Available online at www.sciencedirect.com

SCIENCE DIRECT

Coordination Chemistry Reviews 250 (2006) 449–467

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

# The migration and cleavage of substituents from donor atoms in coordination compounds of the transition metals

Adrian W. Parkins*

*Department of Chemistry, King's College London, Strand, London WC2R 2LS, UK*

Received 4 April 2005; accepted 3 August 2005
Available online 12 September 2005

## Contents

## Abstract

The review brings together reactions involving the cleavage of organic substituents from donor atoms in coordination and organometallic compounds. In some cases the substituent is lost, in others it migrates to the metal. A few cases of migration from the metal to the donor atom are included. The information is scattered widely in the literature, and has been compiled as a survey of groups of the periodic table.

*Keywords:* Coordination compounds; Substituent migration; Cleavage reactions

## 1. Introduction

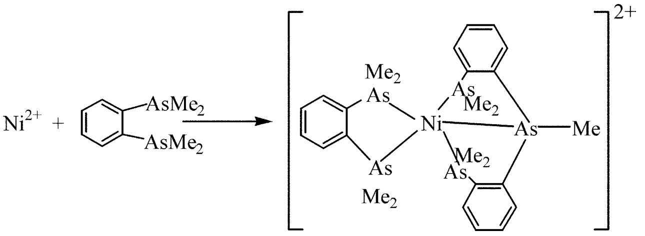
In 1974 Kraihanzel [1] reviewed the reactions of coordinated group 15 ligands, and cited the nickel chemistry reported by Nyholm [2] in 1950, as the first example of a reaction involving the cleavage of an As–C bond in a coordination compound. In this case, it was not until a crystal structure was carried out many years later, showing a five coordinate complex with a tridentate ligand formed by loss of a methyl group from the original diars ligand, that the cleavage reaction was revealed (Eq. (1)) [3]. There is an earlier reaction involving C–O cleavage of a phosphite coordinated to platinum, which is described in the platinum section, but the cleavage is not from the atom coordinated to the metal.

---

*Abbreviations:* Cp, cyclopentadienyl; diars, 1,2-bis(dimethylarseno) benzene; dmpm, bis(dimethylphosphino)methane; dppe, 1,2-bis(diphenylphosphino)ethane; dppm, bis(diphenylphosphino)methane; hfac, hexafluoroacetylacetonate; HMPT, hexamethylphosphoric triamide

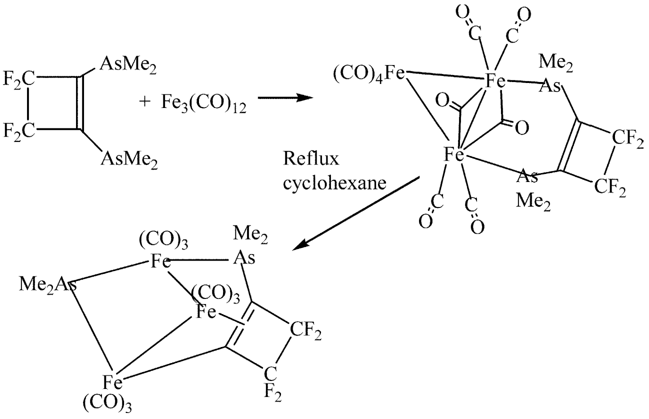
* Tel.: +44 20 7848 1148; fax: +44 20 7848 2810.
*E-mail address:* adrian.parkins@kcl.ac.uk.

0010-8545/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2005.08.001



(1)

Cullen et al. [4] subsequently showed that the cleavage of As–C bonds is not a rarity, and the structures were reported by Einstein et al. (Eq. (2)) [5]



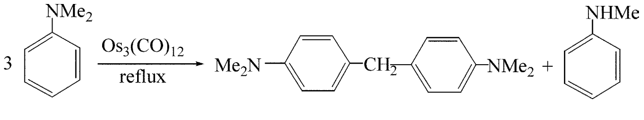
(2)

However, it is in the area of homogeneous catalysis involving transition metal complexes that many of the cleavage reactions have been discovered. The majority of these involve the cleavage of phosphorus–carbon (P–C) rather than arsenic–carbon (As–C) bonds. This is because more work has been carried out with phosphine rather than arsine complexes, not because P–C bonds are cleaved more easily than As–C bonds. The mean bond enthalpies for P–C and As–C bonds in the trimethyl derivatives are 276 and 229 kJ mol$^{-1}$, respectively; but this does not necessarily mean that the energy required for the breakage of one bond is in the same proportion [6]. Some relevant observations on the fragmentation processes occurring in the mass spectrometry of $Ar_3E$ (E = N, P, As, Sb and Bi) have been published by Grützmacher and co-workers [7]. The reviews by Garrou [8] and Michman [9] give good coverage of the breakdown of phosphorus ligands in homogeneous catalysts, and this theme has been taken up more recently by van Leeuwen [10]. In the case of antimony where the bond enthalpy is 214 kJ mol$^{-1}$ very little work has been reported although $Ph_3Sb$ is the source of Sb in the rhodium cluster anion $[Rh_{12}Sb(CO)_{27}]^{3-}$ [11]. An appreciation of the dispersed nature of the literature on this topic can be gained from the remark made in 2000, that P–C bond cleavage reactions are “relatively rare” [12]. Such an opinion is probably due to the very scattered nature of the subject. As early as 1975 Carty and co-workers [13] remarked that “Numerous other examples of facile P–C cleavage in reactions of phosphine with low-valent metals are known”. A theoretical treatment of migration reactions by Hoffmann and co-workers appeared as early as 1984 [14].

The situation with sulfur–carbon (S–C) bonds is similar to phosphorus in terms of bond energy, but the valencies are different, so that whereas cleavage of a P–C bond often gives rise to a bridging phosphido group, with thiols the formation of a metal sulfide can occur. The S–C cleavage reaction is important in the hydrodesulfurisation of petroleum feedstocks, for example in the water–gas shift reaction where sulfur sensitive catalysts are employed preliminary to ammonia synthesis in the Haber process. Polyhedron has issued a Symposium in Print covering desulfurisation [15], and the field has been reviewed by Brorson et al. [16]. Curtis, who has carried out extensive studies in this field using clusters of cobalt and molybdenum, has made comparisons with commercial hydrodesulfurisation catalysts [17].

A reaction, which could, perhaps justifiably, be described as rare is the cleavage of nitrogen carbon (N–C) bonds by transition metals. The mean bond enthalpy in this case is much higher (314 kJ mol$^{-1}$) and so the paucity of examples is not surprising. In 1979 N–C cleavage promoted by palladium was reported by Murahashi and Yano [18] and there has been a small number of examples subsequently. These are dealt with in the group survey under palladium, technetium and rhenium.

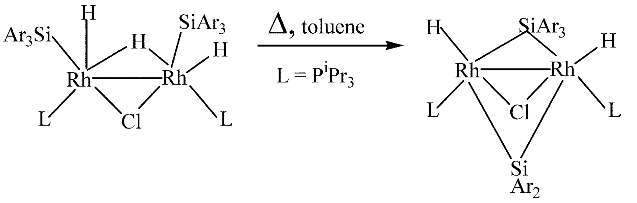
C–N cleavage is also uncommon with transition metal cluster compounds. Choo Yin and Deeming found that $Os_3(CO)_{12}$ reacted with trimethylamine and dimethylaniline with C–N cleavage give trinuclear clusters containing C=N [19] and subsequently reported that $Os_3(CO)_{12}$ catalyses the formation of $Me_2NC_6H_4CH_2C_6H_4NMe_2$ from *N*,*N*-dimethylaniline, with a turnover number of 742 (Eq. (3)). Although the detailed mechanism was not established, the *N*-methyl groups are the source of the central $CH_2$ group [20].



(3)

Several groups have reported that metal carbonyl clusters catalyse the redistribution of alkyl groups between tertiary amines [21]. Aime et al. [22] isolated and characterised $(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}CH_3C{=}N{-}CH_2CH_3)Ru_3(CO)_9$ in which one of the ethyl groups has been lost, from the reaction of triethylamine with $Ru_3(CO)_{12}$ in the presence of $Fe_2(CO)_4(\mu\text{-}SEt_2)_2(PPh_3)_2$. Adams et al. have reported that the exchange of alkyl groups on amines is catalysed by $(\mu\text{-H})_2(\mu_3\text{-}S)(CHNMe_2)Os_3(CO)_8$ [23].

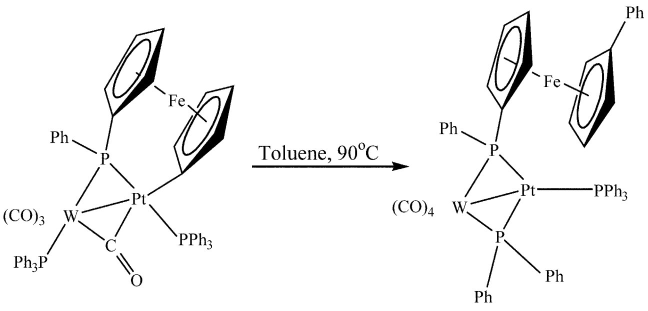
The mean bond enthalpy of a C–Si bond is 311 kJ mol$^{-1}$, and there is an example of C–Si cleavage in rhodium chemistry (Eq. (4)) [24]. In the product one silicon atom is bonded to three aryl groups, but the other silicon atom has only two aryl groups. Some related chemistry has been discussed by Braunstein and Boag [25].



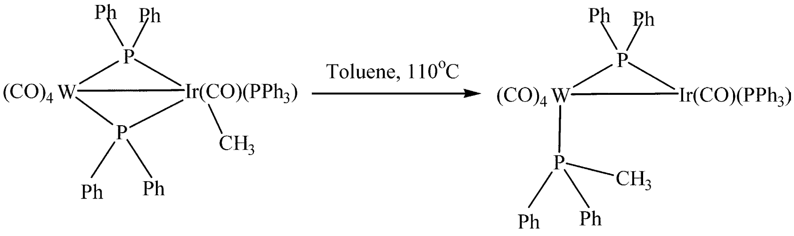
(4)

There are many examples of substituents on donor atoms migrating onto the metal atom or being lost through cleavage, but in addition there are now examples of the reverse, in other words, the reaction leads to the formation of a bond between a substituent and a donor atom. For example, the bridging diphenylphosphido group in a tungsten–iridium complex becomes a terminal diphenylmethylphosphine coordinated to tungsten when the methyl group migrates from iridium to phosphorus (Eq. (5)).

One further reaction in which a metal to ligand migration has been postulated is in a tungsten–platinum derivative of ferrocene, in which a phenyl group migrates from triphenylphosphine to the ferrocene ring possibly via an intermediate with the phenyl group bonded to the platinum (Eq. (8)) [29]. An additional example is given in the ruthenium section.

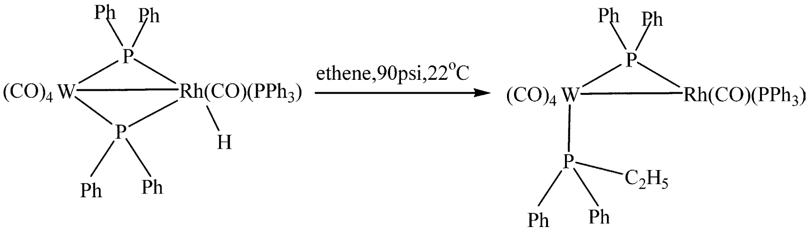


(8)



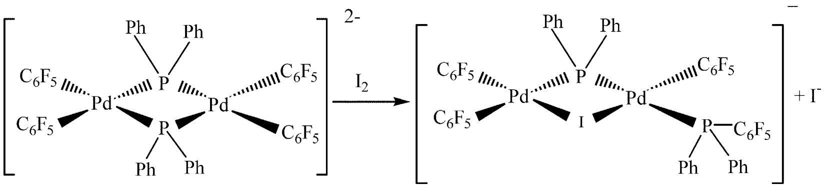
(5)

The same research group reported the reaction of an analogous tungsten–rhodium hydride with ethene. In this case the product was a terminal diphenylethylphosphine, and the rhodium ethyl complex was the suggested intermediate (Eq. (6)) [26,27]. This reaction is on the very blurred border between a migration reaction and a reaction of the coordinated ligand. There are a number of reactions in this review where this distinction is not useful.



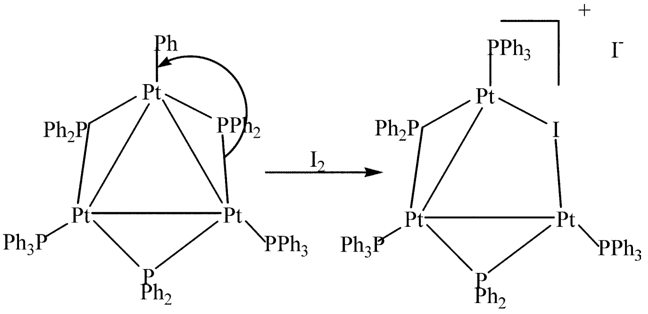
(6)

Another example of a reverse migration is the formation of a diphenylpentafluorophenylphosphine ligand in a dinuclear palladium complex (Eq. (7)) [28].



