPh}_3)_3$ with $\text{CoMe}[(p\text{-MePh})_3\text{P}]_3$ in equivalent amounts gave the same products in a ratio of 1:4:9. Only para-substituted biaryls were obtained from para-substituted-aryl phosphines. The low temperature at which such species react indicate an exceptionally easy P-C bond cleavage in such reactions. During their studies on transfer hydrogenation and transfer hydrogenolysis Nishiguchi and co-workers²³⁻²⁵ observed extensive hydrogenolysis of PPh_3 coordinated to transition metals. When $\text{RhCl}(\text{PPh}_3)_3$ was heated at 140 °C for 1 h in several organic compounds that served as both hydrogen source and solvent, the yield of benzene varied as shown in Table II. The influence of solvents on the benzene yield was investigated by heating $\text{RhCl}(\text{PPh}_3)_3$ and pyrrolidine or indoline in solvents that were inert to hydrogen transfer under reaction conditions. The effect of the solvents are shown in Table III. The yield of benzene vs. reaction time was studied and a 1.5-h induction period was observed. It was speculated that this induction period was due to the transformation of $\text{RhCl}(\text{PPh}_3)_3$ to $\text{RhH}(\text{PPh}_3)_4$, however the similarity between reaction time and benzene yield when $\text{RhH}(\text{PPh}_3)_4$ was substituted as catalyst does not support that contention. No reaction intermediates were isolated. Radical inhibitors did not retard the reaction and radical initiators did not speed up the reaction or increase the yield of benzene, indicating the hydrogenolysis did not proceed by a radical process. The examination of a variety of tran-

TABLE IV. Transfer Hydrogenolysis of the PPh_3 Ligands of Various Transition-Metal- PPh_3 Complexes

complex	H donor	mol of C_6H_6 /mol of complex
$\text{RhH}(\text{PPh}_3)_4$	pyrrolidine	10.4
	2-propanol	11.2
$\text{RhCl}(\text{PPh}_3)_3$	pyrrolidine	8.0
	2-propanol	2.8
$\text{RuH}_2(\text{PPh}_3)_4$	pyrrolidine	9.6
	2-propanol	10.4
$\text{RuCl}_2(\text{PPh}_3)_3$	pyrrolidine	7.8
	2-propanol	0.6
$\text{PtCl}_2(\text{PPh}_3)_2$	pyrrolidine	3.0
$\text{Pt}(\text{PPh}_3)_4$	pyrrolidine	1.8
$\text{PdCl}_2(\text{PPh}_3)_2$	pyrrolidine	2.6

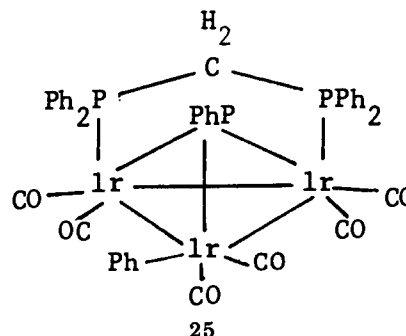
sition-metal-tertiary-phosphine complexes generated the results shown in Table IV. It is clear from these data that in some cases PPh_3 undergoes complete hydrogenolysis to give 3 mol of benzene and presumably PH_3 . All of the reactions appeared to be inhibited by the presence of excess phosphine.

Thermal degradation of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ occurs in a wide variety of solvents above 80 °C.²⁶ After overnight reflux in nonane a green solid was obtained. X-ray crystallography revealed the molecular structure to be 23. When the nonane solution was kept under 60 psig



of CO/H_2 24 was isolated as a brown complex.²⁷ The potential importance of such species in Rh-catalyzed hydroformylation will be discussed later.

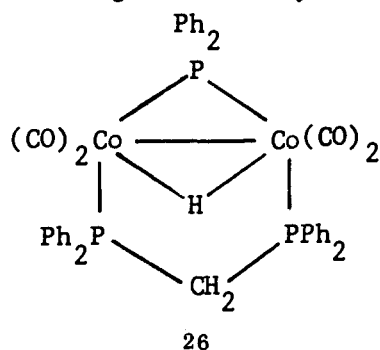
PPh_3 was found to be catalytically degraded by $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, and/or $\text{Rh}_{12}(\text{CO})_{30}^{2-}$ in the presence of paraformaldehyde to give 98% yields of benzaldehyde.²⁸ In the case of tri-*p*-tolylphosphine, *p*-tolualdehyde was the exclusive product. Reaction of $\text{IrCl}(\text{CO})_2(\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2)$ with $\text{CH}(\text{PPh}_2)_3$ at 90 °C in the presence of Zn and CO produced a low yield of 25.²⁹



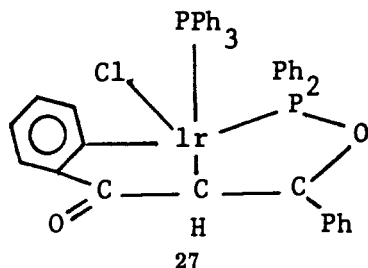
One edge of the Ir triangle is bridged by dppm (bis(diphenylphosphino)methane) and a phenyl group is σ bonded to the third Ir atom. Thus, the initial tridentate phosphine ligand has undergone P-C bond cleavage followed by protonation of the central carbon atom to give dppm and PPh_2 . The PPh_2 moiety has undergone

further P-Ph bond cleavage to give a μ_3 -PPh ligand and form the Ir-Ph bond.

In a similar fashion the reaction of $\text{Co}_2(\text{CO})_6\text{dppm}$ with H_2 resulted in the cleavage of the dppm ligand to give phosphido-bridged **26** in 20% yield.

