Chemical Reviews

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

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Contents

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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 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 Trofimenko[1] 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 interchangably. 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 cyclometalation 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 Nyholm[4-6] and later Deeming[7,8] on the reaction of $Os_3(CO)_{12}$ with PPh_3. Reaction of $Os_3(CO)_{12}$ 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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4

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1

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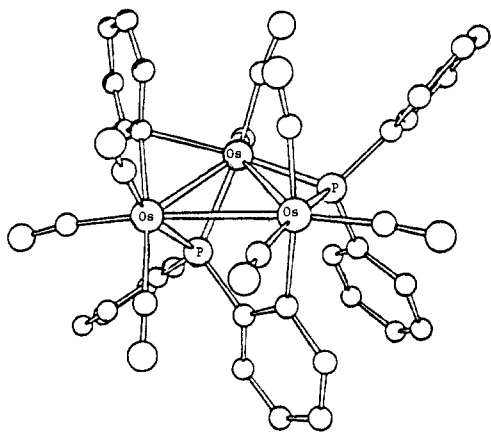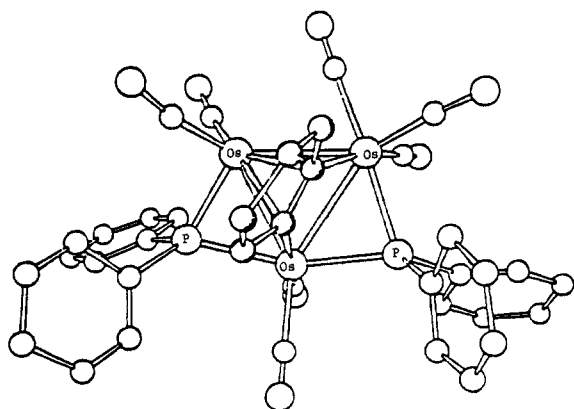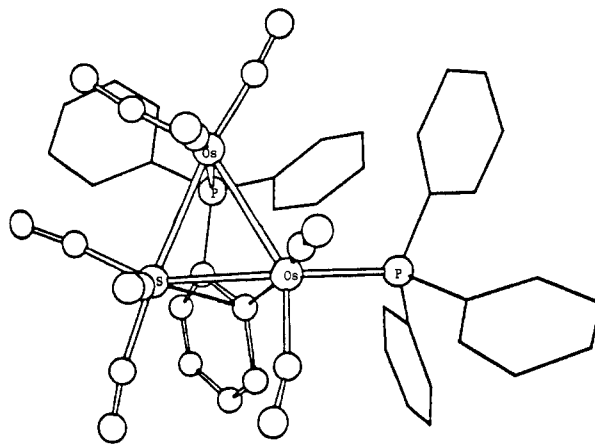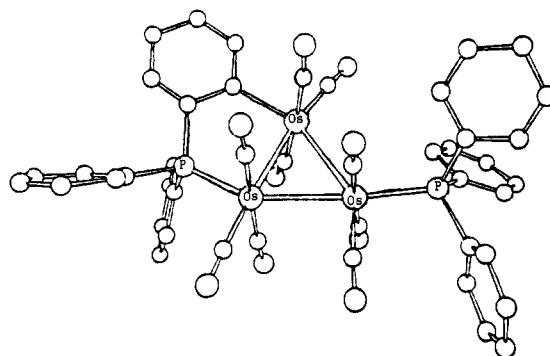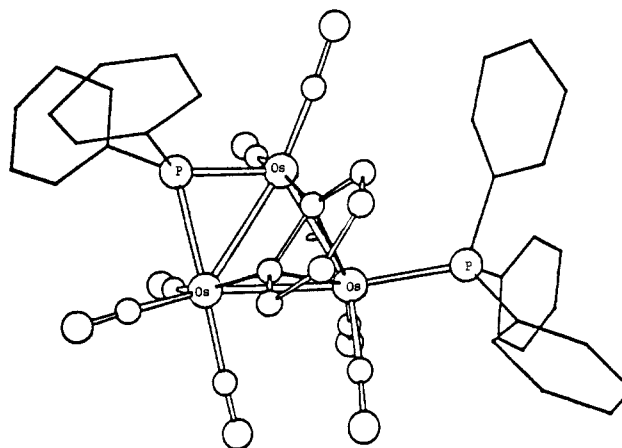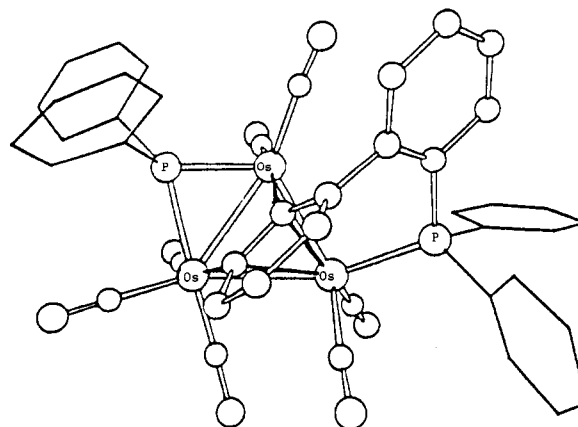
6

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 $Os_3(CO)_{10}(PPh_3)_2$ 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 $Os_3(CO)_{12-x}(PPhMe_2)_x$ in refluxing octane resulted in the isolation of analogues to **2**, **5**, and **6**. When PMe_3 was reacted with $Os_3(CO)_{12}$ 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 $P(alkyl)_3$, phosphorus–alkyl bond cleavage was not.


7a   7b
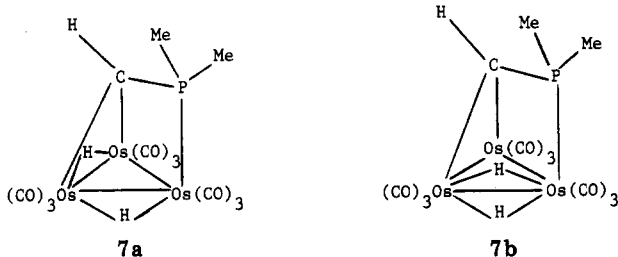
The reaction of $Ru_3(CO)_{12}$ with PR_3 (R = Ph, p-MeC_6H_4, m-MeC_6H_4, $MePh_2$) in refluxing decalin produced **8**, **9**, **10**, and **11**.[9] The structures were assigned

8   9


10   11
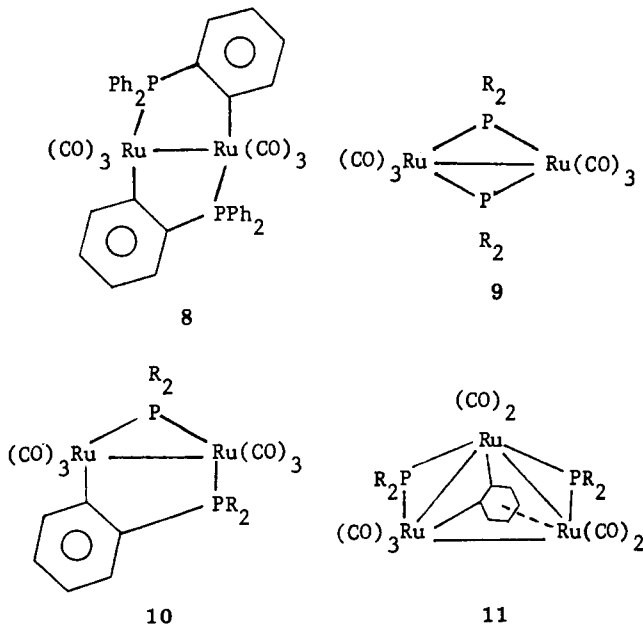
based on IR and NMR data and by analogy to their Os analogues. In contrast to the Os work one observes a preponderance of binuclear ruthenium complexes and no isolable ruthenium hydride species. In similar fashion, C–H activation by a metal not bound to the phosphorus and the bridging phenyl group, achieved via P–Ph cleavage (**2** vs. **11**) appear to be stable structures attained by both systems.