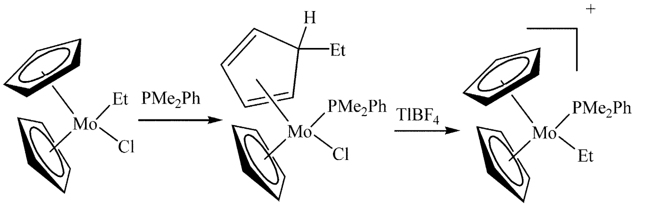
(7)

Cluster chemistry also has examples of the reverse migration reaction and Braunstein and co-workers reported an example involving the formation of triphenylphosphine on a platinum cluster in 1996 (Eq. (9)) [30].



(9)

This review is primarily concerned with migration and cleavage from donor atoms. However, there are many reactions involving hydrocarbons which are coordinated when the carbon skeleton undergoes a cleavage or migration reaction. An example of this, and one of the few examples in which the migration occurs in both directions, is provided by the molybdenum chemistry described by Benfield and Green [31] (Eq. (10)). Further examples of cyclopentadiene to π-cyclopentadienyl reactions involving C–C cleavage are given in the iron and iridium sections. A review of “Transition Metal Catalysis of Pericyclic Reactions” was published by Mango in 1975 [32] and Tantillo and Hoffmann have commented on the ring-opening of cyclobutene more recently [33]. Murakami and Ito have surveyed the “Cleavage of Carbon–Carbon Single Bonds By Transition Metals” [34].



(10)

With literature spanning several decades, and several donor elements presenting relevant cases, and most of the transition metals exhibiting cleavage behaviour, we cannot hope to be exhaustive in this survey. The formation of phosphido bridged dinuclear complexes occurs frequently in this review, but we are particularly aware that we have not dealt with metal cluster compounds comprehensively. Reactions of compounds with two or more metal atoms provide a rich area for migration and cleavage reactions. A useful review with the title “Cluster Assisted Ligand Transformations” with 323 references has been published by Lavigne [35]. The reviews of “Ligand Centered Reactivity of Organometallic Radicals” [36] and “Homolytic Cleavage and Aggregation Processes in Cyclopentadienyl Chemistry” [37] are complementary to this review. We will not cover the cleavage of P–C bonds by alkali metals, other than to say that this is a synthetically useful reaction, which has been known for many years [38–40]. We hope that by bringing together a large range of material, which is long overdue for review, we have shone some light on the topic. To misquote Mallory, “we did it, because it wasn’t there.”

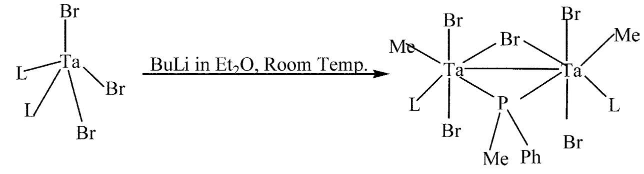
## 2. Titanium, zirconium and hafnium

The ions of group 4 are normally considered to be hard acids, and so only a few complexes of phosphine ligands have been reported. However, Coucouvanis and co-workers have reported a number of examples of S–C cleavage brought about by zirconium species, which give products containing inorganic sulfide (Eq. (11)) [41].

$$\mathrm{Zr(BH_4)_4} + 13\ t\text{-}\mathrm{BuSH} + 2\mathrm{THF} \longrightarrow \mathrm{Zr_3S_3}(t\text{-}\mathrm{BuS})_2\mathrm{(BH_4)_4(THF)_2} + 8/3(\mathrm{BH_2S}\text{-}t\text{-}\mathrm{Bu})_3 + 13\mathrm{H_2} + 3t\text{-}\mathrm{BuH} \qquad (11)$$

## 3. Vanadium, niobium and tantalum

A surprising reaction occurs when tribromobis(dimethylphenylphosphine)tantalum reacts with BuLi at room temperature. Although phenyl groups generally migrate more readily than methyl, in this case, a methyl transfers from phosphorus to tantalum with the formation of a phosphido bridge (Eq. (12)) [42]. The structure of the starting material has been challenged by Cotton et al. [43], who consider it to be $(\mathrm{Me_2PhP})_2\mathrm{TaCl}_x\mathrm{Br}_{4-x}$.

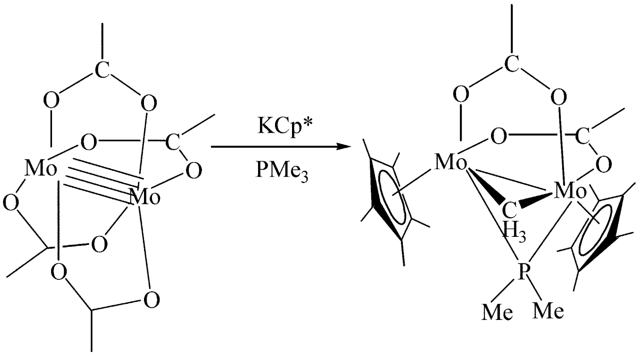


L= PPhMe2

(12)

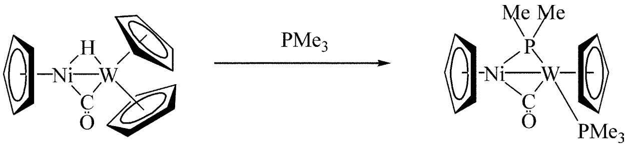
## 4. Chromium, molybdenum and tungsten

The reaction between dimolybdenum tetraacetate and potassium pentamethylcyclopentadienide in the presence of trimethylphosphine gives a complex with a bridging methyl group as well as a bridging dimethylphosphido group. Trimethylphoshine is known to undergo C–H activation in some transition metal complexes, but here P–C cleavage has occurred in preference to C–H activation (Eq. (13)) [44].



(13)

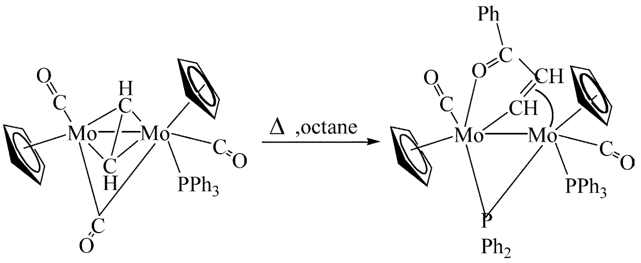
Trimethylphosphine undergoes a similar transformation on reaction with a dinuclear cyclopentadienyl nickel tungsten carbonyl hydride (Eq. (14)) [45].



(14)

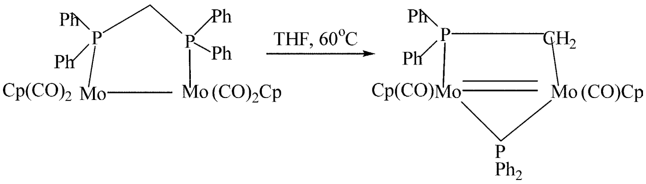
Mays and co-workers found that the alkynyl phosphine $Ph_2P–C≡C–Ph$ can undergo C–P cleavage on reaction with the heterobimetallic complexes $Cp(OC)_2W(\mu\text{-}R^1CCR^2)Co(CO)_3$, but that depending on $R^1$ and $R^2$ the P–C bond may be retained [46]. The dinuclear complexes $M_2(\mu\text{-}PPh_2)_2(CO)_8$ M = Mo or W are formed in a reaction involving $CH_2–P$ cleavage when the hexacarbonyls react with a macrocyclic ligand containing a $CH_2PPh_2$ side chain [47].

A dinuclear molybdenum complex brings about P–C cleavage of triphenyl phosphine with the formation of a diphenylphosphido complex and the bridging ethyne is converted into phenyl vinyl ketone (Eq. (15)) [48].



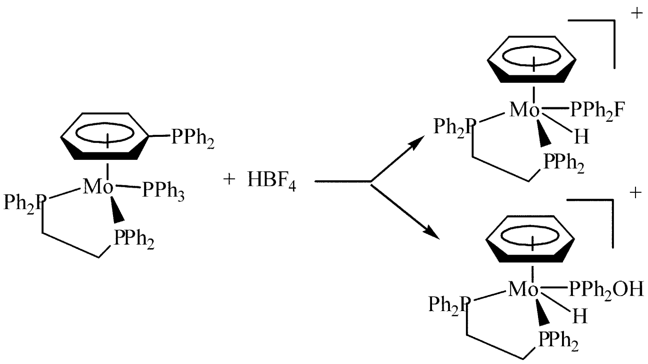
(15)

Work with dppm and molybdenum has also been reported (Eq. (16)) [49].



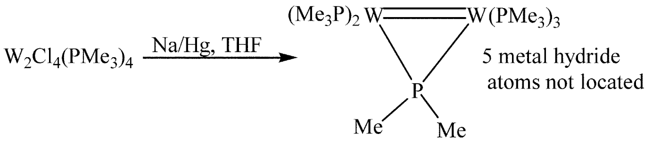
(16)

While many of the reactions involving cleavage and migration are thermally induced, the reaction of a triphenylphosphine π-bonded to molybdenum is promoted by $HBF_4$ (Eq. (17)) [50].



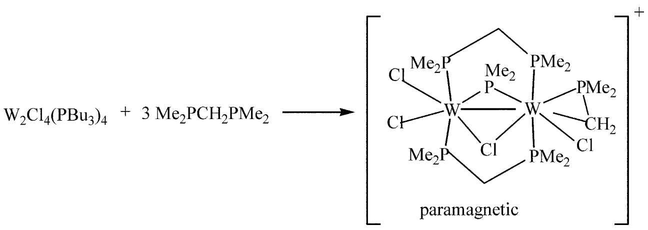
(17)

Wilkinson and co-workers have reported another example in which a phosphorus-methyl bond is cleaved (Eq. (18)) [51].



(18)

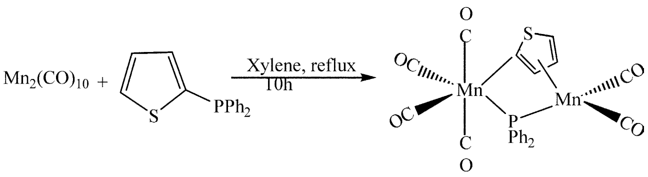
Cotton et al. have reported a somewhat different result with dmpm to give a paramagnetic cation (Eq. (19)) [52].



(19)

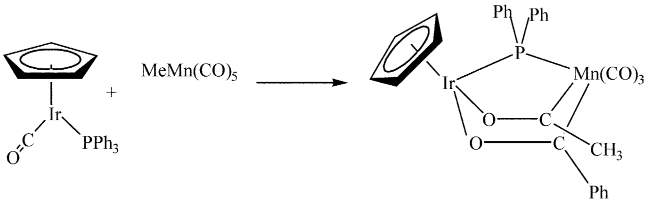
## 5. Manganese, technetium and rhenium

A reaction from manganese chemistry involving diphenyl-2-thienylphosphine provides an interesting case because the ligand contains both P–C and S–C bonds, but in this case it is the P–C bond, which undergoes cleavage (Eq. (19)) [53].



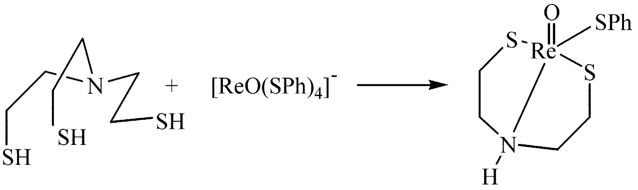
(20)

When methylmanganese carbonyl is reacted with an $CpIr(CO)PPh_3$ a dinuclear species with a bridging diphenylphosphido group results. An acetyl and benzoyl group are also formed (Eq. (21)) [54,55]. A cleavage similar to Eq. (65) has been reported for a manganese carbonyl complex of dmpm (see below).



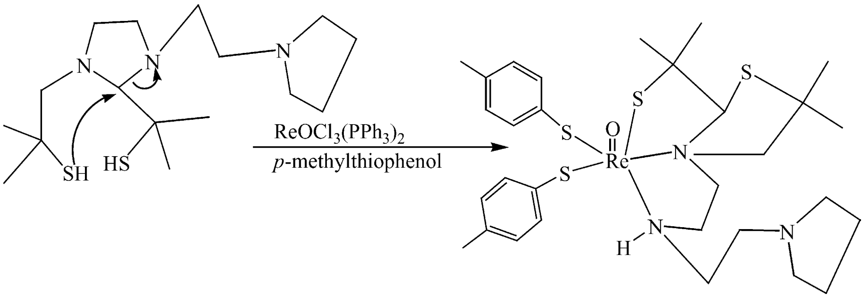
(21)

There are three examples in this triad, which involve N–C bond cleavage. The first was observed when Schiff bases derived from 2-aminobenzenethiol were reacted with solutions of Tc(V) gluconate. The resulting complex was simply the 2-aminobenzenethiolate complex. The technetium ion was considered to participate in the hydrolysis, as under the reaction conditions the rate of alkaline hydrolysis is very slow [56]. The second example cannot be explained as a hydrolysis reaction and involves the tripod ligand 2,2′,2″-nitrilotris (ethanethiol) and $[ReO(SPh)_4]^-$. In this case the ligand loses one of its arms and the result is a tridentate rather than a tetradentate ligand in the product (Eq. (22)) [57].