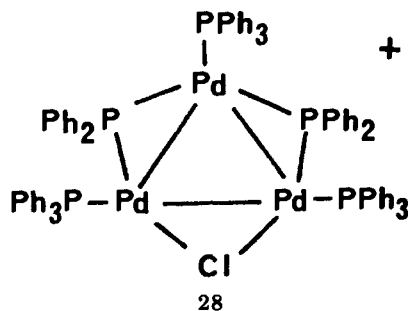


The reaction of $\text{IrCl}(\text{PPh}_3)_3$ with dibenzoyldiazomethane in refluxing THF resulted in the formation of **27** in which an unusual tridentate ligand was formed by loss of a phenyl group from PPh_3 and condensation of the dibenzoylmethylene moiety with the PPh_2 fragment.³¹

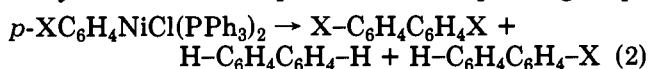


C. Nickel Subgroup

During attempts to prepare $\text{Pd}(\text{PPh}_3)_2$ from $\text{Pd}(\text{PPh}_3)_4$ by the use of PdCl_2 as a scavenger of PPh_3 , Coulson³² observed that reaction at 130 °C in Me_2SO produced *trans*- $\text{Pd}(\text{Ph})\text{Cl}(\text{PPh}_3)_2$ and $\text{Pd}_3\text{Cl}_2(\text{PPh}_2)_2(\text{PPh}_3)_3$ in addition to the expected $\text{PdCl}_2(\text{PPh}_3)_2$. The structure was later shown to be $\text{Pd}_3\text{Cl}_2(\text{PPh}_2)_2(\text{PPh}_3)_3^+\text{Cl}^-$, **28**.³³

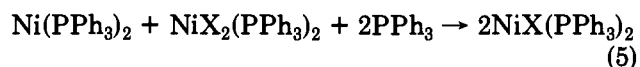
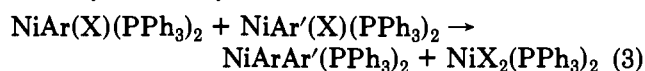


Thermal decomposition of *trans*- $\text{NiBr}(\text{Ph})(\text{PPh}_3)_2$ in the presence of excess PPh_3 gave biphenyl and $\text{NiBr}(\text{PPh}_3)_3$.³⁴ Unexpectedly, however, meta- or para-substituted aryl-nickel complexes gave three different biaryls as shown in eq 2. The corresponding tri-*p*-



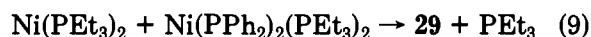
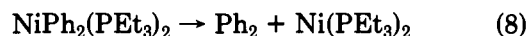
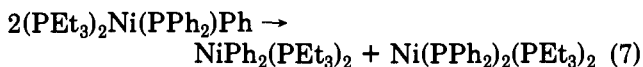
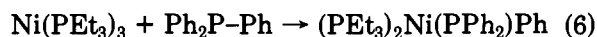
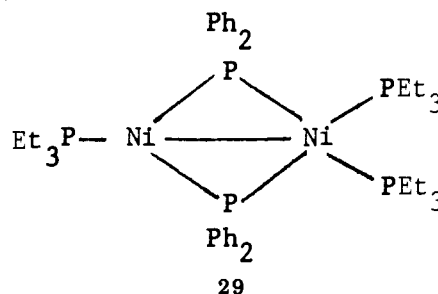
tolyolphosphine complex, $\text{NiCl}(\text{Ph})[\text{P}(p\text{-MeC}_6\text{H}_4)_3]_2$, also gave three diaryls confirming aryl transfer from phosphine to nickel had taken place. They proposed that the biaryl formation was not due to the coupling of aryl

free radicals since no abstraction of hydrogen from the solvent was observed for $\text{NiCl}(\alpha\text{-naphthyl})(\text{PPh}_3)_2$ and no radical polymerization occurred during the thermal reaction in the presence of acrylonitrile or methyl acrylate. They proposed eq 3-5 as the sequence of reactions that were responsible for the initial production of biaryl.³⁵ They then envisioned Ni(I) attack on a



P-aryl bond to give Ni(II)RX phosphido species which could undergo reactions similar to eq 3-5 to produce biaryl derived from the phosphine ligand. The fact that mixed species were observed indicated that the reactions were occurring simultaneously. The importance of Ni(I) species was supported by the lack of biaryl formation during thermolysis of $\text{NiX}_2(\text{PPh}_3)_2$ or $\text{Ni}(\text{PPh}_3)_4$ while biaryl was observed during the thermolysis of $\text{NiX}(\text{PPh}_3)_3$.

In a similar study Fahey and Mahan³⁷ observed that when $\text{Ni}(\text{PEt}_3)_3\text{PPh}_3$ was heated in hydrocarbon solutions $\text{Ni}_2(\text{PPh}_3)_2(\text{PEt}_3)_3$, PEt_3 , and biphenyl were obtained in 77, 115, and 84% yields, respectively. They proposed that the biphenyl resulted from oxidative addition of a P-Ph bond to $\text{Ni}(\text{PEt}_3)_3$ followed by phenyl redistribution. Subsequent biphenyl elimination and reaction with $\text{Ni}(\text{PEt}_3)_2$ would give **29** (eq 6-9). As added evidence for a Ni-Ph intermediate, when the reaction was run in the presence of CO and ROH, $\text{ROC}(\text{O})\text{Ph}$ was observed.



Thermolysis of the aryl complexes *cis*- $\text{PtAr}_2(\text{PAR}'_3)_2$ showed that more than 1 equiv of biaryl was produced in addition to benzene.³⁸ A comparative study of $\text{Pt}(p\text{-MeC}_6\text{H}_4)_2(\text{PPh}_3)_2$ and $\text{PtPh}_2[\text{P}(p\text{-MeC}_6\text{H}_4)_3]_2$ showed that the aryl groups originally bonded to the platinum were eliminated quantitatively as biaryl and the extra biaryl and arene were derived from the ligands. These results are in contrast to the previously discussed Ni results where aryl mixing was shown to occur. Once again, however, arene and biaryl were produced via insertion of Pt into an aryl-P bond.

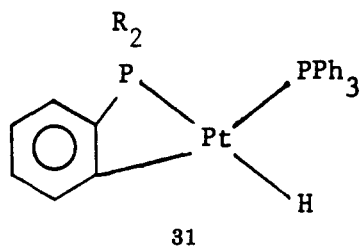
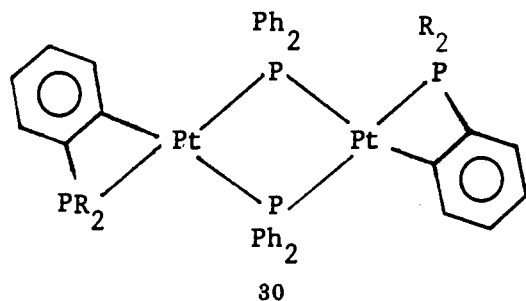
PtPh_2dppm ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) undergoes thermolysis in the presence of excess dppm at 125 °C to give, among other products, PPh_2Me .³⁹ PtPh_2dppe

(dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) undergoes thermolysis at 215 °C to give, among other products, $\text{PPh}_2(\text{vinyl})$. The appearance of both of these PR_3 cleavage products was explained by metal insertion into a $\text{CH}_2\text{-P}$ bond followed in the latter case by β -elimination and in the former case by reductive elimination of Ph_2PCH_2 and H to give PPh_2Me .