Carty and co-workers[10] have carried out extensive investigations on the reactions of metal clusters with the phosphinoacetylene $PPh_2C\equiv CR$. 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

$$P-C_{sp} > P-C_{sp^2} > P-C_{sp^3}$$
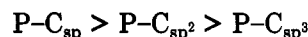
The conditions observed for P–C cleavage during the reaction of such iron-subgroup clusters are shown in Table I. All of the complexes have been structurally characterized by X-ray diffraction. $Fe_2(CO)_6(PPh_2)$-$(C\equiv CPh)$, **12**, revealed the molecular geometry shown.

12
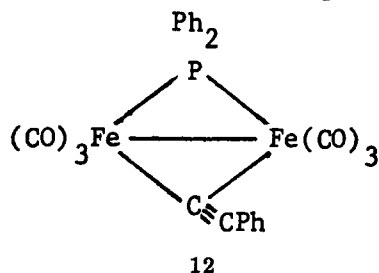
The two $Fe(CO)_3$ fragments are joined by a metal–metal bond, a bridging diphenylphosphido group and a unique acetylide ligand which is σ bonded to one Fe and π bonded to the other.

The reaction of $RuH(NO)(PPh_3)_3$ in refluxing decalin resulted in the formation of **13** in 25% yield.[11]

13

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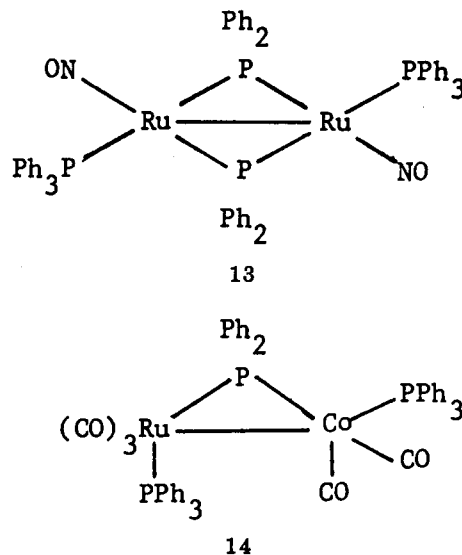
Geoffroy and co-workers[12] examined the reaction of $NaCo(CO)_4$ with $RuHCl(PPh_3)_3(CO)$ at 40 °C (eq 1) and isolated 28% of **14**. **14** was characterized by

$$RuHCl(CO)(PPh_3)_3 + NaCo(CO)_4 \rightarrow$$
$$14 + RuHCl(CO)_2(PPh_3)_2 + Ru(CO)_3(PPh_3)_2 \quad (1)$$
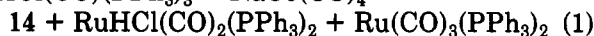
spectroscopic methods and a complete X-ray diffraction study. Benzene was detected in the THF solvent after the reaction implying that the phosphido bridge formed via the reaction of a PPh_3 phenyl group with a hydride initially on Ru.

In a similar fashion reaction of $NaMn(CO)_5$ with $RuCl_2(PPh_3)_3$ produced $Ru(CO)_3(PPh_3)_2$ 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.

15
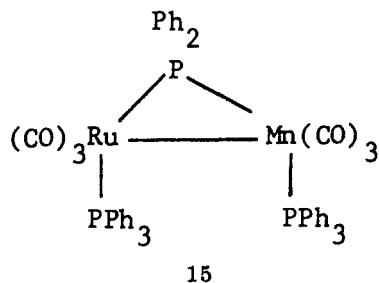
The interaction of RuHCl(PPh₃)₃ with KOH in THF led to a red tetranuclear complex of stoichiometry Rh₄H₄(OH)₂(PPh₂)₂(CO)₂(PPh₃)₆.[14] Spectroscopic data did not allow for stereochemical assignment.

Carty and coworkers[15] observed the facile reduction of μ-PPh₂ groups in Ru₃(CO)₉(μ₃-PPh)(μ₂-H)₂ via an intermediate electron-deficient hydride, 16, which contains a weak P–Ph interaction to a Ru atom. 16

16   17
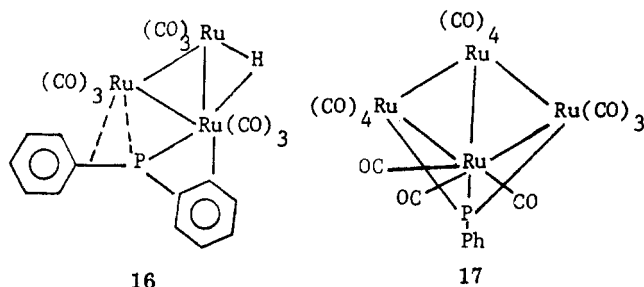
offers a unique view of an intermediate stage in P–C bond activation and cleavage. Reaction of 16 with H₂ at 80 °C resulted in 17 in which a molecule of benzene has been lost and cluster rearrangement has occurred. Carty accurately pointed out that this reactivity of phosphido ligands under reducing conditions would limit their utility in cluster catalysis.

Reaction of the carbonyl anion Fe₄(CO)₁₃²⁻ with strong acids in the presence of diphenylphosphine affords the trinuclear phosphido-bridged cluster Fe₃(μ-H)₂(μ-PPh₂)₂(CO)₈, 18, which was characterized by X-ray diffraction.[16] Reaction of 18 with CO at room temperature yields the complex Fe₃(μ-PPh)₂(CO)₉ via elimination of benzene.

18
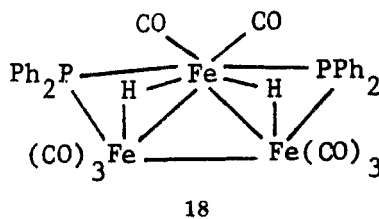
B. Cobalt Subgroup

Two groups[17,18] simultaneously discovered that refluxing IrHCO(PPh₃)₃ in a high-boiling solvent resulted in the separation of purple, diamagnetic crystals of 19.

19
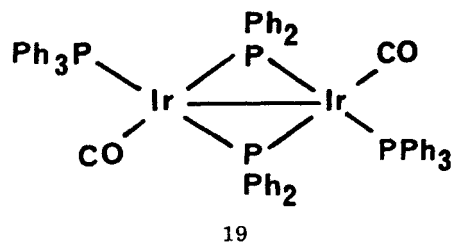
TABLE I. P–C Bond Cleavage during the Reaction of PPh₂(C≡CR) with Iron-Subgroup Clusters

cluster	temp, °C	time, h	product	ref
Fe₃(CO)₁₁(PPh₂C≡CR)	60	2	Fe₂(CO)₆(PPh₂)-(C≡CR)	16a
Ru₃(CO)₁₁(PPh₂C≡CR)	80	8	Ru₂(CO)₆(PPh₂)-(C≡CR)	16a
Os₃(CO)₁₁(PPh₂C≡CR)	203	0.33	Os₂(CO)₆(PPh₂)-(C≡CR)	16a
Ru₃(CO)₉(PPh₂C≡CR)₃	80	1	Ru₃(CO)₆(PPh₂)₂-(C≡CR)-(PPh₂C≡CR)	16b

Interaction of MCp(CO)PPh₃ (M = Rh or Ir) and MnMe(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-

20   21
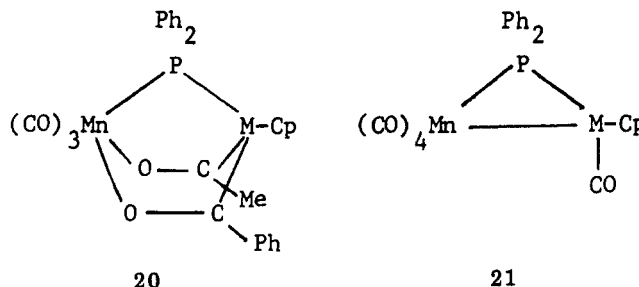
mation of the acetyl and benzoyl groups must involve migration of methyl and phenyl groups from metal to coordinated carbonyls. The presence of a phenyl group on the Rh or Ir was thought to arise from cleavage of coordinated PPh₃ on MCp(CO)PPh₃ to give MCp-(Ph)(PPh₂)(CO). The diphenylphosphide group could then bridge the MnMe(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 MeC(O)Ph. This sequence of reactions is indeed complex. The major point is that the P–aryl bond was cleaved in refluxing toluene.