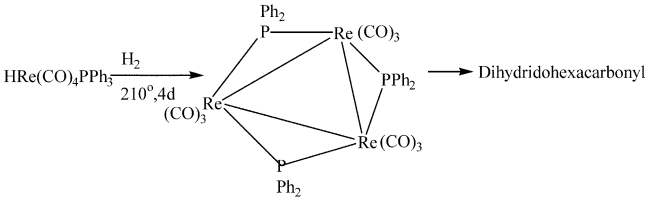
(22)

The third example involves the rearrangement of a ligand on complexation to rhenium. The reaction involves the cleavage of a C–N bond of a tertiary amine (Eq. (23)) [58].



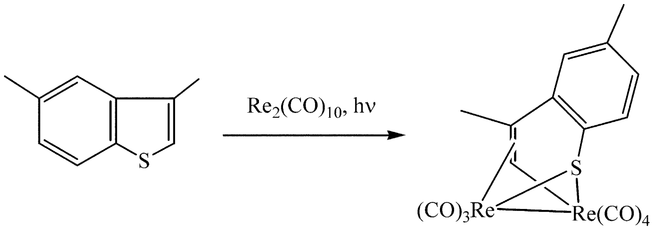
(23)

The cleavage of a phenyl group by thermolysis of a triphenylphosphine complex with the formation of diphenylphosphido bridged trinuclear rhenium cluster was reported by Haupt et al. (Eq. (24)) [59,60].



(24)

Angelici and co-workers have studied the interaction of benzothiophenes with rhenium carbonyl and have found several examples of C–S bond cleavage (Eq. (25)) [61]. Reactions with hydrogen were also studied and the compounds are considered as a model for hydrodesulfurisation.



(25)

## 6. Iron, ruthenium and osmium

The study of the reactions of the iron carbonyl complexes of variously substituted bisdiphosphinomethane ligands constitute one of the few systematic attempts to understand the factors which control the susceptibility of P–C bonds to cleavage. The reactions are summarised in Fig. 1. Some of the older work involving dppm is covered in a review [62].

The priorities involved are subtle and although the complexes often contain P–Ph and P–Me bonds, it is the bond to the central $CH_2$ group, which is usually cleaved. The generalisation [8] that (using the language of hybridisation) the ease of cleavage is $P–C_{sp} > P–C_{sp2} > P–C_{sp3}$ does not help in understanding the preferences observed here. Thus heating the complex (A) of the unsymmetrical diphosphine $Me_2PCH_2PPh_2$ does not lead to C–Ph cleavage, but to complex (B) with a dimethylphosphido bridge formed by cleavage of a $P–CH_2$ bond. Complex (C) which has a diphenylphos-

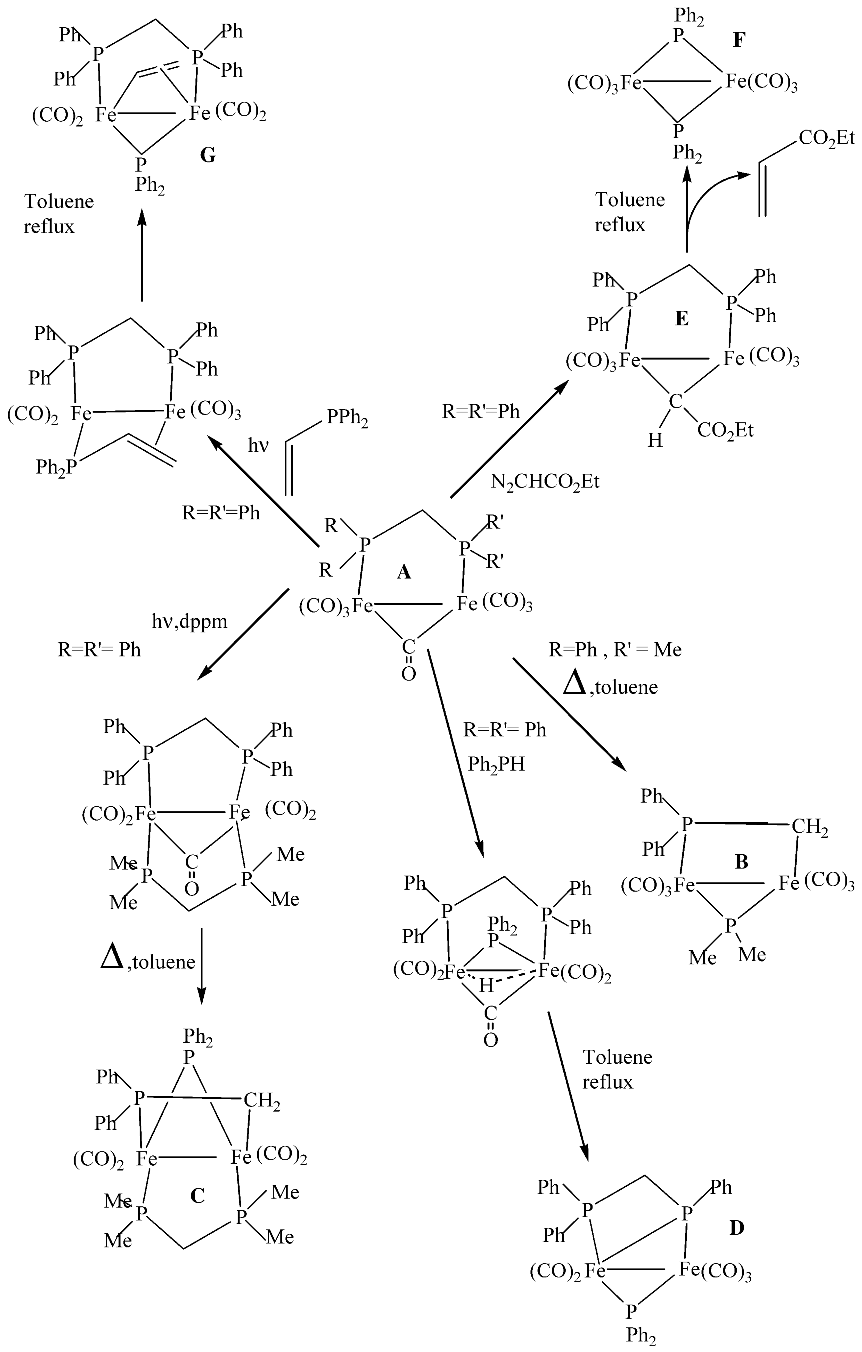
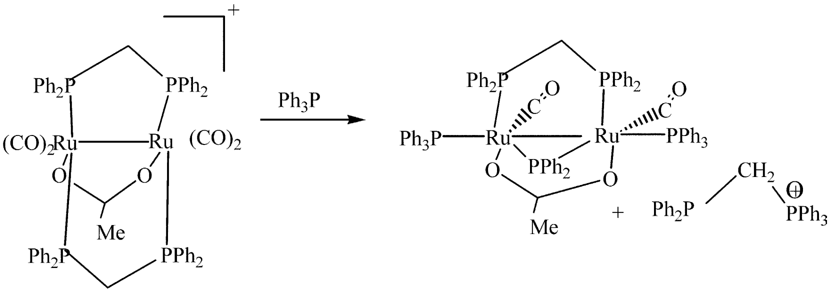


Fig. 1.

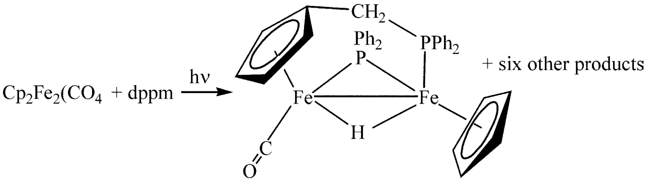
phido bridge is obtained by heating in toluene the photochemical product from (A) and dppm [63,64]. Reaction of (A) with diphenylphosphine also leads to a diphenylphosphido bridge [65], and heating this in toluene leads to P–Ph cleavage and complex (D) [66]. When the bridging carbonyl group of (A) is replaced by the bridging substituted methylene group $CHCO_2Et$ (E), the final product is again a complex with a diphenylphosphido bridge (F), but in addition ethyl acrylate is eliminated. This involves a multistep reaction path, which presumably occurs within the coordination sphere of the complex [67]. Photochemical reaction of A with diphenylvinylphosphine causes the bridging carbonyl group to be replaced by the phosphine, and on heating the P-vinyl group is cleaved to give a complex (G) which exhibits fluxional behaviour at 108 °C [68]. Further reactions involving P–C cleavage on this dinuclear iron system have been reported by the same group [69–71], and by Carty and coworkers [72].

Shiu and co-workers have studied a related ruthenium system (Eq. (26)) [73], and a case of Ph–P cleavage in a bimetallic Ru–Rh complex has been reported by Poilblanc and co-workers [74].



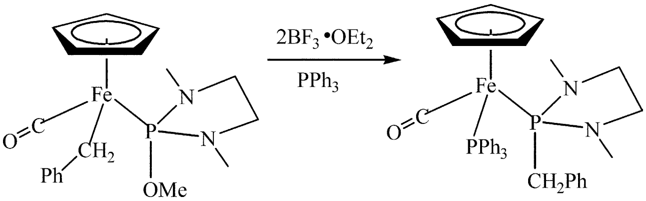
(26)

The photochemical reaction between $Cp_2Fe_2(CO)_4$ and dppm leads to seven products not all of which involve P–C cleavage. In some of the products a cyclopentadienyl ring is attacked as shown (Eq. (27)) [75]. The photochemistry of $Cp_2M_2(CO)_4$ systems has been reviewed [76].



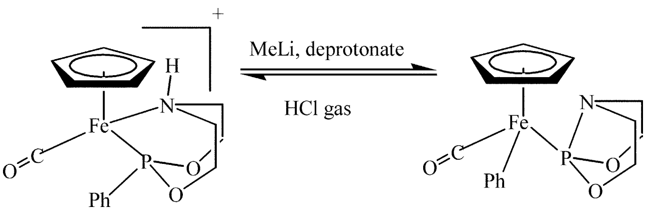
(27)

A migration of an alkyl group from iron to phosphorus has been reported to occur when some cyclopentadienyliron-aminophosphite complexes are treated with boron trifluoride etherate (Eq. (28)) [77].



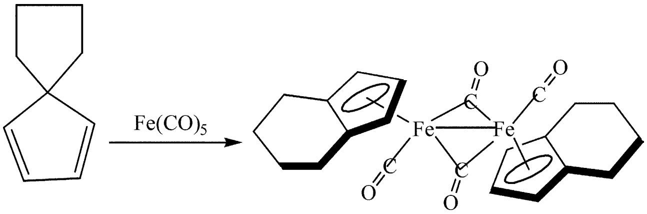
(28)

The reaction involving the transfer of a phenyl group from phosphorus to iron with the formation of a bicyclic ligand is remarkable for being reversible (Eq. (29)) [78].



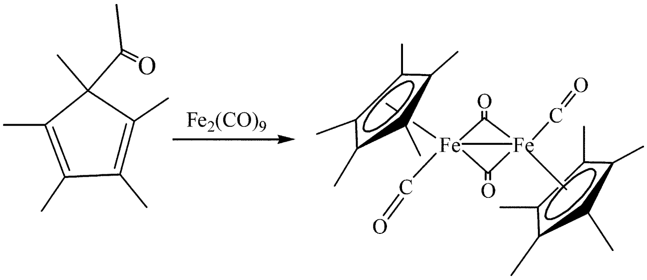
(29)

Hallam and Pauson reported that skeletal isomerisation occurred when a spirocyclopentadiene reacted with iron pentacarbonyl Eq. (30) [79].



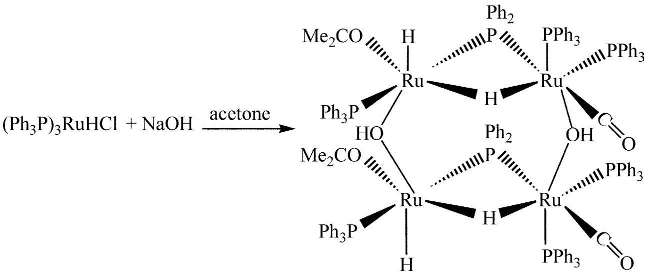
(30)

This is just one example of a considerable volume of work involving 5,5-disubstituted cyclopentadienes with iron carbonyls. King and Efarty carried out the reaction between 5-acetyl-pentamethylcyclopentadiene and $Fe_2(CO)_9$ under a variety of conditions. In refluxing 2,2,5-trimethylhexane the main product is pentamethylcyclopentadienyliron dicarbonyl dimer (Eq. (31)) [80]. Eilbracht and co-workers have also published several papers in this area [81,82].



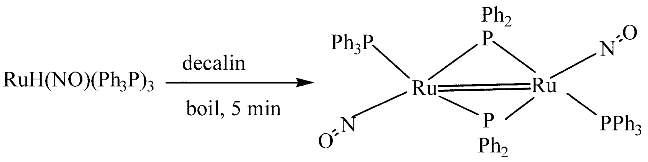
(31)

Wilkinson and co-workers reported that the well known catalyst $(Ph_3P)_3RuHCl$ on treatment with NaOH in acetone gives rise to a tetranuclear compound with bridging diphenylphosphido groups (Eq. (32)) [83].