Examination of the thermolysis (300 °C) products of complexes of the type $\text{PdCl}(\text{X})\text{L}_2$ ($\text{X} = \text{CH}_2\text{CN}$ or $\text{HC}=\text{CHCN}$; $\text{L}_2 = 2\text{PPh}_3$ or $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) revealed products such as PhCl , PhCH_2CN , and PhPh that could only have come from cleavage of phenyl from a tertiary phosphine during thermolysis.⁴⁰

While studying the reductive elimination of ethane from $\text{Pd}(\text{Me})_2(\text{PPh}_2\text{CD}_3)_2$ Stille et al.⁴¹ observed ethane- d_3 and ethane- d_6 indicating the phosphorus methyl groups become involved in the reaction. They proposed a catalytic oxidative addition of a phosphorus-methyl bond to a $\text{Pd}(0)$ species generated by elimination of ethane- d_0 .

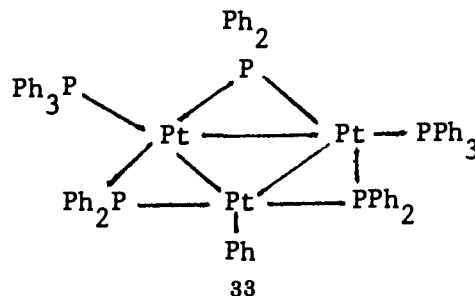
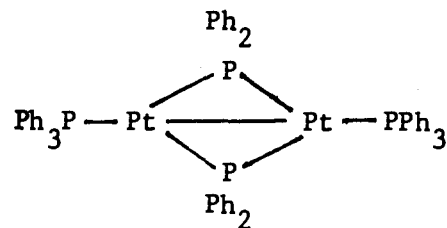
Passing N_2 through an o-xylene solution of $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ at 25 °C over 24 h resulted in loss of ethylene and benzene, with a 50% conversion into a species formulated as **30**.⁴² It was concluded that the



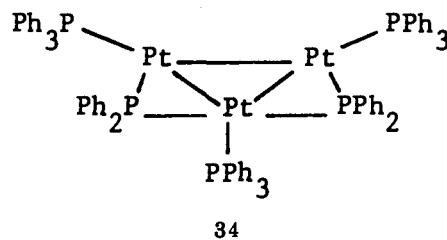
elimination of ethylene was followed by ortho metalation to give the hydride intermediate **31** which would give **30** by elimination of benzene. The mechanism of benzene elimination was not discussed.

Upon heating $\text{Pt}(\text{PPh}_3)_4$ in benzene for several days under argon, a deep red solution resulted from which two crystalline complexes, **32** and **33** were obtained.⁴³ **32** consists of a binuclear molecule with a strong metal-metal bond, two bridging diphenylphosphido groups, and two terminal PPh_3 ligands. The structure of **33** is based on an open Pt_3 cluster with two Pt-Pt bonds and three bridging phosphido groups. The unique Pt atom is coordinated to two phosphido groups and a σ -bonded phenyl group. This is one of the earliest structures where the aryl remnant of a P-C cleavage remains coordinated to the metal.

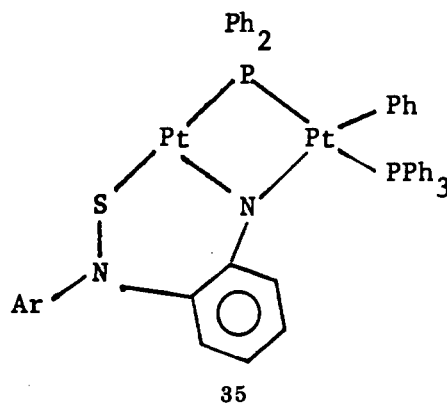
While studying the photochemical reactivity of oxalato bis(triphenylphosphine)platinum(II) Blake and Nyman⁴⁴ observed the evolution of 0.3 mol of benzene per mole of complex. No biphenyl was detected. In a similar fashion the complex $\text{Pt}_3(\text{PPh}_3)_3(\mu\text{-PPh}_2)_2(\mu\text{-H})^+$



BF_4^- , **34**, was prepared by UV irradiation of $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{O}_4)$ under H_2 , followed by precipitation by NaBF_4 .⁴⁵

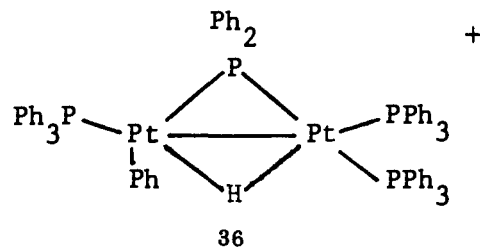


Vrieze and co-workers⁴⁶ isolated **35** from the reaction of $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ and 5,6-dimethyl-2,1,3-benzothiadiazole in refluxing ethyl ether. The crystal



structural determination clearly reveals a Pt has inserted into one of the $\text{N}=\text{S}$ bonds and the two Pt atoms are bridged by a diphenylphosphido group which has formed by insertion of the other Pt atom into a P-phenyl bond.

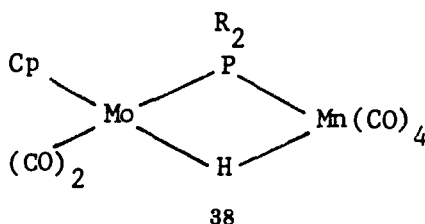
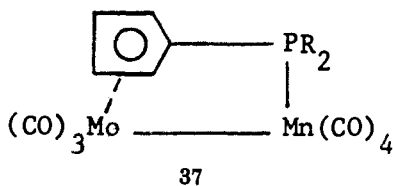
The cation **36** was obtained from the reaction of $\text{Pt}(1,5\text{-C}_8\text{H}_{12})_2$, $\text{trans-PtPh}(\text{MeCOMe})(\text{PPh}_3)_2^+$, PPh_3 , and H_2 .⁴⁷ The question of whether the phenyl group



bonded to the Pt originated from the initial Pt-Ph cation or from cleavage of PPh_3 was resolved by substituting *trans*-Pt(*p*-MeC₆H₄)(MeCOMe)(PPh₃)₂⁺ in the reaction. Since 36 was still the product it was concluded that the σ -bonded phenyl group came from cleavage of PPh₃.