RhCl(PPh₃)₃ undergoes thermal decomposition above 140 °C in solution or in the solid state to yield biphenyl.[21] It was shown that rhodium compplexes of para-substituted tertiary phosphine ligands form exclusively 4,4'-disubstituted biphenyls. Mixtures of RhCl(PAr₃)₃ and RhCl(PAr'₃)₃ result in cross-coupling products. The mechanism was once again thought to involve oxidative addition of dissociated phosphine to RhCl(PPh₃)₂ to give an intermediate such as 22. Al-

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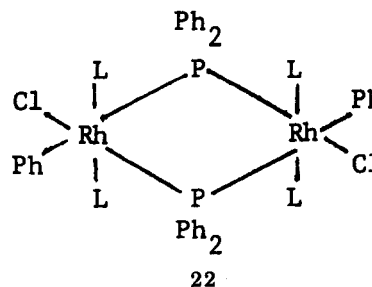
though no phenyl–rhodium complex was isolated, its participation was confirmed by an experiment in which styrene was added as solvent and 1,1-diphenylethylene and trans-stilbene were formed along with biphenyl. No mechanisms were proposed for the biaryl formation;

TABLE II. Benzene Formation vs. Hydrogen-Donating Ability in the Transfer Hydrogenolysis of the PPh₃ Ligands of RhCl(PPh₃)₃

H donor	mol of C_6H_6/mol of RhCl(PPh₃)₃
pyrrolidine	8.0
piperidine	6.9
piperazine	6.2
2-propanol	5.8
n-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 PPh₃ Ligands of RhCl(PPh₃)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] RhCl(PPh₃)₃ (0.05 M) and H donor (0.45 M) at 140 °C for 3 h in the designated solvent.

TABLE IV. Transfer Hydrogenolysis of the PPh₃ Ligands of Various Transition-Metal–PPh₃ Complexes

complex	H donor	mol of C_6H_6/mol of complex
RhH(PPh₃)₄	pyrrolidine	10.4
	2-propanol	11.2
RhCl(PPh₃)₃	pyrrolidine	8.0
	2-propanol	2.8
RuH₂(PPh₃)₄	pyrrolidine	9.6
	2-propanol	10.4
RuCl₂(PPh₃)₃	pyrrolidine	7.8
	2-propanol	0.6
PtCl₂(PPh₃)₂	pyrrolidine	3.0
Pt(PPh₃)₄	pyrrolidine	1.8
PdCl₂(PPh₃)₂	pyrrolidine	2.6

however, one could envision redistribution sequences similar to those observed for Ni.[34,37]

CoMe(PR₃)₃ (R = Ph, 4-MePh, 3-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 PR₃ seems neither to suppress nor to increase the yield of biphenyl, free PR₃ must be involved in the reaction since addition of (4-MePh)₃P to CoMe(PPh₃)₃ resulted in the formation of biphenyl, 4-methylbiphenyl, and 4,4′-dimethylbiphenyl in the ratio of 16:10:2. Crossover experiments of CoMe(PPh₃)₃ with CoMe[(p-MePh)₃P]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-workers[23-25] observed extensive hydrogenolysis of PPh₃ coordinated to transition metals. When RhCl(PPh₃)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 RhCl(PPh₃)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 RhCl(PPh₃)₃ to RhH-(PPh₃)₄, however the similarity between reaction time and benzene yield when RhH(PPh₃)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-

sition-metal–tertiary-phosphine complexes generated the results shown in Table IV. It is clear from these data that in some cases PPh₃ undergoes complete hydrogenolysis to give 3 mol of benzene and presumably PH₃. All of the reactions appeared to be inhibited by the presence of excess phosphine.

Thermal degradation of RhH(CO)(PPh₃)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

23

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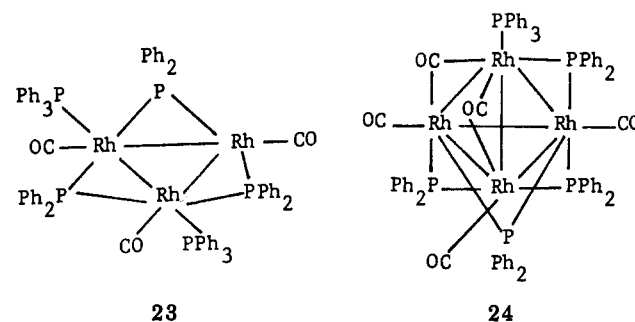
of CO/H₂ 24 was isolated as a brown complex.[27] The potential importance of such species in Rh-catalyzed hydroformylation will be discussed later.

PPh₃ was found to be catalytically degraded by Rh₄(CO)₁₂, Rh₆(CO)₁₆, and/or Rh₁₂(CO)₃₀²⁻ 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 IrCl(CO)₂(CH₃C₆H₄NH₂) with CH(PPh₂)₃ at 90 °C in the presence of Zn and CO produced a low yield of 25.[29]

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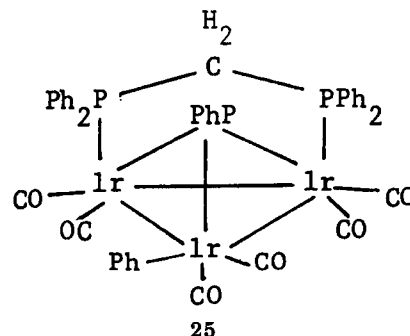
One edge of the Ir triangle is bridged by dppm (bis-(diphenylphosphino)methane) and a phenyl group is σ bonded to the third Ir atom. Thus, the initial tridentate phosphine ligand has undergone P–C bond cleavage followed by protonation of the central carbon atom to give dppm and PPh₂. The PPh₂ moiety 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 $Co_2(CO)_6$dppm with H_2 resulted in the cleavage of the dppm ligand to give phosphido-bridged 26 in 20% yield.

26
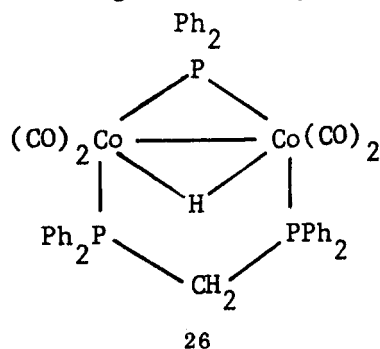
The reaction of $IrCl(PPh_3)_3$ with dibenzoyldiazomethane in refluxing THF resulted in the formation of 27 in which an unusual tridentate ligand was formed by loss of a phenyl group from PPh_3 and condensation of the dibenzoylmethylene moiety with the PPh_2 fragment.[31]

27
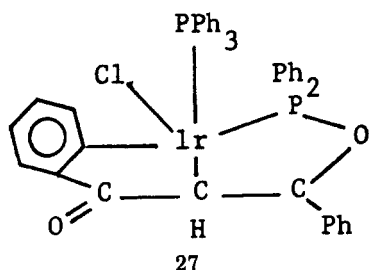
C. Nickel Subgroup

During attempts to prepare $Pd(PPh_3)_2$ from Pd-$(PPh_3)_4$ by the use of $PdCl_2$ as a scavenger of PPh_3, Coulson[32] observed that reaction at 130 °C in Me_2SO produced $trans$-$Pd(Ph)Cl(PPh_3)_2$ and $Pd_3Cl_2(PPh_2)_2$-$(PPh_3)_3$ in addition to the expected $PdCl_2(PPh_3)_2$. The structure was later shown to be $Pd_3Cl_2(PPh_2)_2$-$(PPh_3)_3{}^+Cl^-$, 28.[33]