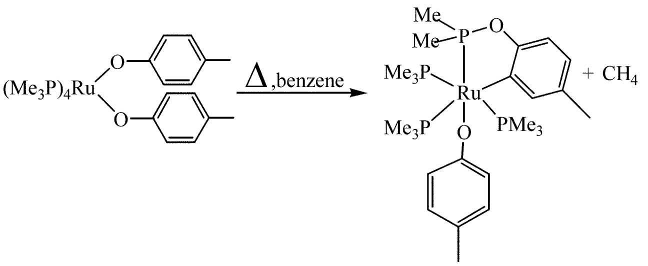
(32)

Eisenberg and co-workers reported the formation of a dinuclear ruthenium nitrosyl complex by thermolysis of the mononuclear triphenylphosphine complex $RuH(NO)(PPh_3)_3$. They also prepared it independently from $Ru(NO)Cl_3$, $PPh_3$ and $LiPPh_2$. The crystal structure determination was carried out on the methyldiphenylphosphine analogue, and had a Ru–Ru distance of 2.629(2) Å, for which a double bond was postulated (Eq. (33)) [84].



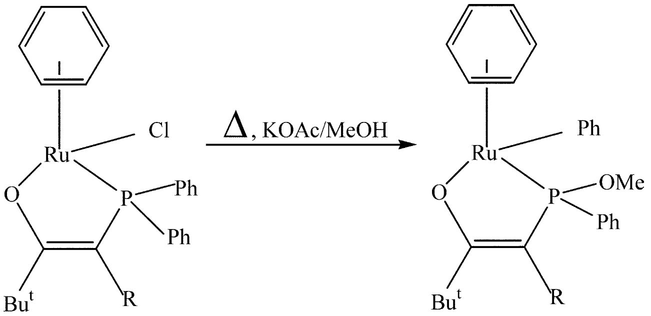
(33)

An unusual reaction which involves the migration of a *p*-methylphenolate ligand from ruthenium to phosphorus (the reverse of the majority of migrations) and *ortho*-metallation of the benzene ring was reported by Bergman and co-workers (Eq. (34)) [85].



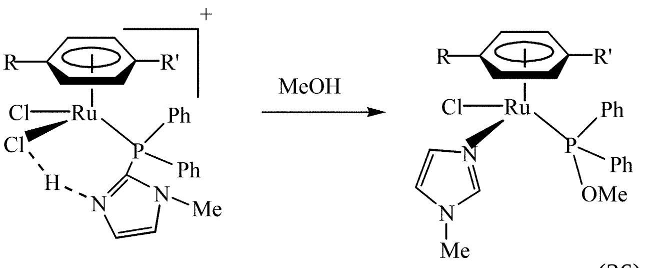
(34)

A reaction involving phenyl migration and methanolysis has been reported by Crochet et al. (Eq. (35)) [86].



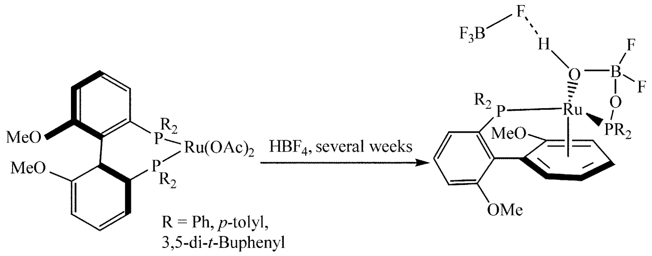
(35)

Another reaction involving the replacement of a P–C bond by P–OMe has been reported by Jalón and co-workers Eq. (36) [87].



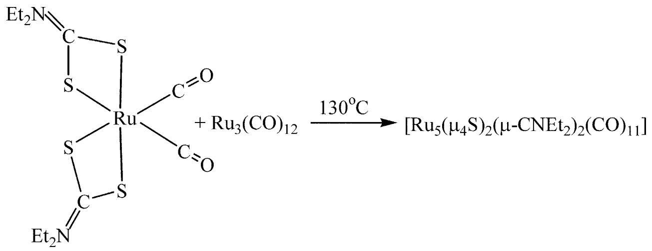
(36)

A complicated rearrangement which also involves the partial hydrolysis of a tetrafluoroborate anion has been reported by Pregosin and co-workers. The C–P bond of one of the phosphorus substituents has been cleaved, and the phosphorus is incorporated as a phosphinito group in a five-membered ring (Eq. (37)). Since the original report of this reaction [88], the work has been considerably extended and reviewed [89].



(37)

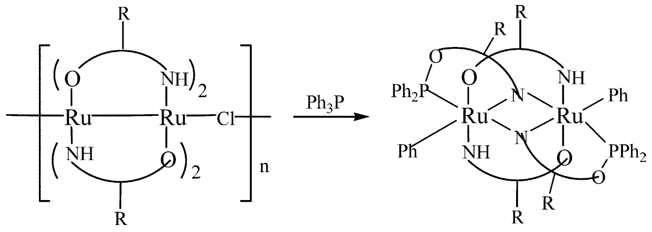
Deeming and Vaish have reported the cleavage of C–S bonds in dithiocarbamates of ruthenium (Eq. (38)) [90]. Analogous results were reported by Bodensieck and co-workers [91].



(38)

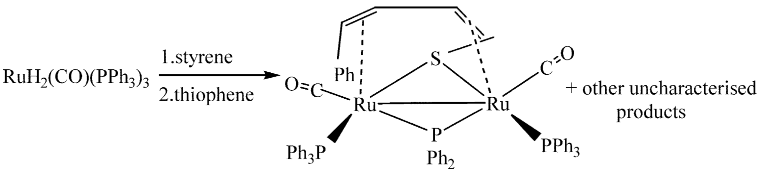
The reaction of the dialkynylsulfide $S(C{\equiv}CSiMe_3)_2$ with $Ru_3(CO)_{12}$ leads to cleavage of a C–S bond in the initial product and on pyrolysis, to a $Ru_4$ cluster with a sulfur atom coordinated to a tetrahedron of ruthenium atoms [92]. All three possible isomers of diphenylphosphinopyrrole react with $Ru_3(CO)_{12}$ to give tetranuclear ruthenium carbonyl clusters. In the case of the isomer in which the phosphorus is bonded to nitrogen the reaction involves the cleavage of a N–P bond [93].

Cotton and co-workers have reported reactions involving polynuclear amide complexes and triphenylphosphine in which a phenyl group is transferred to the ruthenium, R = dimethoxyphenyl (Eq. (39)) [94,95].



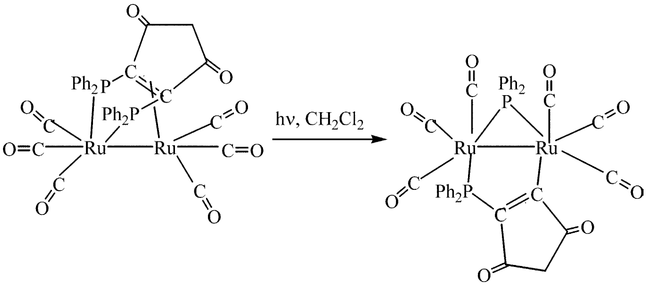
(39)

An example from ruthenium chemistry which includes both C–P and C–S cleavage and a subsequent C–C bond formation to the phenyl group was reported by Onishi and co-workers, who also suggest a mechanism for the formation of the dinuclear complex (Eq. (40)) [96].



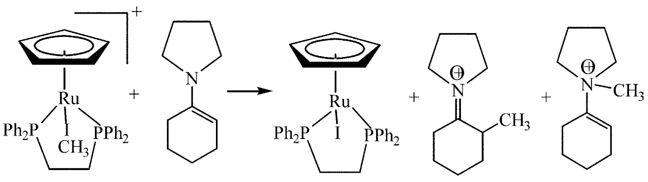
(40)

Dinuclear compounds of ruthenium can also bring about C–P bond cleavage (Eq. (41)) [97].



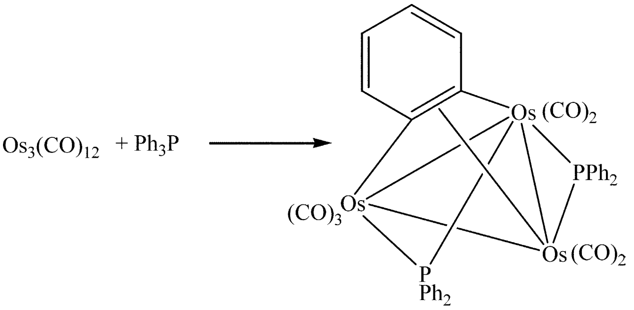
(41)

There is not a great range of complexes of haloalkanes, but it is not surprising that the alkylating ability of iodomethane is retained on coordination to ruthenium, a reaction which leads to the cleavage of a iodine–carbon bond (Eq. (42)) [98].



(42)

Some of the early work on P–C cleavage reactions was carried out using triphenylphosphine with $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. Nyholm and co-workers [99] reported the isolation of $Os_3(CO)_7(\mu_2\text{-}PPh_2)_2(\mu_3\text{-}C_6H_4)$ which was shown by X-ray crystallography to contain a bridging doubly metallated benzene ligand, as well as two bridging diphenylphosphido groups (Eq. (43)) [100,101]. Analogous work with $Me_2PhP$ was reported by Deeming et al. [102] and the products of the thermolysis of $Os_3(CO)_{11}(AsPh_3)$ in refluxing nonane have been reported by Tay and Leong [103].

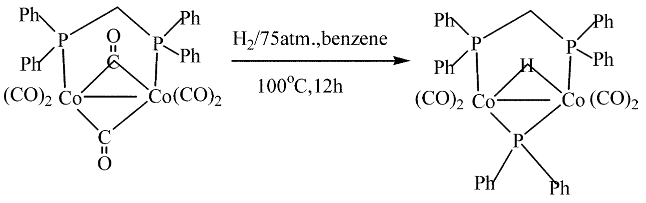


(43)

The analogous ruthenium compound $Ru_3(CO)_7(\mu_2\text{-}PPh_2)_2(\mu_3\text{-}C_6H_4)$ was reported by Stone and co-workers although with ruthenium there is a tendency to form dinuclear complexes [104]. A comparison of the structures of the ruthenium and osmium compounds shows them to be very similar in their molecular dimensions [105]. This area was subsequently developed by Knox and co-workers [106], who later found that the dimetallated benzene ruthenium complex is a good catalyst for the hydrogenation of alkynes [107].

## 7. Cobalt, rhodium and iridium

In dinuclear compounds the formation of phosphido bridges is a common occurrence. $DppmCo_2(CO)_6$ reacts with hydrogen under pressure to give a tetracarbonyl with a bridging diphenylphosphido ligand by cleavage of P–C bond to the central methylene group (Eq. (44)) [108].

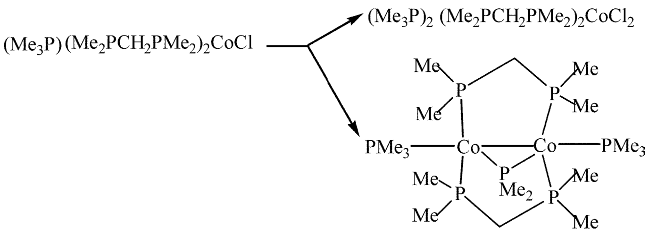


(44)

A similar diphenylphosphido bridged dicarbonyl compound can be made from $CoCl_2{\cdot}6H_2O$ with dppm and carbon monoxide at atmospheric pressure. With nickel a cation is produced [109].

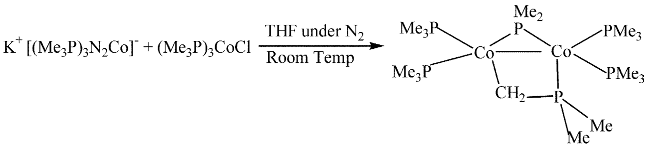
An unusual paramagnetic dimethylphosphido bridged cobalt compound arises from reactions involving trimethylphosphine and dmpm (Eqs. (45) and (46)) [110]. The magnetic moment of the dinuclear compound is 1.85 $\mu_B$ per dimeric unit.

$$(Me_3P)_3CoCl + Me_2PCH_2PMe_2 \longrightarrow (Me_3P)(Me_2PCH_2PMe_2)_2CoCl \tag{45}$$



(46)

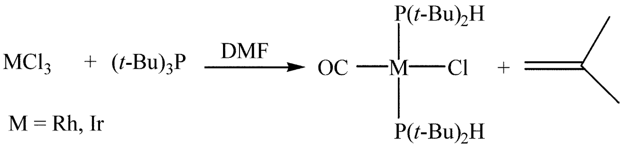
A reaction reported by Klein and co-workers has both a C–H bond activation and a C–P bond cleavage (Eq. (47)) [111].



(47)

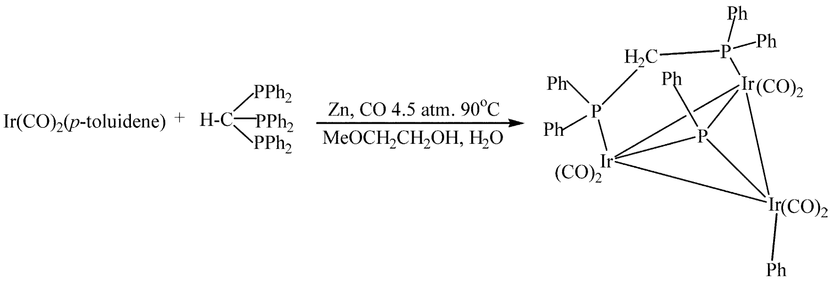
$(Ph_3P)_3CoCl$ reacts with $[S_2C{=}C(CN)_2]^{2-}$ to give a pentanuclear cluster in which one C–S bond has been cleaved [112].