D. Others

Casey and co-workers⁴⁸ have recently reported that photolysis of 37 under an atmosphere of H₂ for 4 days led to the isolation of 38. The low-temperature ¹H



NMR spectrum of 38 established the presence of a Cp ligand, of nonequivalent *p*-tolyl groups on phosphorus, and of a bridging metal hydride. They concluded that the use of such C₅H₄P(*p*-MeC₆H₄)₂ ligands in catalysis would be limited if such P-Cp cleavage was found to be facile.

III. Phosphorus-Carbon Bond Cleavage Observed during Catalytic Reactions

A. Hydroformylation

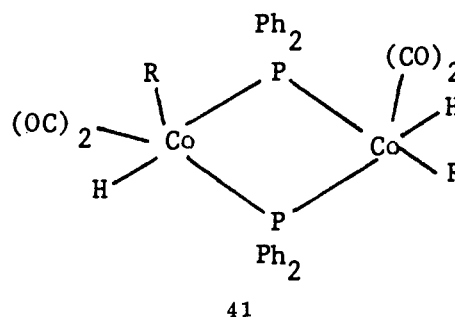
Hydroformylation, discovered by Roelen in 1938, continues to be one of the most industrially important and most extensively investigated homogeneously catalyzed reactions. In order to stabilize the Co₂(CO)₈ catalyst, ligand "modifiers" are added. In the 1960s Slauch and Mullineaux⁴⁹ pioneered the use of tertiary phosphines as catalyst modifiers. Such phosphine-modified systems have a number of properties that have led to their industrial application in the Shell process to produce "higher" alcohols. The addition of PR₃ to the cobalt systems (a) increases the linearity of the product; (b) increases the hydrogenating power of the catalyst system resulting in high selectivity to alcohol products; (c) stabilizes the catalyst system allowing lower partial pressures of CO to be used; (d) requires reaction temperatures of 180–200 °C.^{50,51}

In a similar fashion the discovery by Wilkinson⁵² that phosphine-modified rhodium catalysts hydroformylate olefins at room temperature and atmospheric pressure led to the commercial Johnson Mathey/Union Carbide/Davy McKee process for the hydroformylation of propylene.⁵³ While there is an enormous volume of literature available on both Co- and Rh-based hydroformylation processes, such studies have failed to detail the stability of tertiary phosphines under reaction conditions.⁵⁴

Although Chini⁵⁶ first noted in 1972 that arene or alkane were produced during Rh₄(CO)₁₂/PR₃ catalyzed hydroformylation, this observation lay dormant for more than 10 years. This industrially significant reaction has recently come under close scrutiny by a number of research groups around the world and phosphorus-carbon bond cleavage has been identified as a catalyst deactivation mode for both the Co and Rh systems.

Phosphorus-carbon bond cleavage was identified⁵⁷ as a mode of catalyst deactivation during a study of 1-hexene hydroformylation catalyzed by triarylphosphine substituted cobalt carbonyl species, Co₂(CO)₈/PR₃, where the PR₃ ligands examined were triphenylphosphine, tri-*p*-tolylphosphine, and tribenzylphosphine. GC analysis of the above catalyst reaction mixtures revealed a release of benzene or toluene. For R = Ph in the presence of 1-hexene substrate (a working catalyst), 0.93 mol of benzene is produced per mole of Co after 8 days. For R = CH₂Ph, in the absence of substrate, 0.89 mol of toluene is produced per mol of Co after 36 h of reaction. If the reactions are carried out without 1-hexene substrate, diarylphosphine, R₂PH (R = Ph, *p*-MeC₆H₄, CH₂Ph), is detected by ³¹P NMR. When substrate 1-hexene is present R₂P(hexyl) is observed by ³¹P NMR.

This is consistent with the observations of Geoffroy and co-workers⁵⁸ who found that Co₂(μ-PPh₂)₂(CO)₆, 39, reacts with 1-hexene under synthesis gas to give Co₂(CO)₆(PPh₂hexyl)₂, 40. This reaction could occur via an intermediate such as 41b, which would eliminate PPh₂hexyl to give HCo(CO)₃(PPh₂hexyl). Removal of the CO/H₂ pressure from the solution of HCo(CO)₃(PPh₂hexyl) would result in dimerization to give 40, the observed product.



During hydroformylation with Co₂(CO)₈/PR₃ it is proposed that the reverse sequence of reactions occurs. Scheme I was offered as a plausible mechanism for catalytic formation of arene (R = Ph) and PPh₂hexyl (R' = C₆H₁₃). PPh₃ could oxidatively add to an unsaturated Co-H to give an intermediate such as 41a (R = Ph). This could eliminate benzene to give 39. In the absence of olefin an intermediate such as 39 (R = Ph) could add H₂ to give a species such as 41a (R = Ph) which would eliminate HCo(CO)₃(PPh₂H) which, under syn gas in the presence of excess PR₃ would exchange phosphine and lead to the observation of free PPh₂H in solution. Insertion of CO into the Co-CH₂CH₂R' bond of 41b would lead to the elimination of CH(O)-CH₂CH₂R' (hydroformylation). Insertion of CO into the Co-Ph bond of 41a would lead to the elimination of benzaldehyde, and under reaction conditions subsequent reduction to benzyl alcohol. Indeed, PhCH₂OH, PhCH₃, and traces of biphenyl and PhCH₂CH₂OH were