28
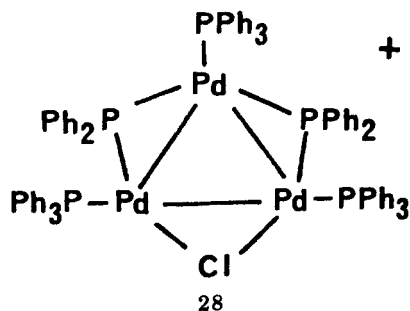
Thermal decomposition of $trans$-$NiBr(Ph)(PPh_3)_2$ in the presence of excess PPh_3 gave biphenyl and NiBr-$(PPh_3)_3$.[34] Unexpectedly, however, meta- or para-substituted aryl–nickel complexes gave three different biaryls as shown in eq 2. The corresponding tri-p-

$$p\text{-}XC_6H_4NiCl(PPh_3)_2 \rightarrow X\text{-}C_6H_4C_6H_4X +$$
$$H\text{-}C_6H_4C_6H_4\text{-}H + H\text{-}C_6H_4C_6H_4\text{-}X \quad (2)$$
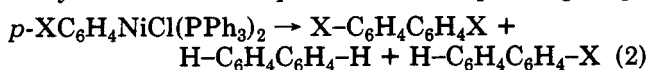
tolylphosphine complex, $NiCl(Ph)[P(p\text{-}MeC_6H_4)_3]_2$, also gave three diaryls confirming aryl transfer from phosphine to nickel had taken place. They proposed that the biaryl formation was not due to the coupling of aryl

free radicals since no abstraction of hydrogen from the solvent was observed for NiCl (α-naphthyl)(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 reponsible for the initial production of biaryl.[35] They then envisioned Ni(I) attack on a

$$NiAr(X)(PPh_3)_2 + NiAr'(X)(PPh_3)_2 \rightarrow$$
$$NiArAr'(PPh_3)_2 + NiX_2(PPh_3)_2 \quad (3)$$

$$NiArAr'(PPh_3)_2 \rightarrow ArAr' + Ni(PPh_3)_2 \quad (4)$$

$$Ni(PPh_3)_2 + NiX_2(PPh_3)_2 + 2PPh_3 \rightarrow 2NiX(PPh_3)_2 \quad (5)$$
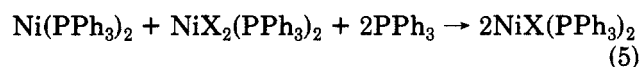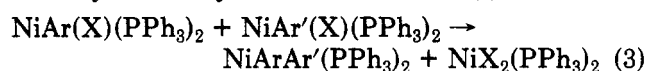
P–aryl bond to give Ni(II)RX phosphido species which could undergo reactions similar to eq 3–5 to produce biaryl derived from the phosphine ligand. The fact that mixed species were observed indicated that the reactions were occurring simultaneously. The importance of Ni(I) species was supported by the lack of biaryl formation during thermolysis of $NiX_2(PPh_3)_2$ or Ni-$(PPh_3)_4$ while biaryl was observed during the thermolysis of $NiX(PPh_3)_3$.

In a similar study Fahey and Mahan[37] observed that when $Ni(PEt_3)_3PPh_3$ was heated in hydrocarbon solutions $Ni_2(PPh_3)_2(PEt_3)_3$, 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 $Ni(PEt_3)_3$ followed by phenyl redistribution. Subsequent biphenyl elimination and reaction with $Ni(PEt_3)_2$ 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, ROC(O)Ph was observed.

29

$$Ni(PEt_3)_3 + Ph_2P\text{-}Ph \rightarrow (PEt_3)_2Ni(PPh_2)Ph \quad (6)$$

$$2(PEt_3)_2Ni(PPh_2)Ph \rightarrow$$
$$NiPh_2(PEt_3)_2 + Ni(PPh_2)_2(PEt_3)_2 \quad (7)$$

$$NiPh_2(PEt_3)_2 \rightarrow Ph_2 + Ni(PEt_3)_2 \quad (8)$$

$$Ni(PEt_3)_2 + Ni(PPh_2)_2(PEt_3)_2 \rightarrow 29 + PEt_3 \quad (9)$$
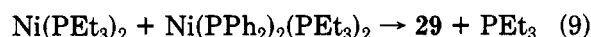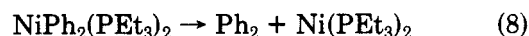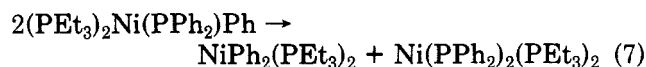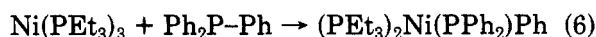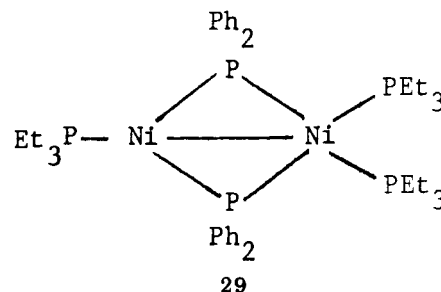
Thermolysis of the aryl complexes cis-$PtAr_2(PAr'_3)_2$ showed that more than 1 equiv of biaryl was produced in addition to benzene.[38] A comparative study of Pt-$(p\text{-}MeC_6H_4)_2(PPh_3)_2$ and $PtPh_2[P(p\text{-}MeC_6H_4)_3]_2$ showed that the aryl groups originally bonded to the platinum were eliminated quantitatively as biaryl and the extra biaryl and arene were derived from the ligands. These results are in constrast 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.

$PtPh_2$dppm (dppm = $Ph_2PCH_2PPh_2$) undergoes thermolysis in the presence of excess dppm at 125 °C to give, among other products, PPh_2Me.[39] $PtPh_2$dppe

(dppe = $Ph_2PCH_2CH_2PPh_2$) undergoes thermolysis at 215 °C to give, among other products, PPh_2(vinyl). The appearance of both of these PR_3 cleavage products was explained by metal insertion into a CH_2–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 $PdCl(X)L_2$ (X = CH_2CN or $HC\!\!=\!\!CHCN$; L_2 = $2PPh_3$ or $Ph_2PCH_2CH_2PPh_2$) 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 $Pd(Me)_2(PPh_2CD_3)_2$ 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 Pd(0) species generated by elimination of ethane-d_0.

Passing N_2 through an o-xylene solution of Pt-$(C_2H_4)(PPh_3)_2$ 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

30

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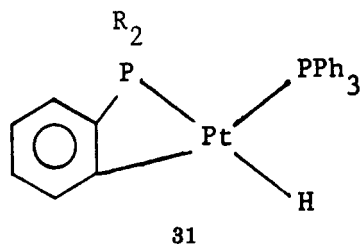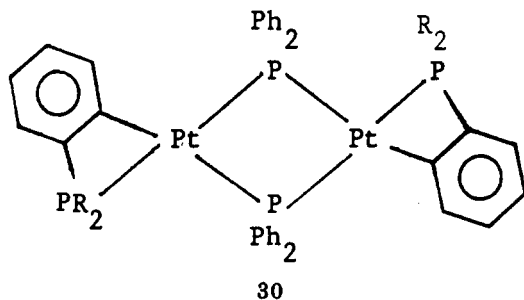
elimination of ethylene was followed by ortho metalation to give the hydride intermediate 31 which would give 30 by elimination of benzene. The mechanism of benzene elimination was not discussed.