The reaction of $(t\text{-}Bu)_3P$ with rhodium or iridium trichloride in DMF leads to cleavage of the tertiary butyl groups from the phosphorus and formation of complexes in the +1 oxidation state (Eq. (50)) [117]. See also Eq. (63) below.



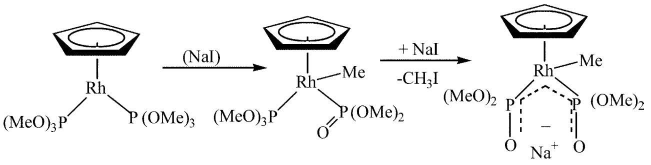
(50)

A reaction involving the formation of a cluster and a P–C cleavage was reported by Smith and co-workers (Eq. (51)) [118].



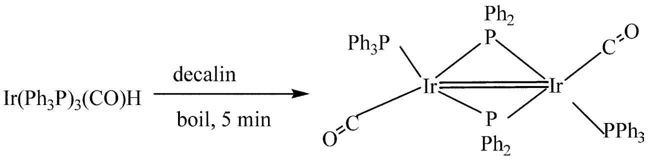
(51)

The Michaelis Arbusov reaction in which a phosphite is converted into a phosphonate on quarternisation has a parallel in coordination chemistry, and has been reported for a cyclopentadienyl rhodium complex (Eq. (48)) [113]. The topic has been reviewed and includes examples of C–O cleavage in complexes of groups 6–10 of the periodic table [114] (see under platinum).



(48)

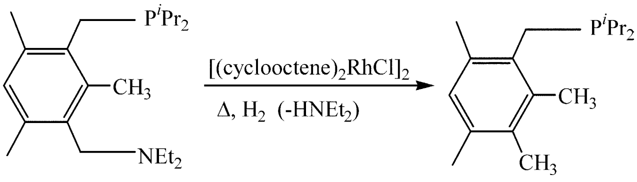
One of the early reports of P–C cleavage concerned the formation of a dinuclear diphenylphosphidoiridium complex by heating $Ir(PPh_3)_3(CO)H$ in decalin. The crystal structure revealed an Ir–Ir distance of 2.554 Å, and electron counting suggests that this is a double bond (Eq. (49)) [115]. This compound was also reported by Bellon and co-workers who used $Ir(PPh_3)_3(CO)H$ or $Ir(PPh_3)_3H_3$ as starting material and carried out the reaction in DMF [116].



(49)

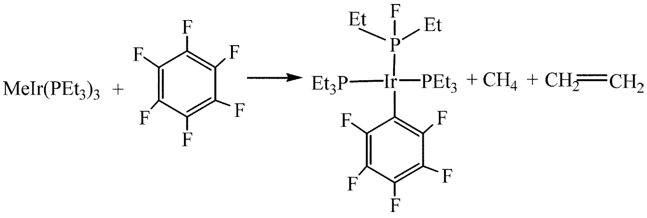
In 1972 Chini and co-workers noted that during the hydroformylation of propene using a $Rh_4(CO)_{12}/PPh_3$ catalyst benzene and cyclohexane could be detected. They proposed that phosphido bridged complexes were probably formed under these conditions [119]. A reaction which occurs during the hydroformylation of propene catalysed by rhodium complexes of triphenylphosphine, is the conversion of the triphenylphosphine to diphenylpropylphosphine [120]. Sakahura studied how different metals affect the P–C bond cleavage [121] and workers at Union Carbide studied the mechanism of formation of diphenylpropylphosphine [122] and the interchange of aryl groups under rhodium catalysed hydroformylation conditions [123]. P–C cleavage also occurs during hydroformylation with cobalt catalysts [124,125]. A summary of the deactivation of hydroformylation catalysts has appeared [126]. A remarkable C–C cleavage reaction was reported by Milstein and co-workers, which involves a coordination compound of rhodium with a pincer ligand based on trimethyl benzene. It was found that the methyl group between the phosphine arms of the pincer ligand 1,3-bis(diisopropylphosphinomethylene)mesitylene was lost when the ligand was reacted with hydrogen in the presence of $[(cyclooctene)_2RhCl]_2$ in dioxane at 180 °C. A postulated mechanism is given in Fig. 2 [127].

In a later study a C–N cleavage reaction was observed (Eq. (52)) [128]. The reactivity of complexes of pincer ligands has been reviewed [129] and extended [130]



(52)

One of the ethyl groups of triethylphosphine coordinated to iridium in MeIr(PEt$_3$)$_3$ is replaced by fluorine on reaction with hexafluorobenzene (Eq. (53)) [131].



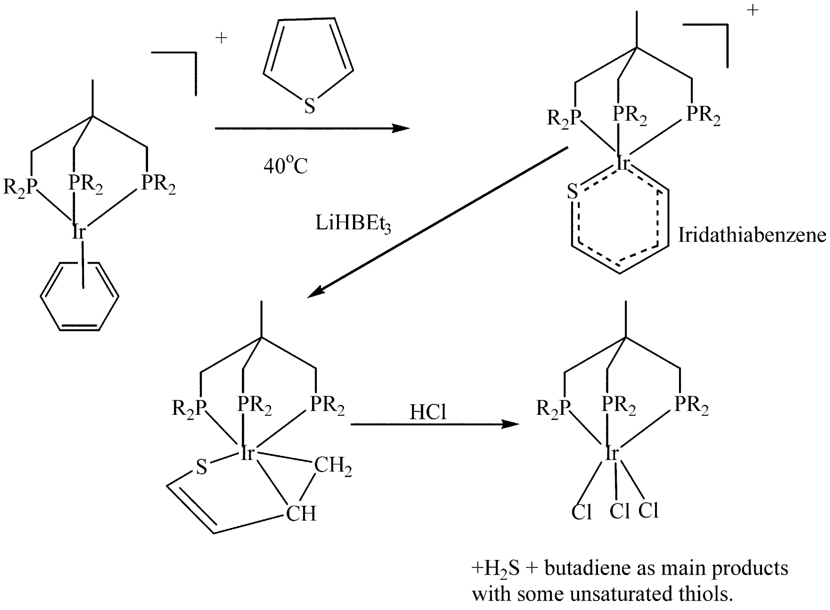
(53)

Bianchini and co-workers have studied the homogeneous hydrodesulfurisation reaction, some steps of which including the C–S cleavage with iridium complexes are illustrated below (Eq. (54)) [132].

A similar reaction with cyclooctane leads to cyclooctene, but in this case the [IrH$_2$($\eta^2$-O$_2$CCF$_3$)(PR$_3$)$_2$] catalyst is deactivated by P–C cleavage [135].

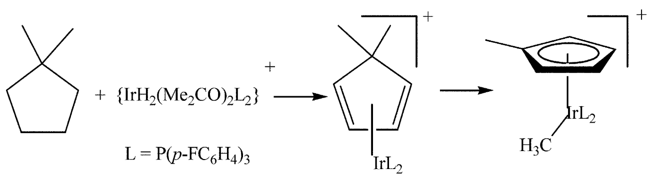
## 8. Nickel, palladium and platinum

Several of the early observations of migration reactions were reported for this triad. Indeed, the reaction involving K$_2$PtCl$_4$ and P(OEt)$_3$ (Eq. (56)), is even earlier than the nickel case referred to in the introduction, but does not involve the bonds to the donor atom. The reaction was reported in 1944 by Grinberg and Troitskaya and gives the hydrogen bridged chelate shown [136,137]. The X-ray structure of the methyl analogue was reported in 1984, although the ethyl compound is disordered [138]. The original workers did recognise that each phosphorus atom had lost an ethyl group.

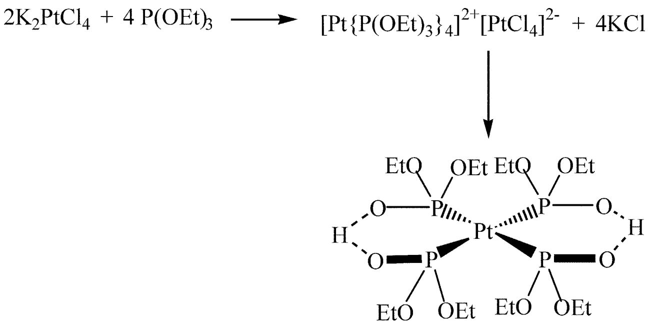


(54)

Iridium complexes can be used to dehydrogenate cycloalkanes, a reaction which recalls the use of iridium in the production of aromatics from petroleum [133]. 5,5-Dimethylcyclopentane undergoes C–C cleavage and dehydrogenation to give a methylcylopentadienyl complex (Eq. (55)) [134].



(55)



(56)

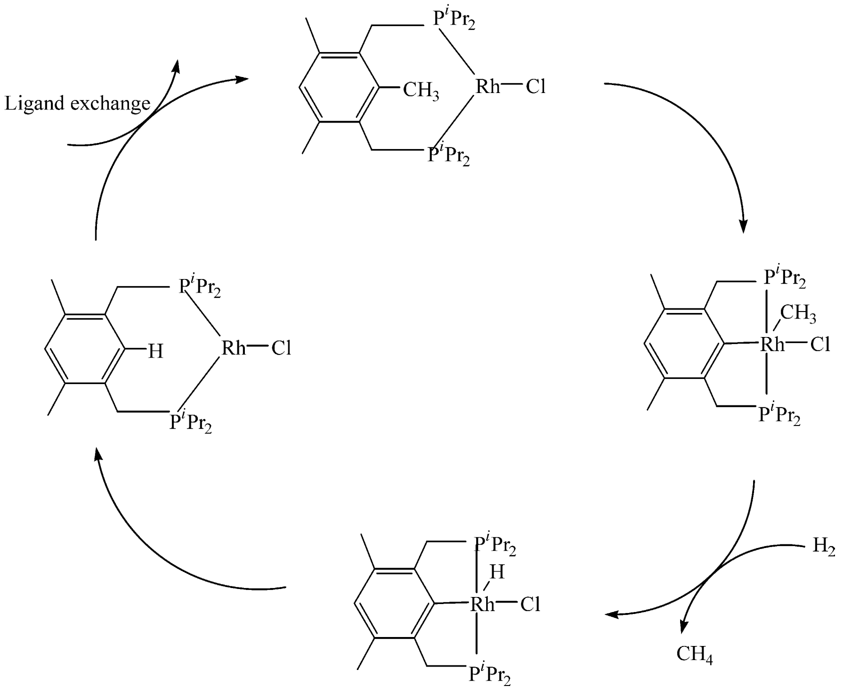
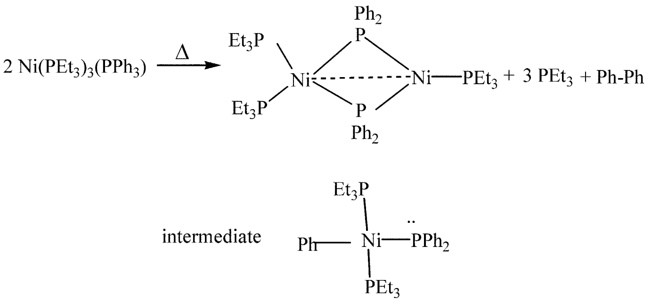


Fig. 2.

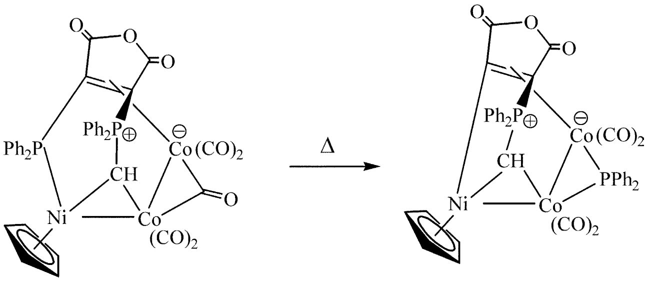
Carty and co-workers [13] prepared the dinuclear $[Pt_2(PPh_3)_2(PPh_2)_2]$ and trinuclear $[Pt_3(PPh_3)_2(PPh_2)_3Ph]$ by heating solutions of $[Pt(PPh_3)_4]$ for several days in benzene (see Eq. (67)). Both compounds were characterised by X-ray diffraction and have bridging diphenylphosphido groups and the trinuclear compound also has a phenyl group σ-bonded to one of the platinum atoms. Similar palladium compounds were suggested by Coulson starting from $[Pd(PPh_3)_4]$, but without structural characterisation [139].

A well-characterised example of a migration reaction involving loss of an organic group from the donor atom of a coordination compound to the metal atom was reported by Fahey and Mahan (Eq. (57)) [140].



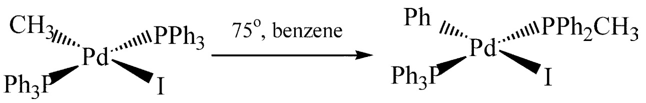
(57)

The thermal reaction shown in Eq. (58) has been reported by Bott and co-workers, who studied the kinetics which were found to be first order with $\Delta H^{\neq} = 131\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\neq} = 88\,\mathrm{JK^{-1}\,mol^{-1}}$ [141].