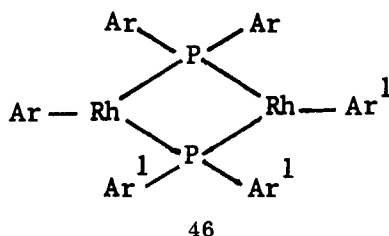
TABLE VI. Relative Rates of Aryl-Group Exchange between PPh₃ and P(*p*-MeC₆H₄)₃ Catalyzed by Group 8–10^a Transition Metals

complex	PR ₃ , M	temp, °C	rel rate	atm
Pd(PPh ₃) ₄	20	170	1	<i>b</i>
Ni(CO) ₂ (PPh ₃) ₂	20	170	1.7	<i>b</i>
Rh ₆ (CO) ₁₆	20	170	2.6	<i>b</i>
Ru ₃ (CO) ₁₂	20	170	19.	<i>b</i>
Os ₃ (CO) ₁₂	20	130	4.8	<i>b</i>
Co ₂ (CO) ₈	20	130	65.3	<i>b</i>
RhCl(CO)(PPh ₃) ₂	10	120	1	<i>c</i>
RhCl(PPh ₃) ₃	10	120	7.7	<i>c</i>
Rh(acac)(CO)PPh ₃	10	120	24.7	<i>c</i>
Rh ₈ (CO) ₁₆	10	120	tr	<i>c</i>

^aIn this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III→3 and 13.) ^bH₂/C₃H₆ (1:1). ^cH₂.

°C while oxygenate production remained fairly constant. No C₄ hydrocarbons, C₅ alcohols, or C₅ aldehydes were observed when P(*n*-Bu)₃ was studied under similar conditions.

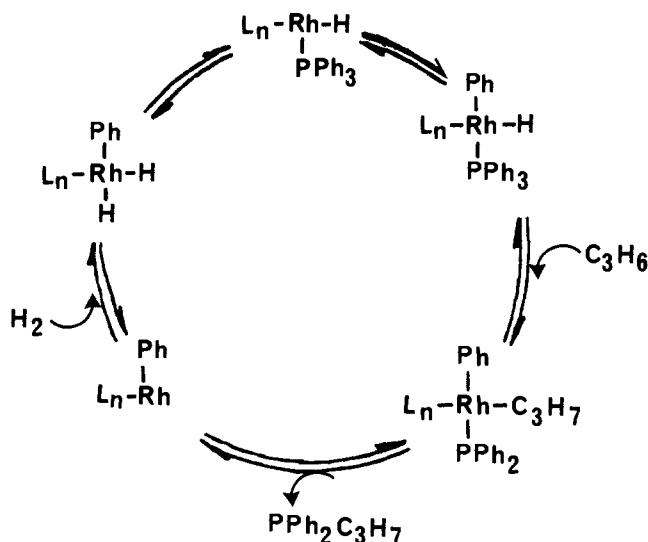
Gregario et al.⁶⁰ recently reported that PPh₃ is slowly converted to PPh₂Pr during rhodium-catalyzed propylene hydroformylation. Union Carbide workers^{61,62} in similar studies observed the facile interchange of aryl groups between different triarylphosphines and alkyl-arylphosphines (eq 11). The relative rates for the catalysis of eq 11 by a variety of transition-metal complexes is given in Table VI. They proposed the intermediacy of a species such as 46 which could eliminate in either of two directions resulting in scrambling of the R groups on phosphorus. Rates varied depending on



the source of rhodium. The scrambling occurred under atmospheres of propylene, hydrogen, or nitrogen. For reaction 11, catalyzed by RhH(CO)(PPh₃)₃ the rate (half-lives) varied with atmosphere as follows: C₃H₆ (3 h), H₂ (4 h), N₂ (18 h). In every instance the solutions turned dark brown indicative of rhodium clustering.²⁷

They found that the conversion of PPh₃ to PPh₂Pr, which is very slow during normal low-pressure rhodium-catalyzed hydroformylation, is greatly accelerated under higher H₂ partial pressures (CO-starved reactions). Benzene was observed in equimolar ratio to PPh₂Pr. As the concentration of PPh₂Pr increased it was slowly converted to PPhPr₂ and further benzene. PPh₃ was shown to inhibit the decomposition reaction.⁶³ Higher propylene concentrations promoted PPh₂Pr formation. Scheme III was proposed to account for all of these observations.

Longoni and co-workers in Milano⁶⁵ reported that kinetics on cyclohexene hydroformylation catalyzed by

SCHEME III. Suggested Mechanism for PPh₃ Cleavage in the Presence of Rh, Propylene, and Hydrogen

the bimetallic Rh/Co PPh₃-substituted carbonyl clusters were impossible to derive because of ligand degradation reactions. In the case of Rh₄(CO)₁₂/PPh₃ catalyst, benzene and benzaldehyde were observed accounting for 30–40% of the available phenyl groups in 30–40 h. Trace amounts of phenol were observed when P(OPh)₃ was used as ligand.

B. Hydrogenation and Dehydrogenation

While studying alkyl group scrambling on primary and secondary amines catalyzed by RuCl₂(PR₃)₃, aryl cleavage was identified as the mode of catalyst deactivation.⁶⁶ At 180–200 °C the RuCl₂(PPh₃)₃-catalyzed reaction revealed an initial first-order dependence on catalyst and amine concentration. As the reaction proceeded, however, extensive catalyst decomposition was observed and thus a tailing off of the reaction rate. Approximately 1 mol of benzene per mole of PPh₃ decomposition was observed at the end of the reaction. A RuCl₃/PBU₃ catalyst system appeared to be much more stable for the amine dehydrogenation–imine hydrogenation sequence identified as the mechanistic pathway.

Recently Crabtree and co-workers⁶⁷ reported that during the dehydrogenation of cyclohexane to benzene, catalyzed by IrH₂[P(*p*-FC₆H₄)₃]₂(Me₂CO)⁺PF₆⁻, 0.8 mol of fluorobenzene per mole of iridium was formed. They concluded that phosphorus–carbon bond cleavage precluded such systems from being catalytically viable. Studies have also been conducted on the catalytic dehydrogenation of cyclooctane to cyclooctene by Ir and Ru polyhydrides.⁶⁸ The best results reported were only 45–70 catalytic turnovers. Phosphorus–carbon bond cleavage was noted to be a mode of catalyst deactivation, although not the only one.⁶⁹ It is probably that the reports of the yellow catalyst solutions turning brown by the end of the reactions,⁶⁶ are related to the earlier observations by Pruett.²⁷

C. Others

The reaction of syn gas and pyridine in the presence of [Co(CO)₃(PPh₃)₂]₂ at 212 °C/1750 psig led to the formation of *N*-formylpiperidine, *N*-methylpiperidine,

N-ethylpiperidine, and higher homologues.⁷⁰ In addition, benzene and toluene were observed indicating P-C cleavage of the PPh₃ ligand. For PR₃ = P(*p*-MeC₆H₄)₃ they observed 37% toluene, 1% *p*-tolualdehyde, 3% *p*-methylbenzyl alcohol, and 6% xylene.