Upon heating $Pt(PPh_3)_4$ 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 diphenylphosphide 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 Nyman[44] observed the evolution of 0.3 mol of benzene per mole of complex. No biphenyl was detected. In a similar fashion the complex $Pt_3(PPh_3)_3(\mu\text{-}PPh_2)_2(\mu\text{-}H)^+$

32

33
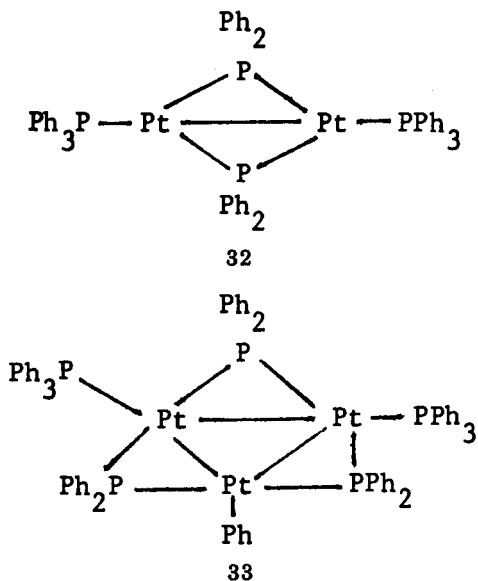
BF_4^-, 34, was prepared by UV irradiation of Pt-$(PPh_3)_2(C_2O_4)$ under H_2, followed by precipitation by $NaBF_4$.[45]

34
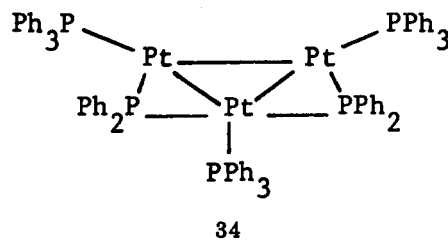
Vrieze and co-workers[46] isolated 35 from the reaction of $Pt(C_2H_4)(PPh_3)_2$ and 5,6-dimethyl-2,1,3-benzothiadiazole in refluxing ethyl ether. The crystal

35
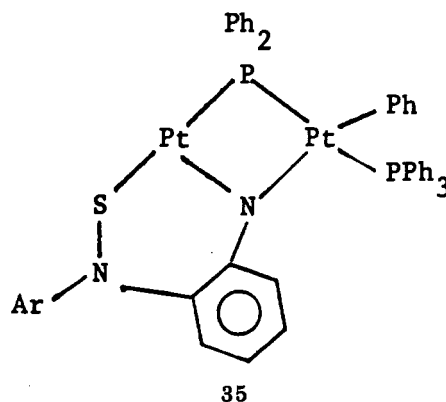
structural determination clearly reveals a Pt has inserted into one of the N=S bonds and the two Pt atoms are bridged by a diphenylphosphido group which has formed by insertion of the other Pt atom into a P–phenyl bond.

The cation 36 was obtained from the reaction of $Pt(1,5\text{-}C_8H_{12})_2$, trans-$PtPh(MeCOMe)(PPh_3)_2^+$, PPh_3, and H_2.[47] The question of whether the phenyl group

36
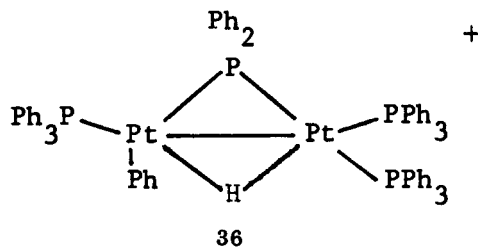
bonded to the Pt originated from the initial Pt–Ph cation or from cleavage of PPh_3 was resolved by substituting trans-Pt(p-MeC$_6$H$_4$)(MeCOMe)(PPh$_3$)$_2$$^+$ in the reaction. Since **36** was still the product it was concluded that the σ-bonded phenyl group came from cleavage of PPh_3.

D. Others

Casey and co-workers[48] have recently reported that photolysis of **37** under an atmosphere of H_2 for 4 days led to the isolation of **38**. The low-temperature ^{1}H

37

38

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 $C_5H_4P(p\text{-}MeC_6H_4)_2$ 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 $Co_2(CO)_8$ catalyst, ligand "modifiers" are added. In the 1960s Slaugh and Mullineaux[49] 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 PR_3 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 Wilkinson[52] 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 Chini[56] first noted in 1972 that arene or alkane were produced during $Rh_4(CO)_{12}/PR_3$ 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 identified[57] as a mode of catalyst deactivation during a study of 1-hexene hydroformylation catalyzed by triarylphosphine substituted cobalt carbonyl species, $Co_2(CO)_8/PR_3$, where the PR_3 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 = CH_2Ph, 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, R_2PH (R = Ph, p-MeC$_6$H$_4$, CH_2Ph), is detected by ^{31}P NMR. When substrate 1-hexene is present $R_2P(hexyl)$ is observed by ^{31}P NMR.

This is consistent with the observations of Geoffroy and co-workers[58] who found that $Co_2(\mu\text{-}PPh_2)_2(CO)_6$, **39**, reacts with 1-hexene under synthesis gas to give $Co_2(CO)_6(PPh_2hexyl)_2$, **40**. This reaction could occur via an intermediate such as **41b**, which would eliminate PPh_2hexyl to give $HCo(CO)_3(PPh_2hexyl)$. Removal of the CO/H_2 pressure from the solution of $HCo(CO)_3(PPh_2hexyl)$ would result in dimerization to give **40**, the observed product.

41

During hydroformylation with $Co_2(CO)_8/PR_3$ 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 PPh_2hexyl (R' = C_4H_9). PPh_3 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 H_2 to give a species such as **41a** (R = Ph) which would eliminate $HCo(CO)_3(PPh_2H)$ which, under syn gas in the presence of excess PR_3 would exchange phosphine and lead to the observation of free PPh_2H in solution. Insertion of CO into the $Co–CH_2CH_2R'$ bond of **41b** would lead to the elimination of $CH(O)$-CH_2CH_2R' (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, $PhCH_2OH$, $PhCH_3$, and traces of biphenyl and $PhCH_2CH_2OH$ were

TABLE V. Product Distribution upon Decomposition of PPh₃ by Rh, Ru, and Co Complexes

phosphine (mmol)	metal (mmol)	conditions			products, mmol				ref
		temp, °C	press, psig	time, h	ArH	ArCHO	ArCH₂OH	other	
PPh₃ (1.0)	Rh (0.2)	200	4410	6	.16	.21			54
	Ru (0.2)	200	4410	6				a	54
	Co (0.2)	200	4410	6	0.06	0.04	0.11	a	54
P(p-MeC₆H₄)₃ (1.0)	Rh (0.2)	200	4410	6	0.07	0.23	0.01		54
	Co (0.2)	200	4410	6		0.01	0.02		54
P(p-ClC₆H₄)₃ (1.0)	Rh (0.2)	200	4410	6	0.12	0.14	0.05		54
	Co (0.2)	200	4410	6	0.03	tr	0.05		54
PPh₃ (6.0)	Co (2.6)	190	2000	16	0.46	tr	0.24		52
P(CH₂Ph)₃ (6.0)	Co (2.6)	190	2000	16	4.2		0.16		52
P(p-MeC₆H₄)₃ (20.0)	Co (3.9)	190	2000	10	2.6		0.8	1.0[b]	52

[a] Trace of corresponding biphenyl. [b] p-xylene.

SCHEME I. Possible Mechanism for Co₂(CO)₈ Catalyzed P–C Cleavage and/or R-Group Scrambling

observed in the reaction solutions. A complete PR₃ decomposition product distribution is shown in eq 10 and Table V. RCH₃ and RCH₂CH₂OH are formed by

$$PR_3 + Co_2(CO)_8 \longrightarrow RH + RR + RCH_2OH \longrightarrow RCH_3$$
$$\longrightarrow RCH_2CH_2OH \quad (10)$$

secondary reactions. It is thought that the traces of phenethanol are formed via known Co-catalyzed homologation.[50,51] Toluene could be produced by hydrogenolysis. Reactions run in ethylbenzene-d_{10} revealed no deuterium incorporation into the arene or oxygenated products, indicating free radicals are not involved in the process. Reaction with PR₃ (R = p-MeC₆H₄) resulted in the production of only the para isomer of methylbenzyl alcohol consistent with an oxidative addition process as shown in Scheme I and not an ortho metalation process which would have resulted in meta products.

Preliminary substituent effect data[57c] reveal the following trends for PR₃ (R = p-XC₆H₄) decomposition

$$p\text{-CF}_3 > p\text{-Cl} > H > p\text{-Me} > p\text{-OMe}$$

Thus, it is clear that the overall decomposition reaction is enhanced by the presence of electron-withdrawing substituents and inhibited by electron-donating substituents.

The mechanism of arene formation is of course harder to trace by labeling experiments. A case could be made for intermediates such as 42 or 43 in which simple

electrophilic substitution or a binuclear electrophilic substitution would lead to RH and phosphido products.