(58)

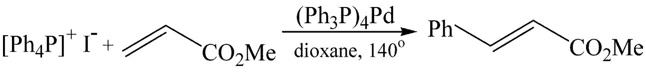
An example of migration from phosphorus to palladium, or more specifically the interchange between the metal and the coordinated phosphorus, was reported by Norton and co-workers in 1995 (Eq. (59)) [142].



(59)

A similar reaction in which two aryl groups interchange was studied by Novak and co-workers who found that in contrast to the alkyl–aryl exchange, the interchange is inhibited by the addition of phosphine [143]. Grushin investigated the effect of changing the halogen on the rate of aryl exchange in $[(Ph_3P)_2Pd(C_6D_5)X]$ X = Cl, Br and I and found that the rate of exchange decreases in the order I > Br > Cl [144]. This interchange of groups from phosphorus to palladium can explain impurities arising in the products of the Heck reaction [145,146].

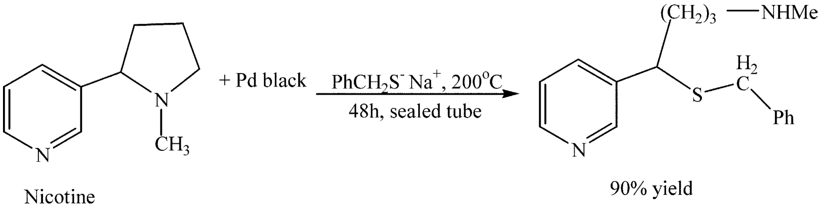
Reactions involving phosphonium salts and palladium complexes have been reported by Yamamoto and co-workers [147]. Although the reactions involve P–C cleavage, this may occur outside the coordination sphere of the palladium. The yields are not spectacular but provide an interesting insight into the reactivity of the P–C bond. Thus a Heck reaction carried out with tetraphenylphosphonium iodide rather than iodobenzene gave methyl cinnamate (Eq. (60))



(60)

Aryl phosphonic acids have also been used as a source of the aryl group in the Heck reaction, and the mechanism is thought to involve a phosphorus to palladium migration [148].

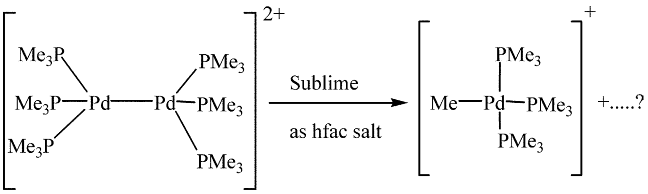
In 1979 Murahashi and Yano reported a procedure for the cleavage of N–C bonds in amines, involving palladium and a thiolate (Eq. (61)) [18].



(61)

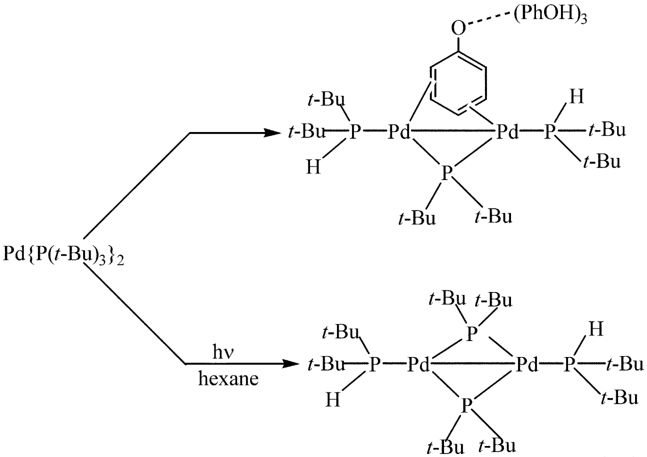
The mechanism was thought to involve nucleophilic attack by the thiolate anion at a coordinated iminium species.

Sublimation of a dinuclear palladium hfac salt leads to methyl transfer (Eq. (62)) [149].



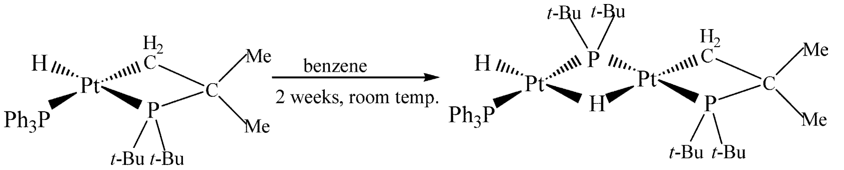
(62)

Tertiary butyl groups bonded to phosphorus are particularly susceptible to cleavage in palladium and platinum complexes. Leoni et al. [150] have described work with $P(t\text{-}Bu)_3$ and palladium. The reaction between $Pd\{P(t\text{-}Bu)_3\}_2$ and phenol gives a compound with a phosphido bridge and a bridging π-bonded phenoxide, the oxygen atom of which is involved in a hydrogen bonded network with three other phenol molecules. Photolysis of the same complex gives rise to a dinuclear complex with two phosphido ligands. In both cases the tertiary phosphine becomes a secondary phosphine by P–C cleavage (Eq. (63)) [151]. See also Eq. (50) above.



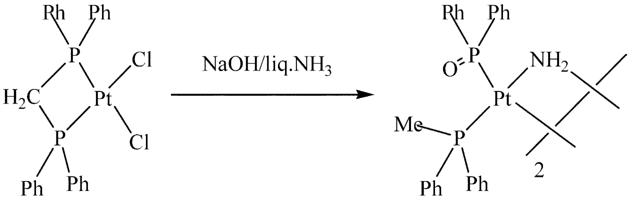
(63)

Goel and Goel reported the formation of a dinuclear platinum complex with a phosphido bridge on standing a solution of a mononuclear complex in benzene for 2 weeks. The low symmetry of the product leads to a very complicated $^{31}P$ NMR spectrum (Eq. (64)) [152].



(64)

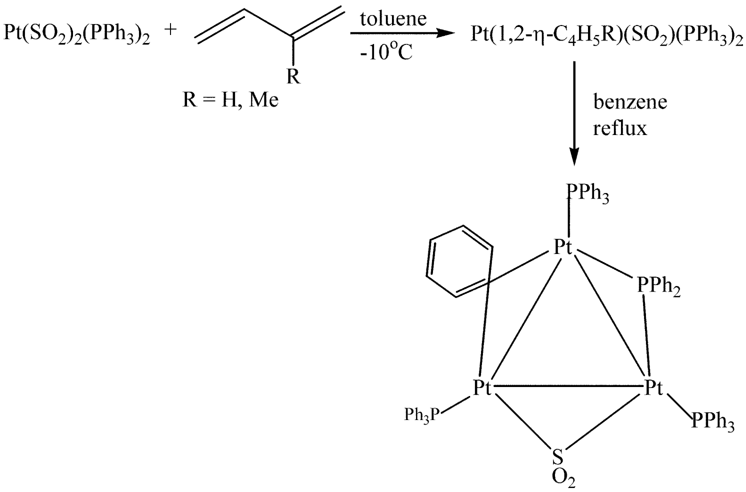
The cleavage of the four-membered ring of a dppm complex of platinum was reported by Alcock et al. (Eq. (65)) [153]. This is similar to the well-known cleavage of substituents from phosphorus using sodium metal in liquid ammonia. A similar cleavage can be brought about by the action of potassium hydroxide on a manganese dmpm complex [154].



(65)

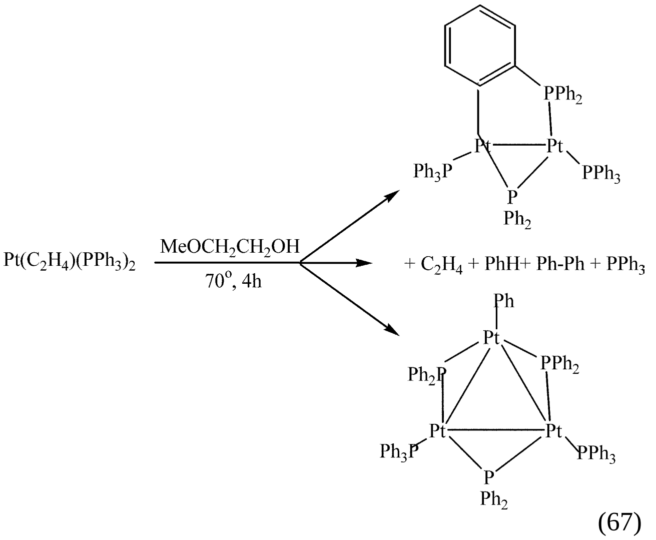
Another example involving the formation of phosphorus oxygen bonds from tertiary phosphines with $Pd(OAc)_2$ was reported by Kikukawa and Matsuda [155] and an analogous case has been recently reported by Helfer and Atwood [156].

In 1980 Mingos and co-workers described the formation of a triangular platinum cluster, which contained both the diphenylphosphido and phenyl groups from triphenyl phosphine (Eq. (66)) [157]. The phenyl group bridges one edge of the triangle.



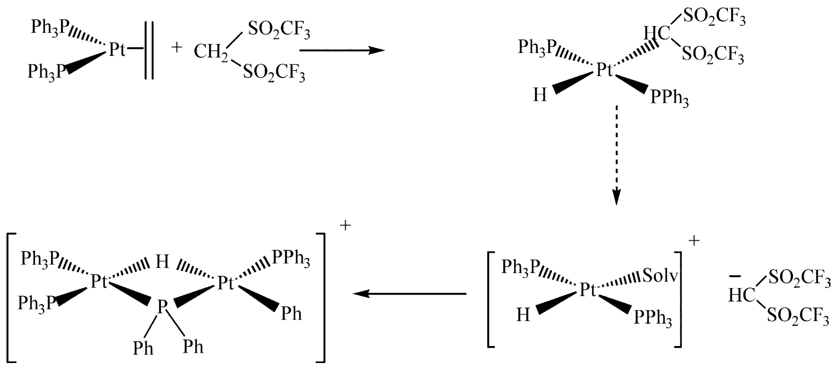
(66)

Work by Braunstein and co-workers showed that controlled thermolysis of $Pt(C_2H_4)(PPh_3)_2$ gave a mixture which contains both di and trinuclear complexes (Eq. (67)) [158]. The trinuclear compound had previously been reported by Carty and co-workers [13].



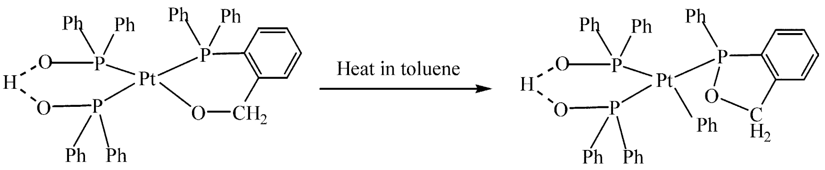
(67)

The work of Siedle and co-workers provides an example from platinum chemistry, in which a phenyl group migrates from a coordinated phosphorus onto platinum (Eq. (68)) [159].



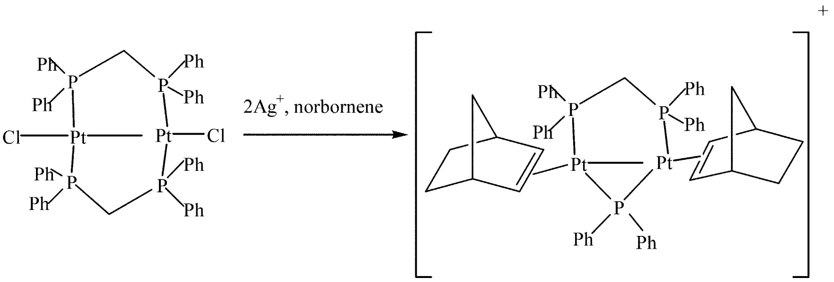
(68)

The same dinuclear cation was made earlier by Venanzi and co-workers [160], and can be made by simply standing a solution of $[(PPh_3)_2Pt(OH_2)H]\ BF_4^-$ in aqueous thf [161]. Banditelli and co-workers [162] have also reported the formation of a dinuclear platinum compound with bridging diphenylphosphido and hydride ligands from 1,4-bis(diphenyl)butane, but in this case the compound could not be definitively characterised. Phenyl migration from phosphorus to platinum was also reported for phosphinito complexes of platinum on heating in toluene (Eq. (69)) [163].



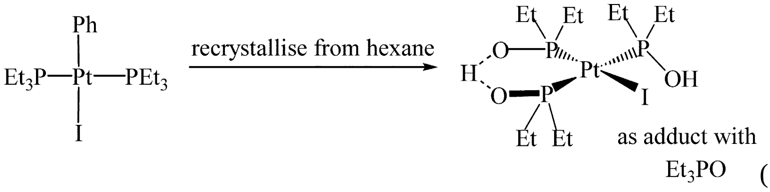
(69)

Peringer and co workers have reported a P–C cleavage which leads to the formation of a norbornene complex with a diphenylphosphido bridge (Eq. (70)) [164].