During an investigation of the reduction of substituted bromobenzenes to arenes catalyzed by Pd(PPh₃)₄, Helquist⁷¹ observed 10% yields of benzene which could not have come from the starting aryl halide. Thus, during the reduction of 2-bromotoluene 17% of the P-Ph bonds were cleaved during the 6-h reaction time.

Reaction of Pd(OAc)₂ with PR₃ (R = *p*-XC₆H₄) in a 1:2 molar ratio, at 100 °C for 5 h, resulted in the formation of 60% 4,4'-disubstituted biphenyl, 18% benzene, and 5% phenyl acetate.⁷² When equimolar mixtures of two tertiary phosphines having different substituents such as *p*-OMe vs. *p*-Cl were reacted in the same fashion, the formation of biaryls having electron-withdrawing substituents was shown to be more facile, pointing towards a nucleophilic character to the overall P-C cleavage reaction. However, preliminary experiments with spin-trapping agents pointed towards a radical mechanism rather than a bimolecular mechanism for the formation of biaryl from the presumed aryl-palladium intermediate.

In a similar fashion, when PdCl₂(PPh₃)₂ was heated to 180–200 °C in toluene under an atmosphere of CO₂ a 15–40% yield of benzoic acid was obtained.⁷³ It was proposed that the benzoic acid formed via CO₂ insertion into a Pd-Ph intermediate.

Mixtures of Ar₃P and Ar'₃P in the presence of catalytic amounts of Pd(II) at 100 °C revealed both scrambling of aryl units to give ArAr'₂P and Ar₂Ar'P and bond scission to give Ar₂, Ar'Ar, Ar'₂, ArH, and Ar'H.⁷⁴

D. Reactions in Which Phosphorus-Carbon Bond Cleavage May Be Involved

A reaction closely related to hydroformylation is the homologation of methanol to ethanol and higher alcohols.⁷⁵ Among the many catalyst systems patented for this reaction are several modifications of the system Co₂(CO)₈ + PR₃ + an iodide source. These reactions are run between 175 and 200 °C. Keister⁷⁶ has shown that tertiary phosphines are unstable under such reaction conditions in the related ruthenium carbonyl catalyzed methyl formate homologation. It is likely that Co/PR₃ methanol homologation catalysts are equally as unstable although stability studies have not been reported.

An area where phosphorus-carbon bond cleavage would be intolerable would be in asymmetric synthesis. Over the last decade work in this field has increased enormously and numerous comprehensive reviews have been published.⁷⁷ Spectacular success has been achieved in the hydrogenation of enamide precursors to amino acids using modifications of Wilkinson's famous RhCl(PPh₃)₃ hydrogenation catalyst at relatively mild temperatures and pressures. When chiral chelating phosphines are used optical purity as high as 95% are reported. It would be fair to say that attempts to induce optical activity in other catalytic reactions have been less successful. There are hints that catalyst stability is a, if not the, major problem. Solodar^{77c} has pointed out that a practical temperature limit of 85–90 °C is imposed during the asymmetric hydrogenation of

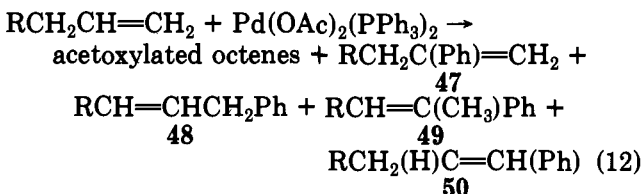
ketones by [Rh(diolefin)L₂]⁺ because catalyst decomposition is observed at higher temperatures. It is clear from his data that higher temperatures result in catalyst deactivation and lower optical purity in the products.

Since the site of asymmetry almost always resides on the tertiary phosphine one must worry about R group scrambling and P-C bond cleavage which is catalyzed by quite a variety of transition-metal complexes. Also, attention should be paid to the ancillary ligands on the metal since the source of metal (Rh) can have a pronounced effect on the rate of PR₃ redistribution (Table VI). Future workers in this field should keep these points in mind and be wary of any decreases in catalyst activity and or product optical purity with time.

The number of transition-metal/tertiary-phosphine catalyzed reactions that might exhibit P-C bond cleavage as a mode of catalyst deactivation is formidable. Examination of the literature reveals that most researchers have been unconcerned with catalyst lifetime in the industrial sense. They generally add 1–5 mol % catalyst and are unconcerned with the fate of the catalyst after the reaction. For example, the following are transformations that RuCl₂(PPh₃)₃ has been shown to catalyze (the temperatures at which the reactions were conducted are in parentheses): *N*-alkylation of amides with alcohols (180 °C),⁷⁸ secondary amine from alcohols and primary amines (180 °C),⁷⁹ rearrangement of diallyl ethers (200 °C),⁸⁰ transfer hydrogenation of α,β-unsaturated carbinols (200 °C),^{81,82} and dehydrogenation of carbinols (186 °C).⁸³ None of these studies have reported phosphine decomposition, yet all involve dehydrogenation/hydrogenation reactions and all are conducted at >180 °C. By analogy with the aforementioned studies on primary to secondary amine transformation⁶⁶ one could expect similar catalyst decomposition would be found if catalyst lifetime studies were conducted.