42

A cluster-mediated reaction is also possible for the generation of insertion products (Scheme II) via an intermediate such as 44 (see 16 for a similar structure where M = Ru). The intermediate M–P–Ph three-center interaction could give a cluster containing a bridging phosphido group and a M–Ph moiety, 45, which could then undergo reaction with either H₂ or CO/H₂ to give the observed products. Such a mechanism would also result in the maintenance of stereochemistry around the phenyl ring, i.e., para products from para-substituted substrates. The exact mechanism by which such phosphorus–carbon bond cleavages occur awaits further mechanistic studies.

Tanaka and co-workers[59] recently reported that tertiary phosphines give P–C cleavage decomposition products when reacted with metal carbonyls such as Rh₄(CO)₁₂, Co₂(CO)₈, or Ru₃(CO)₁₂ under synthesis gas (see Table V). They report that the ability to cleave the phoshorus–aryl bond follows the order Rh > Ru > Co. Higher syn-gas pressures resulted in higher oxygenate/arene ratios. The production of arene drastically increased with temperature between 180 and 200

SCHEME II. Possible Cluster-Mediated P–C Bond Cleavage

TABLE VI. Relative Rates of Aryl-Group Exchange between PPh_3 and $P(p\text{-}MeC_6H_4)_3$ Catalyzed by Group 8-10[a] Transition Metals

complex	PR_3, M	temp, °C	rel rate	atm
$Pd(PPh_3)_4$	20	170	1	b
$Ni(CO)_2(PPh_3)_2$	20	170	1.7	b
$Rh_6(CO)_{16}$	20	170	2.6	b
$Ru_3(CO)_{12}$	20	170	19.	b
$Os_3(CO)_{12}$	20	130	4.8	b
$Co_2(CO)_8$	20	130	65.3	b
$RhCl(CO)(PPh_3)_2$	10	120	1	c
$RhCl(PPh_3)_3$	10	120	7.7	c
$Rh(acac)(CO)PPh_3$	10	120	24.7	c
$Rh_6(CO)_{16}$	10	120	tr	c

[a] In 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.) [b] H_2/C_3H_6 (1:1). [c] H_2.

°C while oxygenate production remained fairly constant. No C_4 hydrocarbons, C_5 alcohols, or C_5 aldehydes were observed when $P(n\text{-}Bu)_3$ was studied under similar conditions.
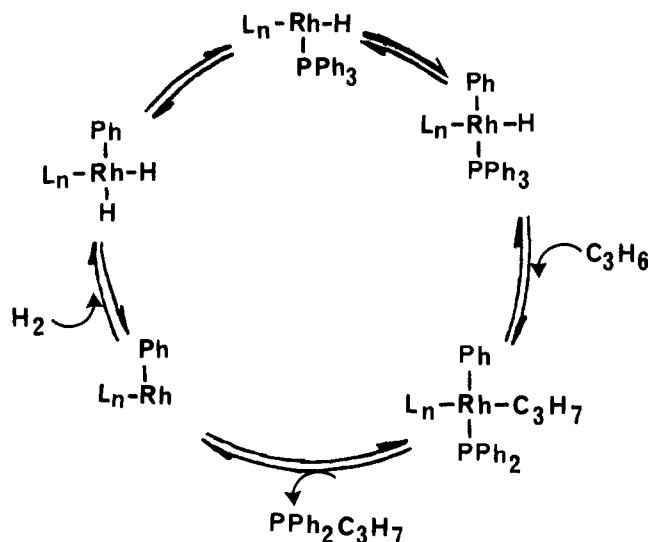
Gregario et al.[60] recently reported that PPh_3 is slowly converted to PPh_2Pr during rhodium-catalyzed propylene hydroformylation. Union Carbide workers[61,62] in similar studies observed the facile interchange of aryl groups between different triarylphosphines and alkylarylphosphines (eq 11). The relative rates for the catalysis of eq 11 by a variety of transition-metal complexes is given in Table VI. They proposed the in-

$$PPh_3 + P(p\text{-}MeC_6H_4)_3 \leftrightarrow PPh_2(p\text{-}MeC_6H_4) + PPh(p\text{-}MeC_6H_4)_2 \quad (11)$$

termediacy 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

46

the source of rhodium. The scrambling occurred under atmospheres of propylene, hydrogen, or nitrogen. For reaction 11, catalyzed by $RhH(CO)(PPh_3)_3$ the rate (half-lives) varied with atmosphere as follows: C_3H_6 (3 h), H_2 (4 h), N_2 (18 h). In every instance the solutions turned dark brown indicative of rhodium clustering.[27]

They found that the conversion of PPh_3 to PPh_2Pr, which is very slow during normal low-pressure rhodium-catalyzed hydroformylation, is greatly accelerated under higher H_2 partial pressures (CO-starved reactions). Benzene was observed in equimolar ratio to PPh_2Pr. As the concentration of PPh_2Pr increased it was slowly converted to $PPhPr_2$ and further benzene. PPh_3 was shown to inhibit the decomposition reaction.[63] Higher propylene concentrations promomted PPh_2Pr formation. Scheme III was proposed to account for all of these observations.

Longoni and co-workers in Milano[65] reported that kinetics on cyclohexene hydroformylation catalyzed by

SCHEME III. Suggested Mechanism for PPh_3 Cleavage in the Presence of Rh, Propylene, and Hydrogen

the bimetallic Rh/Co PPh_3-substituted carbonyl clusters were impossible to derive because of ligand degradation reactions. In the case of $Rh_4(CO)_{12}/PPh_3$ 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 $RuCl_2(PR_3)_3$, aryl cleavage was identified as the mode of catalyst deactivation.[66] At 180–200 °C the $RuCl_2(PPh_3)_3$-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 PPh_3 decomposition was observed at the end of the reaction. A $RuCl_3/PBu_3$ catalyst system appeared to be much more stable for the amine dehydrogenation–imine hydrogenation sequence identified as the mechanistic pathway.

Recently Crabtree and co-workers[67] reported that during the dehydrogenation of cyclohexane to benzene, catalyzed by $IrH_2[P(p\text{-}FC_6H_4)_3]_2(Me_2CO)^+PF_6^-$, 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,[68] are related to the earlier observations by Pruett.[27]

C. Others

The reaction of syn gas and pyridine in the presence of $[Co(CO)_3(PPh_3)]_2$ 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 PPh_3 ligand. For $PR_3 = P(p\text{-}MeC_6H_4)_3$ 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 $Pd(PPh_3)_4$, Helquist[71] 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 PR_3 ($R = p\text{-}XC_6H_4$) 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 $PdCl_2(PPh_3)_2$ was heated to 180–200 °C in toluene under an atmosphere of CO_2 a 15–40% yield of benzoic acid was obtained.[73] It was proposed that the benzoic acid formed via CO_2 insertion into a Pd–Ph intermediate.

Mixtures of Ar_3P 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 $Ar_2Ar'P$ and bond scission to give Ar_2, $Ar'Ar$, 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 $Co_2(CO)_8$ + PR_3 + an iodide source. These reactions are run between 175 and 200 °C. Keister[76] 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/PR_3 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 $RhCl(PPh_3)_3$ 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
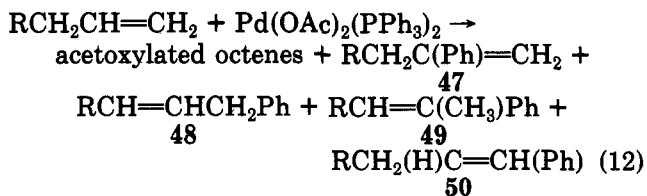
ketones by $[Rh(diolefin)L_2]^+$ because catalyst decomposition is observed at higher temperatures. It is clear from his data that higher temperatures result in catalyst deactivation and lower optical purity in the products.