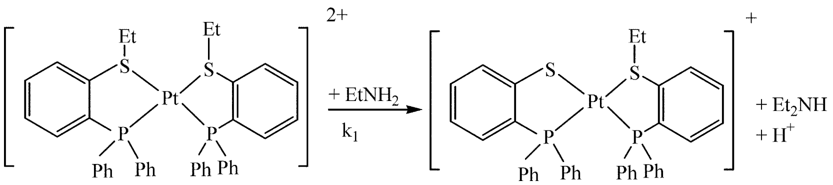
(70)

Another reaction involving P–C cleavage in this case together with Pt–C cleavage is the transformation which occurred on recrystallising *trans*-$(Et_3P)_2Pt(I)Ph$ (Eq. (71)) [165].



(71)

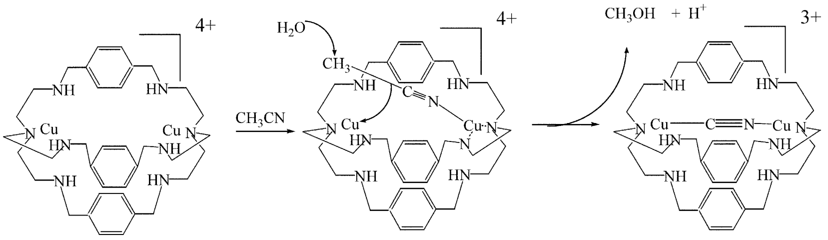
The majority of examples quoted in this review are preparative results often obtained serendipitously, but the final example from platinum chemistry is concerned with the kinetics of the ethyl transfer reaction from sulfur to nitrogen. Both $k_1$ and $k_2$ for the second ethyl transfer were measured (Eq. (72)) [166].



(72)

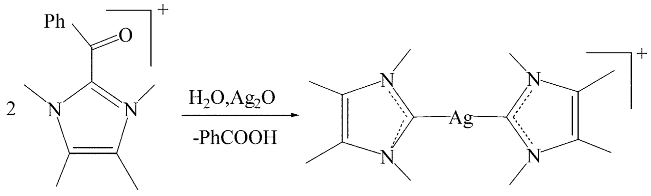
## 9. Copper, silver and gold

Very recently the cleavage of the C–C bond in acetonitrile has been reported (Eq. (73)) [167]. The reaction involves a dinuclear copper (II) cryptate and at the end of the reaction, which takes about a day at room temperature, the cyanide occupies a bridging position between the two copper ions.



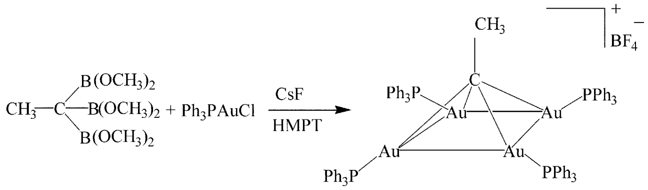
(73)

Crabtree and co-workers have very recently reported the cleavage of a C–C bond on reaction between an imidazolium salt and silver oxide Eq. (74) [168].



(74)

There are a number of gold cluster complexes the formation of which involve cleavage of substituents from another reactant (Eq. (75)) [169–171].



(75)

It is not clear in the quoted examples for silver and gold whether the reactions can really be classified as reactions occurring within the coordination sphere of the metal ion.

## 10. Conclusion

The survey shows that the reactions involving cleavage and migration are very varied in nature and the resulting structures unpredictable. Nearly all the structures in this review have been identified by X-ray diffraction. The range of the chemistry is enormous and it is difficult to uncover general principles, which help to predict where future examples will be found. It has not been possible to discuss the mechanisms of these migration and cleavage reactions, as the reports of the reactions seldom include even a speculative mechanism. In the majority of cases we have simply stated the outcome of the reaction, because the mechanisms are unknown.

## Acknowledgements

I wish to thank Professor Tony Deeming and Dr. Graeme Hogarth of University College London, for providing information and helpful criticism of the manuscript. I am also grateful to a referee for drawing my attention to three references which have extended the coverage of this review.

## References

[1] C.S. Kraihanzel, J. Organomet. Chem. 73 (1974) 137.
[2] R.S. Nyholm, J. Chem. Soc. (1950) 2061.
[3] B. Bosnich, R.S. Nyholm, P.J. Pauling, M.L. Tobe, J. Am. Chem. Soc. 90 (1968) 4741.
[4] W.R. Cullen, B.V. Harbourne, B.V. Liengme, J.R. Sams, Inorg. Chem. 9 (1970) 702.
[5] F.W.B. Einstein, A.M. Pilotti, R. Restivo, Inorg. Chem. 10 (1971) 1947.
[6] C. Elschenbroich, A. Salzer, Organometallics, VCH, Weinheim, 1989, p. 10.
[7] H.-F. Grützmacher, D. Kirchhoff, H. Grützmacher, Organometallics 20 (2001) 3738.
[8] P.E. Garrou, Chem. Rev. 85 (1985) 171.
[9] M. Michman, Israel J. Chem. 27 (1986) 241.
[10] P.W.N.M. van Leeuwen, Appl. Catal. (A) 212 (2001) 61.
[11] J.L. Vidal, J.M. Troup, J. Organomet. Chem. 213 (1981) 351.
[12] C.J. den Reijer, M. Wörle, P.S. Pregosin, Organometallics 20 (2000) 309.
[13] N.J. Taylor, P.C. Chieh, A.J. Carty, J.C.S. Chem. Commun. (1975) 448.
[14] J.V. Ortiz, Z. Havlas, R. Hoffmann, Helv. Chim. Acta 67 (1984) 1.
[15] M.H. Chisholm, Polyhedron 16 (1997) 3071.
[16] M. Brorson, J.D. King, K. Kiriakidou, F. Presttopino, E. Nordlander, in: P. Braunstein, L.A. Oro, P.R. Raithby (Eds.), Metal Clusters in Chemistry, Wiley–VCH, Weinheim, 1999, p. 741.
[17] M.D. Curtis, J. Cluster Sci. 7 (1996) 247.
[18] S.I. Murahashi, T. Yano, J. Chem. Soc. Chem. Commun. (1979) 270.
[19] C. Choo Yin, A.J. Deeming, J. Organomet. Chem. 133 (1977) 123.
[20] C. Choo Yin, A.J. Deeming, J. Organomet. Chem. 144 (1978) 351.
[21] R.M. Laine, D.W. Thomas, L.W. Cary, J. Am. Chem. Soc. 104 (1982) 1763.
[22] S. Aime, R. Gobetto, F. Padovan, M. Botta, E. Rosenberg, R.W. Gellert, Organometallics 6 (1987) 2074.
[23] R.D. Adams, J.E. Babin, H.S. Kim, J.T. Tanner, T.A. Wolfe, J. Am. Chem. Soc. 112 (1990) 3426.
[24] K. Osakada, T. Koizumi, T. Yamomoto, Angew. Chem. Int. Ed. Engl. 37 (1998) 349.
[25] P. Braunstein, N.M. Boag, Angew. Chem. Int. Ed. Engl. 40 (2001) 2427.
[26] G.L. Geoffroy, S. Rosenberg, P.M. Shulman, R.R. Whittle, J. Am. Chem. Soc. 106 (1984) 1519.
[27] P.M. Shulman, E.D. Burkhardt, E.G. Lundquist, R.S. Pilato, G.L. Geoffroy, A.L. Rheingold, Organometallics 6 (1987) 101.
[28] N. Chaouche, J. Fornies, C. Fortuno, A. Kribii, A. Martin, P. Karipidis, A.C. Tsipis, C.A. Tsipis, Organometallics 23 (2004) 1797.
[29] T. Mizuta, M. Onishi, T. Nakazono, H. Nakazawa, K. Miyoshi, Organometallics 21 (2002) 717.
[30] C. Archambault, R. Bender, P. Braunstein, A. Decian, J. Fischer, Chem. Commun. (1996) 2729.
[31] F.W.S. Benfield, M.L.H. Green, J. Chem. Soc. Dalton Trans. (1974) 1324.
[32] F.D. Mango, Coord. Chem. Rev. 15 (1975) 109.
[33] D.J. Tantillo, R. Hoffmann, J. Am. Chem. Soc. 123 (2001) 9855.
[34] M. Murakami, Y. Ito, in: S. Murai (Ed.), Activation of Unreactive Bonds and Organic Synthesis, Springer, Berlin, 1999.
[35] G. Lavigne, in: D.F. Shriver, H.D. Kaesz, R.D. Adams (Eds.), The Chemistry of Metal Cluster Complexes, VCH, New York, 1990, p. 201.
[36] K.E. Torraca, L. McElwee-White, Coord. Chem. Rev. 206–207 (2000) 469.
[37] Z. Weng, L.Y. Goh, Acc. Chem. Res. 37 (2004) 187.
[38] W. Hewertson, H.R. Watson, J. Chem. Soc. (1962) 1490.
[39] W. Gee, R.A. Shaw, B.C. Smith, Inorg. Syn. 9 (1967) 19.
[40] J. Dogan, J.B. Schulte, G.F. Swiegers, S.B. Wild, J. Org. Chem. 65 (2000) 951.
[41] D. Coucouvanis, R.K. Lester, M.G. Kanatzidis, D.P. Kessissoglou, J. Am. Chem. Soc. 107 (1985) 8279.
[42] N. Hovnanian, L.G. Hubert-Pfalzgraf, J. Organomet. Chem. 299 (1986) C29.
[43] F.A. Cotton, M.P. Diebold, W.J. Roth, Inorg. Chem. 25 (1986) 1728.