IV. Tertiary Phosphines as the Source of Aryl or Alkyl Groups in Synthetic Applications

The reaction of styrene, triphenylphosphine, and palladium acetate in acetic acid/dioxane produced *trans*-stilbene in 64% yield.⁸⁴ The reaction of tri-*p*-tolylphosphine with styrene produced a 41% yield of *trans*-*p*-methylstilbene. Kikukawa and co-workers^{85,86} have carried out extensive studies on the arylation and alkylation of olefins by tertiary phosphine/metal complexes. The reaction of 1-octene and Pd(OAc)₂(PPh₃)₂ in acetic acid resulted in the products shown in eq 12 in a 47/48/49/50 ratio of 9/39/12/40. When *p*-

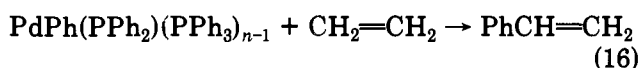
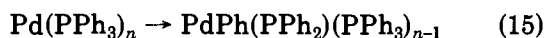
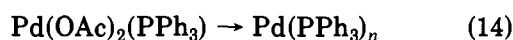


tolylphosphine was reacted in the place of triphenylphosphine, the arylation proceeded to give *p*-tolyl analogues. It was therefore concluded that the reaction proceeded in two phases; cleavage of the aryl-phosphorus bond to give a palladium-aryl intermediate followed by palladation of the olefin to give the observed products. Similar reactions were examined for

styrene, vinyl acetate, ethyl acrylate, and acrylonitrile. Reaction of $P(n\text{-Bu})_3$ or $P(n\text{-octyl})_3$ resulted in the observation of considerable butene or octene.⁸⁷ The observation of olefin was explained by cleavage of the phosphorus-alkyl bond to give a palladium-alkyl intermediate which subsequently decomposes to olefin and palladium hydride. Increasing the PR_3/Pd ratio depressed both the rate and yield of phenylation. $NiCl_2(PPh_3)_2$, $CoCl_2(PPh_3)_2$, and $PdCl_2(PPh_3)_2$ reacted with *p*-tolyllithium or *p*-tolylmagnesium bromide at room temperature to give biphenyl, 4-methylbiphenyl, tri-*p*-tolylphosphine, di-*p*-tolylphenylphosphine, and *p*-tolylidiphenylphosphine, indicating that the aryl-phosphorus bond was cleaved and re-formed under the influence of the transition metal.⁸⁸ In similar fashion *trans*-bis(triethylphosphine)mesitylnickel(II)bromide, *trans*-bis(triethylphosphine)dimesitylnickel, and *trans*-bis(triethylphosphine)dimesitylcobalt were reacted together at 30 °C to give, among other products, 2,4,6-trimethylstyrene which presumably resulted via ethyl transfer from phosphorus to metal.

Green, Felkin, and co-workers⁸⁹ similarly examined the reaction of $NiCl_2(PPh_3)_2$ with $MeMgBr$ and found detectable amounts of benzene, toluene, biphenyl, PPh_2Me , and $PPhMe_2$ in less than 15 min. They proposed the intermediacy of a "phosphorane" and metal-mediated R group scrambling.

The importance of the PR_3/Pd ratio, the reaction atmosphere, and the presence of ethanol on the Pd(II)-catalyzed phosphorus-carbon cleavage were also studied.⁹⁰ Ryabov and Yatsimirsky⁹¹ proposed that $Pd(OAc)_2$ is first reduced to a Pd(0) followed by oxidative addition of a P-Ph bond as shown in eq 13-16.



V. Relevance of Phosphorus-Carbon Bond Cleavage to Polymer-Immobilized Catalyst Systems

During the past decade it has been envisaged that homogeneous catalysts would replace many, if not all, of their heterogeneous (bulk metal or metal oxide) counterparts since homogeneous catalysts exhibit high activity (theoretically one active site per metal atom) and high degrees of selectivity vs. their heterogeneous counterparts. To the contrary, however, although receiving a great deal of attention, homogeneous catalysts have found only limited industrial use chiefly due to the difficulty of their separation from reaction products.

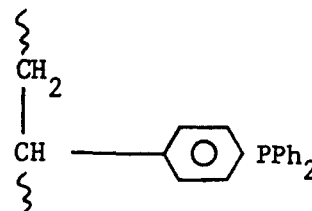
Attachment of transition-metal complexes, either covalently or ionically, to organic polymers has been investigated as a means of forming heterogenized transition-metal catalysts that are as active and selective as their homogeneous counterparts while having the additional quality of being easily separable.⁹² Needed polymer characteristics include such physical properties as attrition resistance, porosity, and thermal stability. In addition it has been assumed that the bond that links the catalyst to the polymer support is chemically stable

under reaction conditions in order to minimize catalyst loss under commercial operating conditions. In industrial chemical processing, the stability of a catalyst is often more important than the activity or selectivity. The literature contains little information in this regard since long lifetime studies are needed to properly evaluate catalysts and such industrial data usually remain proprietary. Because of its dominant role in numerous catalytic reactions,^{93,94} trivalent phosphorus has been the ligand link by which metals have been covalently bonded to a variety of organic polymers.^{92,95} For catalytic reactions examined at relatively low temperatures, macroreticular, high surface area, cross-linked phosphinated polystyrene has been the predominant support due both to its commercial availability,⁹⁶ in various bead sizes with varying degrees of cross-linking, and to the ease with which it can be prepared in the academic laboratory.⁹⁵

Although such phosphinated polystyrene resins have been examined in numerous catalytic reactions^{92,95} many researchers⁹⁷⁻¹⁰⁰ have noted that the polystyrene beads are inherently mechanically and thermally unstable. It is known that macroporous styrene-divinylbenzene resins will slough off polymer, particularly in solvents that swell the beads. Furthermore, numerous catalytic reactions require temperatures at or above the ceiling temperature of polystyrene ($T_c = 150$ °C).

A reaction of considerable industrial significance is the $Co_2(CO)_8/PR_3$ catalyzed hydroformylation reaction, especially as it pertains to the production of alcohols from olefins⁴⁹⁻⁵¹ where typical reaction temperatures are 180-200 °C. Although it appears obvious that a phosphinated polystyrene catalyst system cannot withstand such reaction temperatures, several patents and literature articles have none the less expounded on the merits of such supports for heterogenized $Co_2(CO)_8/PR_3$ catalysis.¹⁰¹⁻¹⁰³ Although researchers have worried about metal-phosphine dissociation resulting in loss of metal under industrial flow conditions, none have concerned themselves with cleavage of the ligating groups under reaction conditions. Such a situation would obviously be intolerable!