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 PR_3 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-phopshine 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 $RuCl_2(PPh_3)_3$ 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 transformation[66] 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 $Pd(OAc)_2(PPh_3)_2$ 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-

$$RCH_2CH{=}CH_2 + Pd(OAc)_2(PPh_3)_2 \rightarrow$$
$$\text{acetoxylated octenes} + \underset{47}{RCH_2C(Ph){=}CH_2} +$$
$$\underset{48}{RCH{=}CHCH_2Ph} + \underset{49}{RCH{=}C(CH_3)Ph} +$$
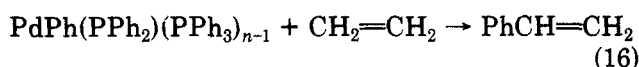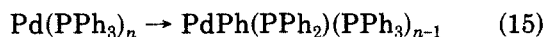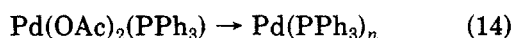$$\underset{50}{RCH_2(H)C{=}CH(Ph)} \quad (12)$$

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-tolyldiphenylphosphine, 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, tran-bis(triethylphosphine)dimesitylnickel, and trans-bis(triethylphosphine)dimesitylcobalt were reacted together at 30 °C to give, among other produces, 2,4,6-trimethylstyrene which presumably resulted via ethyl transfer from phosphorus to metal.

Green, Felkin, and co-workers[89] 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 Yatsimirsky[91] 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.

$$Pd(OAc)_2(PPh_3)_2 \rightarrow Pd(OAc)_2(PPh_3) + PPh_3 \quad (13)$$

$$Pd(OAc)_2(PPh_3) \rightarrow Pd(PPh_3)_n \quad (14)$$

$$Pd(PPh_3)_n \rightarrow PdPh(PPh_2)(PPh_3)_{n-1} \quad (15)$$

$$PdPh(PPh_2)(PPh_3)_{n-1} + CH_2{=}CH_2 \rightarrow PhCH{=}CH_2 \quad (16)$$

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 property 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 researchers[97–100] have noted that the polystryene 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 olefins[49–51] 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
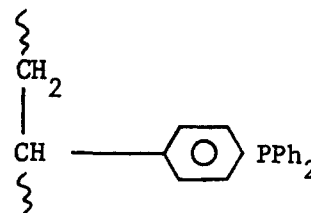
51

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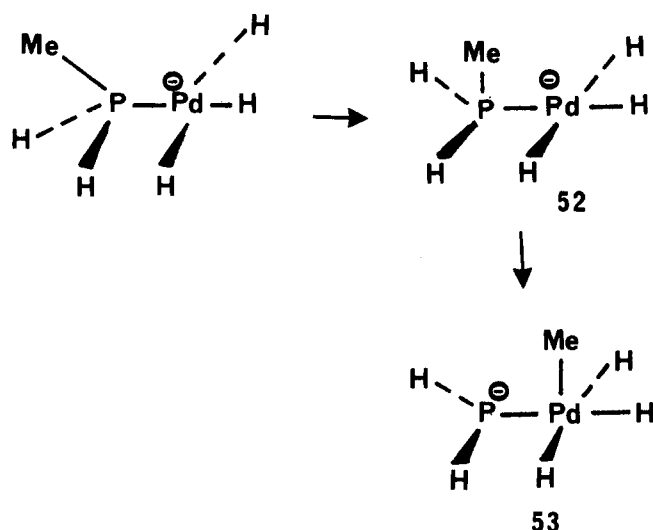
out the need for phosphorus analysis of the effluent streams. It is clear that further work needs to be done with careful examination of the polymer-immobilized supports as a primary goal of the research.

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] Rh,[21] 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 determing 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$_2$P–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$_2$PMe–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 Patrick[105] have recently conducted low-pressure pyrolysis studies on PEt$_3$ and derived a ΔH_{298} of 68 $\pm$ 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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References

(1) Trofimenko, S. *Inorg. Chem.* **1973**, *12*, 1215.
(2) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139.
(3) Garrou, P. E.; Dubois, R. A.; Jung, C. W. *CHEMTECH* **1985**, 123.
(4) Bradford, C. W.; Nyholm, R. S. *J. Chem. Soc., Chem. Commun.* **1972**, 87.
(5) Bradford, C. W.; Nyholm, R. S. *J. Chem. Soc., Dalton Trans.* **1973**, 529.
(6) Gainsford, G. J.; Guss, J. M.; Ireland, P. R.; Mason, R.; Bradford, C. W.; Nyholm, R. S. *J. Organomet. Chem.* **1972**, *40*, C70.
(7) Deeming, A. J.; Kimber, R. E.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2589.
(8) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1973**, 2727.
(9) Bruce, M. I.; Shaw, G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 2094.
(10) (a) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113 and references therein. (b) Carty, A. J.; Taylor, N. J.; Smith, W. F. *J. Chem. Soc., Chem. Commun.* **1979**, 750.
(11) Reed, J.; Schultz, A. J.; Pierpoint, C. G.; Eisenberg, R. *Inorg. Chem.* **1973**, *12*, 2949.
(12) Foley, H. C.; Finch, W. C.; Pierpoint, C. G.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 1379.
(13) Sabo, S.; Chaudret, B.; Gervais, D. *J. Organomet. Chem.* **1983**, *258*, C19.
(14) Chaudiet, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546.
(15) Maclaughlin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* **1982**, *60*, 88.
(16) Patel, V. D.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 99.
(17) Mason, R.; Sotofte, I.; Robinson, S. D.; Uttley, M. F. *J. Organomet. Chem.* **1972**, *46*, C61.
(18) Bellon, P. L.; Benedicenti, C.; Caglio, G.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1973**, 946.
(19) Blickensderfer, J. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 2681.
(20) Blickensderfer, J. R.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 2686.
(21) Lewin, M.; Aizenshtat, Z.; Blum, J. *J. Organomet. Chem.* **1980**, *184*, 255.
(22) Michman, M.; Kaufman, V. D.; Nussbaum, S. *J. Organomet. Chem.* **1979**, *182*, 547.
(23) Nishiguchi, T.; Kazuo, F. *J. Organomet. Chem.* **1974**, *80*, C42.
(24) Nishiguchi, T.; Tanaka, K.; Fukuzumi, K. *J. Org. Chem.* **1978**, *43*, 2968.
(25) Nishiguchi, T.; Tanaka, K.; Fukuzumi, K. *J. Organomet. Chem.* **1980**, *193*, 37.
(26) Billig, E.; Jamerson, J. D.; Pruett, R. L. *J. Organomet. Chem.* **1980**, *192*, C49.
(27) Jamerson, J. D.; Pruett, R. L.; Billig, E.; Fiato, F. A. *J. Organomet. Chem.* **1980**, *193*, C43.
(28) Kaneda, K.; Sano, K.; Teranishi, S. *Chem. Lett.* **1979**, 821.
(29) Harding, M. M.; Nicholls, B. S.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1983**, 1479.
(30) Hanson, B. E.; Fanwick, P. E.; Mancici, J. S. *Inorg. Chem.* **1982**, *21*, 3811.
(31) Cowie, M.; Gauthler, M. D.; Loeb, S. J.; McKeer, I. R. *Organometallics* **1983**, *2*, 1057.
(32) Coulson, D. R. *J. Chem. Soc., Chem. Commun.* **1968**, 1530.
(33) Dixon, K. R.; Rattray, A. D. *Inorg. Chem.* **1978**, *17*, 1099.
(34) Nakamura, A.; Otsuka, S. *Tetrahedron Lett.* **1974**, 463.
(35) Aryl and halide redistributions of this type are now viewed as commonplace.[36]
(36) Garrou, P. E. *Adv. Organomet. Chem.* **1984**, *23*, 95.
(37) Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4499.
(38) Brateman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1306.
(39) Brakerman, P. S.; Cross, R. J.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1310.
(40) Oehme, G.; Bandisch, H. *Tetrahedron Lett.* **1974**, 4129.
(41) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.
(42) Glockling, F.; McBride, T.; Pollock, R. J. *J. Chem. Soc., Chem. Commun.* **1973**, 650.
(43) Taylor, N. J.; Chieh, P. C.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 448.
(44) Blake, D. M.; Nyman, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 5360.
(45) Bellon, P. L.; Ceriotti, A.; Demartin, F.; Longoni, G.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1982**, 1671.
(46) Meij, R.; Stuffkens, D. J.; Vrieze, K.; Browers, A. M. F.; Overbeek, A. R. *J. Organomet. Chem.* **1978**, *155*, 123.
(47) Jans, J.; Naegeli, R.; Venanzi, L. M.; Albinati, A. *J. Organomet. Chem.* **1983**, *247*, C37.