[44] J.H. Shin, G. Parkin, Chem. Commun. (1998) 1273.
[45] T. Nakajima, I. Shimazu, K. Kobayashi, Y. Wakatsuki, Inorg. Chem. 36 (1997) 6440.
[46] J.E. Davies, M.J. Mays, P.R. Raithby, K. Sarveswara, G.A. Solan, J. Chem. Soc. Dalton Trans. (2001) 1269.
[47] P. Planinic, D. Matkovic-Calogovic, Struct. Chem. 12 (2001) 439.
[48] G.R. Doel, N.D. Feasey, S.A.R. Knox, A.G. Orpen, J. Webster, J. Chem. Soc. Chem. Commun. (1986) 542.
[49] G. Garcia, M.E. Garcia, S. Melon, V. Rieva, M.A. Ruiz, F. Villafane, Organometallics 16 (1997) 624.
[50] R.H. Morris, J.F. Sawyer, C.T. Schweitzer, A. Sella, Organometallics (1989) 2099.
[51] K.W. Chiu, R.A. Jones, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1981) 1892.
[52] F.A. Cotton, J.A.M. Canich, R.L. Luck, K. Vidyasagar, Organometallics 10 (1991) 352.
[53] A.J. Deeming, M.K. Shinhmar, A.J. Arce, Y. De Sanctis, J. Chem. Soc. Dalton Trans. (1999) 1153.
[54] J.R. Blickensdorfer, H.D. Kaesz, J. Am. Chem. Soc. 97 (1975) 2681.
[55] J.R. Blickensdorfer, C.B. Knobler, H.D. Kaesz, J. Am. Chem. Soc. 97 (1975) 2686.
[56] H. Spies, H.-J. Pietzsch, Inorg. Chim. Acta 161 (1989) 151.
[57] M. Glaser, H. Spies, R. Berger, F.E. Hahn, T. Lügger, J. Johannsen, Inorg. Chim. Acta 257 (1997) 143.
[58] K. Chryssou, M. Pelecanou, I.C. Pirmettis, M.S. Papadopoulos, C. Raptopoulou, A. Terzis, E. Chiotellis, C.I. Stassinopoulos, Inorg. Chem. 41 (2002) 4653.
[59] H.J. Haupt, P. Balsaa, U. Flörke, Angew. Chem. Int. Ed. Engl. 27 (1988) 263.
[60] H.J. Haupt, P. Balsaa, U. Flörke, Inorg. Chem. 27 (1988) 280.
[61] M.A. Reynolds, I.A. Guzei, R.J. Angelici, J. Am. Chem. Soc. 124 (2002) 1689.
[62] B. Chaudret, B. Delavaux, R. Poilblanc, Coord. Chem. Rev. 86 (1988) 191.
[63] N.M. Doherty, G. Hogarth, S.A.R. Knox, K.A. Macpherson, F. Melchoir, A.G. Orpen, J. Chem. Soc. Chem. Commun. (1986) 540.
[64] N.M. Doherty, G. Hogarth, S.A.R. Knox, K.A. Macpherson, F. Melchoir, D.A.V. Morton, A.G. Orpen, Inorg. Chim. Acta 198–200 (1992) 257.
[65] G. Hogarth, M.H. Lavender, J. Chem. Soc. Dalton Trans. (1992) 2759.
[66] G. Hogarth, M.H. Lavender, J. Chem. Soc. Dalton Trans. (1993) 143.
[67] G. Hogarth, S.A.R. Knox, M.L. Turner, Chem. Commun. (1990) 145.
[68] G. Hogarth, J. Organomet. Chem. 407 (1991) 91.
[69] N.J. Grist, G. Hogarth, S.A.R. Knox, B.R. Lloyd, D.A.V. Morton, A.G. Orpen, Chem. Commun. (1988) 673.
[70] G. Hogarth, S.A.R. Knox, B.R. Lloyd, K.A. Macpherson, D.A.V. Morton, A.G. Orpen, Inorg. Chim. Acta 251 (1996) 167.
[71] G. Hogarth, S.A.R. Knox, B.R. Lloyd, K.A. Macpherson, D.A.V. Morton, A.G. Orpen, Chem. Commun. (1988) 360.
[72] A.A. Cherkas, S. Doherty, M. Cleroux, G. Hogarth, L.H. Randall, S.M. Breckenbridge, N.J. Taylor, A.J. Carty, Organometallics 11 (1993) 1701.
[73] K.B. Shiu, S.W. Jean, H.J. Wang, S.L. Wang, F.L. Liao, J.C. Wang, L.S. Liou, Organometallics 16 (1997) 114.
[74] B. Delavaux, B. Chaudret, R. Poilblanc, Organometallics 4 (1985) 935.
[75] C.M. Alvarez, B. Galan, M.E. Garcia, V. Riera, M.A. Ruiz, J. Vaissermann, Organometallics 22 (2003) 5504.
[76] T.E. Bitterwolf, Coord. Chem. Rev. 206–207 (2000) 419.
[77] H. Nakazawa, Y. Yamaguchi, T. Mizuta, S. Ichimura, K. Miyoshi, Organometallics 14 (1995) 4635.
[78] P. Vierling, J.G. Riess, A. Grand, J. Am. Chem. Soc. 103 (1981) 2466.
[79] B.F. Hallam, P.L. Pauson, J. Chem. Soc. (1958) 646.
[80] R.B. King, A. Efraty, J. Am. Chem. Soc. 94 (1972) 3773.
[81] P. Eilbracht, P. Dahler, Chem. Ber. 113 (1980) 542.
[82] P. Eilbracht, U. Mayser, Chem. Ber. 113 (1980) 2211.
[83] B.N. Chaudret, D.J. Cole-Hamilton, R.S. Nohr, G. Wilkinson, J. Chem. Soc. Dalton Trans. (1977) 1546.
[84] J. Reed, A.J. Schultz, C.G. Pierpoint, R. Eisenberg, Inorg. Chem. 12 (1973) 2949.
[85] J.F. Hartwig, R.G. Bergman, R.A. Anderson, J. Organomet. Chem. 394 (1990) 417.
[86] P. Crochet, B. Demerson, C. Rocaboy, Organometallics 15 (1996) 3048.
[87] A. Caballero, F.A. Jalón, B.R. Manzano, G. Espino, M. Pérez-Manrique, A. Mucientes, F.J. Poblete, M. Maestro, Organometallics 23 (2004) 5694.
[88] C.J. den Reijer, H. Rüegger, P.S. Pregosin, Organometallics 17 (1998) 5213.
[89] T.J. Geldbach, P.S. Pregosin, Eur. J. Inorg. Chem. (2002) 1907.
[90] A.J. Deeming, R. Vaish, J. Organomet. Chem. 460 (1993) C8.
[91] U. Bodensieck, H. Stoeckli-Evans, G. Rheinwald, G. Süss-Fink, J. Organomet. Chem. 433 (1992) 167.
[92] M.I. Alcalde, A.J. Carty, Y. Chi, E. Delgado, B. Donnadieu, E. Hernández, K. Dallmann, J. Sánchez-Nieves, J. Chem. Soc. Dalton Trans. (2001) 2502.
[93] A.J. Arce, A.J. Deeming, Y. De Sanctis, S.K. Johal, C.M. Martin, M. Shinkar, D.M. Speel, A. Vassos, Chem. Commun. (1998) 233.
[94] A.K. Chakravarty, F.A. Cotton, D.A. Tocher, J. Am. Chem. Soc. 106 (1984) 6409.
[95] A.K. Chakravarty, F.A. Cotton, Inorg. Chem. 24 (1985) 3584.
[96] H. Kawano, H. Narimatsu, D. Yamamoto, K. Tanaka, K. Hirai, M. Onishi, Organometallics 21 (2002) 5526.
[97] H. Shen, S.G. Bott, M.G. Richmond, Organometallics 14 (1995) 4625.
[98] R.J. Kulawiec, R.H. Crabtree, Organometallics 7 (1988) 1891.
[99] C.W. Bradford, R.S. Nyholm, J. Chem. Soc. Dalton Trans. (1973) 529.
[100] G.J. Gainsford, J.M. Guss, P.R. Ireland, R. Mason, J. Organomet. Chem. 40 (1972) C70.
[101] C.W. Bradford, R.S. Nyholm, G.J. Gainsford, J.M. Guss, P.R. Ireland, R. Mason, J. Chem. Soc. Chem. Commun. (1972) 87.
[102] A.J. Deeming, R.E. Kimber, M. Underhill, J. Chem. Soc. Dalton Trans. (1973) 2589.
[103] C.T. Tay, W.K. Leong, J. Organomet. Chem. 625 (2001) 231.
[104] M.I. Bruce, G. Shaw, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1972) 2094.
[105] M.I. Bruce, J.M. Guss, R. Mason, B.W. Skelton, A.H. White, J. Organomet. Chem. 251 (1983) 261.
[106] S.A.R. Knox, B.R. Lloyd, D.A.V. Morton, S.M. Nicholls, A.G. Orpen, J.M. Vinas, M. Weber, G.K. Williams, J. Organomet. Chem. (1990) 385.
[107] M. Castiglioni, S. Deabate, R. Giordano, P.J. King, S.A.R. Knox, E. Sappa, J. Organomet. Chem. 571 (1998) 251.
[108] B.E. Hanson, F.E. Fanwick, J.S. Mancini, Inorg. Chem. 21 (1982) 3811.
[109] D.J. Elliot, D.G. Holah, A.N. Hughes, H.A. Mirza, E. Zawada, J. Chem. Soc. Chem. Commun. (1990) 32.
[110] H.H. Karsh, B. Milewski-Mahrla, J.O. Besenhard, P. Hofmann, P. Stauffert, T.A. Albright, Inorg. Chem. 25 (1986) 3811.
[111] H.F. Klein, J. Wenniger, U. Schubert, Z. Naturforsch. B 34 (1979) 1391.
[112] M. Hong, W. Su, R. Cao, F. Jiang, H. Liu, J. Lu, Inorg. Chim. Acta 274 (1998) 229.
[113] H. Werner, R. Feser, Z. Anorg. Allg. Chem. 458 (1979) 301.
[114] T.B. Brill, S.J. Landon, Chem. Rev. 84 (1984) 577.
[115] R. Mason, I. Søtofte, S.D. Robinson, M.F. Uttley, J. Organomet. Chem. 46 (1972) C61.

[116] P.L. Bellon, C. Benedicenti, G. Caglio, M. Mannassero, J.C.S. Chem. Commun. (1973) 946.

[117] R.G. Goel, W.O. Ogini, Organometallics 1 (1982) 652.

[118] M.M. Harding, B.S. Nicholls, A.K. Smith, J. Chem. Soc. Dalton Trans. (1983) 1479.

[119] P. Chini, S. Martinengo, G. Garlaschelli, Chem. Commun. (1972) 709.

[120] S. Gregorio, G. Montrasi, M. Tampieri, P. Cavaliero d'Oro, G. Pagani, A. Andretta, Chem. Ind. (Milan) 62 (1980) 389.

[121] T. Sakakura, T.A. Tobayashi, T. Hayashi, Y. Kawabata, M. Tanaka, I. Ogata, J. Organomet. Chem. 267 (1984) 171.

[122] A.G. Abatjoglou, E. Billig, D.R. Bryant, Organometallics 3 (1984) 923.

[123] A.G. Abatjoglou, D.R. Bryant, Organometallics 3 (1984) 932.

[124] R.A. Dubois, P.E. Garrou, K.D. Lavin, H.R. Allcock, Organometallics 5 (1986) 460.

[125] R.A. Dubois, P.E. Garrou, Organometallics 5 (1986) 466.

[126] C.D. Frohning, C.W. Kohlpainter, H.W. Bohnen, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Wiley–VCH, Weinheim, 2002, p. 60.

[127] S.-Y. Liou, M.E. van der Boom, D. Milstein, Chem. Commun. (1998) 687.

[128] M. Gandelman, D. Milstein, Chem. Commun. (2000) 1603.

[129] M.E. van der Boom, D. Milstein, Chem. Rev. 103 (2003) 1759.

[130] L. Fan, L. Yang, C. Guo, B.M. Foxman, O.V. Ozerov, Organometallics 23 (2004) 4778.

[131] O. Blum, F. Frolow, D. Milstein, J.C.S. Chem. Commun. (1991) 258.

[132] A.M. Bianchini, M. Peruzzi, F. Vizza, P. Frediani, V. Herrera, R.A. Sanchez-Delgado, J. Am. Chem. Soc. 115 (1993) 2731.

[133] F. Garin, G. Maire, Acc. Chem. Res. 22 (1989) 100.

[134] R.H. Crabtree, R.P. Dion, D.J. Gibboni, D.V. McGrath, E.M. Holt, J. Am. Chem. Soc. 108 (1986) 7222.

[135] M.J. Burk, R.H. Crabtree, J. Am. Chem. Soc. 109 (1987) 8025.

[136] A.A. Grinberg, A.D. Troitskaya, Bull. Acad. Sci. URSS Classe Sci. Chim. (1944) 178.

[137] Reference 136 is abstracted in Chem. Abs. 39 (1945) 1604.

[138] J.M. Solar, R.D. Rogers, W.R. Mason, Inorg. Chem. 23 (1984) 373.

[139] D.R. Coulson, Chem. Commun. (1968) 1530.

[140] D.R. Fahey, J.E. Mahan, J. Am. Chem. Soc. 98 (1976) 4499.

[141] S.G. Bott, K. Yang, K.A. Talafuse, M.G. Richmond, Organometallics 22 (2003) 1383.

[142] D.K. Morita, J.K. Stille, J.R. Norton, J. Am. Chem. Soc. 117 (1995) 8576.

[143] F.E. Goodson, T.I. Wallow, B.M. Novak, J. Am. Chem. Soc. 119 (1997) 12441.

[144] V.V. Grushin, Organometallics 19 (2000) 1888.

[145] W.A. Herrmann, C. Brossmer, K. Öfele, M. Beller, H. Fischer, J. Organomet. Chem. 491 (1995) C1.

[146] N.J. Whitcombe, K.K. Hii, S.E. Gibson, Tetrahedron 57 (2001) 7449.

[147] M. Sakamoto, I. Shimizu, A. Yamamoto, Chem. Lett. (1995) 1101.

[148] A. Inoue, H. Shinokubo, K. Oshima, J. Am. Chem. Soc. 125 (2003) 1484.

[149] W.B. Lin, S.R. Wilson, G.S. Girolami, Inorg. Chem. 33 (1994) 2265.

[150] P. Leoni, M. Sommovigo, M. Pasquali, P. Sabatino, D. Braga, J. Organomet. Chem. 423 (1992) 263.

[151] M. Sommovigo, M. Pasquali, P. Leoni, D. Braga, P. Sabatino, Chem. Ber. 124 (1991) 97.

[152] A.B. Goel, S. Goel, Inorg. Chim. Acta 90 (1984) L33.

[153] N.W. Alcock, P. Bergami, T.J. Kemp, P.G. Pringle, J.C.S. Chem. Commun. (1987) 235.

[154] R. Quesada, J. Ruiz, V. Riera, S. Garcia-Granda, M.R. Diaz, Chem. Commun. (2003) 1942.

[155] K. Kikukawa, T. Matsuda, J. Organomet. Chem. 235 (1982) 243.

[156] D.S. Helfer, J.D. Atwood, Organometallics 23 (2004) 2412.

[157] D.G. Evans, G.R. Hughes, D.M.P. Mingos, J.-M. Bassett, A.J. Welch, J.C.S. Chem. Commun. (1980) 1255.

[158] R. Bender, S.E. Bouaoud, P. Braunstein, Y. Dusausoy, N. Merabet, J. Raya, D. Rouag, J. Chem. Soc. Dalton Trans. (1999) 735.

[159] A.R. Siedle, R.A. Newmark, W.B. Gleason, J. Am. Chem. Soc. 108 (1986) 767.

[160] J. Jans, R. Naegeli, L.M. Venanzi, A. Albinati, J. Organomet. Chem. 247 (1983) C37.

[161] A.W. Parkins, C.J. Richard, J.W. Steed, Inorg. Chim. Acta 358 (2005) 2827.

[162] A.L. Bandini, G. Banditelli, G. Minghetti, J. Organomet. Chem. 595 (2000) 224.

[163] P.W.N.M. van Leeuwen, C.F. Roobeek, A.G. Orpen, Organometallics 9 (1990) 2179.

[164] H. Wachtler, W. Schuh, K.-H. Ongania, K. Wurst, P. Peringer, Organometallics 17 (1998) 5640.

[165] M.G. Crisp, L.M. Rendina, E.R.T. Tiekink, Z. Kristallogr. NCS 216 (2001) 243.

[166] A. Benefial, D.M. Roundhill, Inorg. Chem. 25 (1986) 4027.

[167] T. Lu, X. Zhuang, Y. Li, S. Chen, J. Am. Chem. Soc. 126 (2004) 4760.

[168] A.R. Chianese, B.M. Zeglis, R.H. Crabtree, Chem. Commun. (2004) 2176.

[169] O. Steigelmann, P. Bissinger, H. Schmidbaur, Z. Naturforsch. B 48 (1993) 72.

[170] H. Schmidbaur, Chem. Soc. Rev. 24 (1995) 391.

[171] H. Schmidbaur, Gold Bull. 33 (2000) 3.