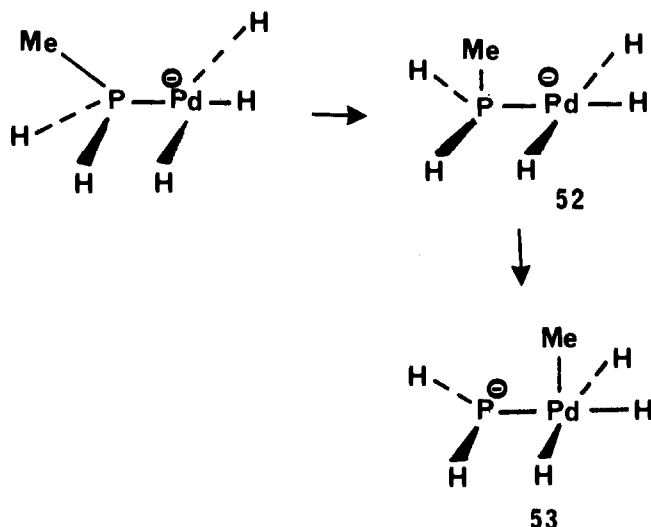
Phosphorus-carbon bond cleavage was in fact identified as a major mode of catalyst deactivation during a study of 1-hexene hydroformylation catalyzed by $Co_2(CO)_8/PR_3$ catalyst systems where the PR_3 ligands examined included diphenylphosphine-functionalized polystyrene, 51.^{57a,c} It was found that Co catalysts



51

derived from 51 lost catalytic activity with time due to both loss of Co and loss of tertiary phosphine functionality. A 15-25% loss of P was observed over a period of 28 h. In addition of 0.5 mol of benzene per mole of cobalt was observed after 48 h. Such results clearly raise questions about previous reports detailing the recycling of such immobilized catalysts and point

SCHEME IV. Proposed Mechanism for Alkyl Transfer from Phosphine to Metal



out the need for phosphorus analysis of the effluent streams. It is clear that further work needs to be done with careful examination of the polymer-immobilized supports as a primary goal of the research.

IV. Thermodynamic and Mechanistic Considerations

Mechanistic information on transition-metal-catalyzed $P-C$ bond scission reactions is rather limited and qualitative. It is clear from an overwhelming quantity of stoichiometric and catalytic data for Ni,³⁴ Co,^{22,57a-c,58,70} Rh,^{28,58,62} Pt,³⁸ and Pd^{84,86,87} that $P-C$ bond scission occurs with retention of configuration. Thus, para-substituted products (biaryls, CO insertion products, etc.) are derived from para-substituted arylphosphines. Phosphorus–carbon cleavage reactions do not involve free radicals, at least in the limited number of cases that have been examined (Ni,³⁴ Rh²¹, Co^{57c}). Substituent effects on the rate of $P-C$ bond cleavage (Rh,²¹ Co,^{57c} Pd^{72,86}) reveal bond scission is enhanced by electron-withdrawing substituents such as CF_3 and inhibited by electron-donating substituents such as OMe in the para position. Further mechanistic studies are needed before such qualitative observations can be related to typical bimolecular nucleophilic aromatic displacement reaction mechanisms where it is known that breaking of the bond to the leaving group is involved in the rate determining step.

Hoffmann and co-workers,¹⁰⁴ have examined the theoretical aspects of the shift of an alkyl or aryl group from a coordinated phosphine to a 16-electron d^8 transition metal to which it is coordinated. They examined the model reaction shown in Scheme IV. From their calculations it appears that the first stage consists of a deformation of the tertiary phosphine ligand from a tetrahedral geometry to one in which the $P-CH_3$ bond is perpendicular to the H_2P-PdH_3 plane. The second stage is the linear migration of R from 52 to 53. They calculated a barrier for the reaction of 23 kcal/mol. For the slightly more realistic case of $H_2PMe-Pd(PH_3)(Me)_2$ a barrier of 31 kcal/mol was calculated. For phenyl migration the barrier is reduced to 1.6 kcal/mol when the transfer occurs with the plane of the phenyl ring perpendicular to the $Pd-P$ axis. They conclude that

from a theoretical standpoint, such migrations of R from phosphorus to metal are symmetry allowed and thermodynamically accessible.

Not much is known about the thermodynamic stability of the starting materials or reaction products of such phosphorus–carbon activation processes. Estimation of the thermodynamic stability of the phosphorus–carbon bond comes from the bond dissociation energy of triethylphosphine. Smith and Patrick¹⁰⁵ have recently conducted low-pressure pyrolysis studies on PEt_3 and derived a ΔH_{298} of 68 ± 2 kcal/mol. This can be compared to values of 104, 102, 88, and 84 kcal/mol for typical $H-H$, CH_3-H , CH_3-OH , and CH_3-CH_3 bonds, respectively. It is known that D_{M-CH} is approximately 30 kcal/mol for a variety of metal complexes.¹⁰⁶ It is also known that $D_{M-Ph} > D_{M-CH_3}$ for a variety of metal and metalloid complexes.¹⁰⁷ Further rationalization based on thermodynamic considerations must await the generation of needed bond dissociation data.

VII. Conclusions

It is now apparent that given the proper circumstances, the generally regarded as inert tertiary phosphine ligand may become significantly involved in the reaction chemistry of the compounds of which they are apart. More than 75 organometallic reactions have been described where net addition of the $P-C$ bond to a variety of transition metals, in low oxidation states, at temperatures as low as 25 °C has been observed. The only common criteria appears to be coordinate unsaturation at the moment of addition.

Such $P-C$ activation reactions appear to be a heretofore unreported but none the less common mode of homogeneous catalyst deactivation in hydroformylation (Rh- and Co-catalyzed) and various other hydrogenation/dehydrogenation reactions. Under syn gas CO insertion products are observed, positively identifying R group migration from P to M as the mechanistic route. Although free radicals have been looked for in several instances, evidence for their presence has not been found. All evidence currently points to a $P-C$ "oxidative addition" to the metal. The limited theoretical data that is available concludes that such R group migrations from phosphorus to metal are symmetry allowed and thermodynamically accessible.

It is clear that future research on M/PR_3 catalyst systems should take such observations into account when concluding or predicting long-term catalyst stability and activity. Research is needed in the polymer-immobilized catalyst area where the recycle of such catalysts cannot be taken for granted or concluded from chemical analysis of the catalyst after a few hundred turnovers. Research is also needed in the area of asymmetric synthesis, to define the relevance of such $P-C$ bond cleavage on the use of chiral tertiary phosphines.

While the past two decades of homogeneous catalysis have been mainly concerned with tertiary phosphine ligands, it is possible that we will see a shift in the next decade to as yet unnamed more chemically stable ancillary ligands.¹⁰⁸

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