(48) Casey, C. P.; Bullock, R. M. *Organometallics* **1984**, *3*, 1100.
(49) Slaugh, L. H.; Mullineaux, R. D. *J. Organomet. Chem.* **1968**, *13*, 469.
(50) Falbe, J. "Carbon Monoxide in Organic Synthesis"; Springer-Verlag: New York, 1970.
(51) Wender, I.; Pino, P. "Organic Synthesis Via Metal Carbonyls"; Wiley-Interscience: New York, 1977.
(52) Osborn, J. A.; Wilkinson, G.; Young, J. F. *J. Chem. Soc., Chem. Commun.* **1965**, 17.
(53) Fowler, R.; Connor, H.; Baehl, R. A. *CHEMTECH* **1976**, 772.
(54) Such data may be available in the proprietary literature of companies commercially involved in hydroformylation, but such data has not been available in the open literature prior to 1984.[55]
(55) With the exception of a communication by the late Paolo Chini.[56]
(56) Chini, P.; Martinengo, S.; Garlaschelli, G. *J. Chem. Soc., Chem. Commun.* **1972**, 709.
(57) (a) Dubois, R. A.; Garrou, P. E.; Lavin, K.; Allcock, H. R. *Organometallics* **1984**, *3*, 649. (b) Dubois, R. A.; Garou, P. E.; Lavin, K.; Allcock, H. R., manuscript in preparation. (c) Dubois, R. A.; Garrou, P. E., manuscript in preparation.
(58) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53.
(59) Sakakura, T.; Kobayashi, T.; Hayashi, T.; Kawabata, Y.; Tanaka, M.; Ogata, I. *J. Organomet. Chem.* **1984**, *267*, 171.
(60) Gregorio, G.; Montrasi, G.; Tampieri, M.; Calvalieri, P.; Pagini, G.; Andreeta, A. *Chim. Ind. (Milan)* **1980**, *62*, 389.
(61) Abatjoglou, A. G.; Bryant, D. R. *Organometallics* **1984**, *3*, 932.
(62) Abatjoglou, A. G.; Billig, E.; Bryant, D. R. *Organometallics* **1984**, *3*, 923.
(63) The use of very high PR_3/Rh ratios is normally comercially practiced. It has been reported[64] that without excess tertiary phosphine ligand in solution, rhodium catalysts deactivate and become difficult to recycle.
(64) Chan, A. S.; Carroll, W. E.; Willis, D. E. *J. Mol. Catal.* **1983**, *19*, 377.
(65) Ceriotti, A.; Garlaschelli, L.; Longoni, G.; Malatesta, C.; Strumolo, D. *J. Mol. Catal.* **1984**, *24*, 309.
(66) Jung, C. W.; Fellmann, J. D.; Garrou, P. E. *Organometallics* **1983**, *2*, 1042.
(67) Burk, M. J.; Crabtree, R. H.; Dion, R. P.; Parnell, C. D.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816.
(68) Felkin, H.; Fillerbeen-Khan, T.; Gault, Y.; Holmes-Smith, R.; Zakrzewski, J. *Tet. Lett.* **1984**, *25*, 1279.
(69) Felkin, H., personal communication.
(70) Masuo, S. T.; Labinger, J. A.; Bonfiglio, J. N.; Grimmett, D. L.; Shearin, E.; Miller, J. S. *C_1 Mol. Chem.* **1984**, *1*, 57.
(71) Zask, A.; Helquist, P. *J. Org. Chem.* **1978**, *43*, 1619.
(72) Goel, A. B. *Inorg. Chim. Acta* **1984**, *84*, L25.
(73) Goel, A. B.; Richards, H. J.; Kyung, J. H. *Tetrahedron Lett.* **1984**, *25*, 391.
(74) Goel, A. B. *Inorg. Chim. Acta* **1984**, *86*, L77.
(75) Fakley, M. E.; Head, R. A. *Appl. Catal.* **1983**, *5*, 3.
(76) Keister, J. B.; Gentile, R. *J. Organomet. Chem.* **1981**, *222*, 143.
(77) (a) Merrill, R. E. *CHEMTECH* **1981**, 118. (b) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106. (c) Solodar, J. *CHEMTECH* **1975**, 421.
(78) Wanatabe, Y.; Ohata, T.; Tsuji, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2647.
(79) Murahashi, S. I.; Kondo, K.; Hakata, T. *Tetrahedron Lett.* **1982**, *23*, 229.
(80) Reuter, J. M.; Salomon, R. G. *J. Org. Chem.* **1977**, *42*, 3360.
(81) Sasson, Y.; Blum, J. *Tetrahedron Lett.* **1971**, 2167.
(82) Blum, J.; Sasson, Y.; Iflah, S. *Tetrahedron Lett.* **1972**, 1015.
(83) Pri-Bar, I.,; Buchman, O.; Blum, J. *Tetrahedron Lett.* **1977**, 1443.
(84) Asano, R.; Moritani, I.; Fujiwara, Y.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2910.
(85) Kikukawa, K.; Yamane, T.; Takagi, M.; Matsuda, T. *J. Chem. Soc., Chem. Commun.* **1972**, 695.
(86) Yamane, T.; Kikukawa, K.; Takagi, M.; Matsuda, T. *Tetrahedron* **1973**, *29*, 955.
(87) Kikukawa, K.; Takagi, M.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1493.
(88) Kikukawa, K.; Yamane, T.; Ohbe, Y.; Takagi, M.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1187.
(89) Green. M. L. H.; Smith, M. J.; Felkin, H.; Scieczewski, G. *J. Chem. Soc., Chem. Commun.* **1971**, 158.
(90) Kikukawa, K.; Matsuda, T. *J. Organomet. Chem.* **1982**, *235*, 243.
(91) Ryabov, A. D.; Yatsimirsky, A. K. *J. Mol. Catal.* **1978**, *4*, 449.

(92) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 110.
(93) Heck, R. F. "Organotransition Metal Chemistry"; Academic Press: New York, 1974.
(94) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980.
(95) Hodge, P.; Sherrington, D. C. "Polymer Supported Reactions In Organic Synthesis"; Wiley: New York, 1980.
(96) Polymer-bound triphenylphosphine on styrene–divinylbenzene is made by Strem Chemicals Inc. and is sold under license of U.S. Patent 3 708 462 owned by the Dow Chemical Company.
(97) Hunter, D. E.; Moore, S. E.; Dubois, R. A.; Garrou, P. E., submitted for publication.
(98) Fellmann, J. D.; Garrou, P. E.; Withers, H. P.; Seyferth, D.; Traficante, D. D. *Organometallics* **1983**, *2*, 818.
(99) Trevillyan, A. E. U.S. Patent 4 045 493, 1977.

(100) Verdet, L.; Stille, J. K. *Organometallics* **1982**, *1*, 380.
(101) Evans, G. O.; Pittman, C. U.; McMullan, R.; Beach, R. T.; Jones, R. J. *J. Organomet. Chem.* **1974**, *67*, 298.
(102) Allen, J. D. U.S. Patent 3 847 997, 1974.
(103) Haag, W. O.; Whitehurst, D., U.S. Patent 4 098 727, 1978.
(104) Ortiz, J. V.; Havias, Z.; Hoffman, K. *Helv. Chim. Acta* **1984**, *67*, 1.
(105) Smith, G. P.; Patrick, R. *Int. J. Chem. Kinet.* **1983**, *15*, 167.
(106) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238.
(107) Cottrell, T. L. "The Strength of Chemical Bonds", 2nd ed.; Butterworths: London, 1958.
(108) It should be noted that the heavier group 15 ligands (As, Sb, Bi) have been observed to undergo cleavage more readily than their PR_3 analogues.[73,82,84,109]
(109) Kawamura, T.; Kikukawa, K.; Takagi, M.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2021.