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Review

TRANSITION METAL–CARBON σ-BOND SCISSION

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In the course of a recent literature search on transition metal σ-alkyl compounds, it became clear that although numerous data on the stabilities of this type of compound are available, there have been as yet few attempts to correlate the data from widely different systems. Furthermore, very few research groups are involved directly in the study of metal—carbon bond scission processes; much of the work in this area has been reported rather haphazardly almost as asides in the literature on complexes containing alkyl ligands, and thus many results are not readily available.

In addition, it is clear that many of the reported observations do not satisfactorily distinguish between thermal stabilities and stabilities with respect to, for instance, air oxidation or hydrolysis. Some estimates of relative thermal stabilities seem to have been inferred only from the relative ease of preparation of a compound; if one compound in a series could not be isolated using a method by which others could be isolated, that compound was regarded as being less stable. Thus it seemed that an examination of the recent literature on metal—carbon bond scission might be timely and appropriate. The results, which follow, are not intended to constitute a comprehensive review of the entire field of transition metal—carbon bond scission, but rather a consideration and a correlation of the main *current* areas of research.

Although binary alkyl transition metal compounds constitute the simplest class of organometallic compounds and have been studied for over a century [1, 2], their chemical and physical properties are not well understood. Much of the earlier work was concerned with preparations by reactions of Grignard reagents with transition metal salts, and was generally hampered by the very low stabilities of the metal alkyls. They appeared to decompose homolytically to give radicals and the metals (eqn. 1) [1], apparently because of an inherent weakness of transition metal—carbon bonds.

$$\begin{tikzcd} n\text{RMgX} + \text{MX}_n \arrow[r] & {[\text{MR}_n]} \arrow[r] & \text{M} + n\text{R}\cdot \arrow[r] \arrow[rrd, dashed, "\text{Solvent}"'] & \text{R}_2 & \\ & & & & \text{RH} \end{tikzcd} \qquad (1)$$

Attention shifted during the 1950s and early 1960s to the possibility of stabilizing metal–carbon σ-bonds by incorporating other, strong field ligands into the molecules. A wide variety of alkyl-transition metal complexes was prepared which also contained ligands such as carbon monoxide, tertiary phosphines and the π-cyclopentadienyl group [3], and a rather convincing and certainly widely-accepted π-bonding theory was proposed to account for the apparent stabilizing properties of these ligands [3]. In effect, it was suggested that if homolytic cleavage of a metal–alkyl σ-bond were to proceed via excitation of an electron from a bonding orbital to a non-bonding or anti-bonding orbital, thus weakening or breaking the bond (yielding a radical?), then the process should be hindered by strong field ligands which can increase the ligand field splitting. The theory became very popular because it was believed that homolytic fission provided a general mechanism for the decomposition of metal-alkyl compounds and, possibly, because of the general optimism with which ligand field theory was regarded at the time [4].

At the same time, there were also reported numerous reversible "insertion" reactions, in which an olefin reacted with a transition metal hydride to form, via an olefin complex, a metal alkyl complex (eqn. 2) [3].

$$RCH=CH_2 + MH \rightleftharpoons (RCH=CH_2)MH \rightleftharpoons RCH(CH_3)M + RCH_2CH_2M \qquad (2)$$

The hydrogen was shown to migrate to the carbon atom β to the metal; the reverse reaction, a β-elimination, provided a mechanism which had been unrecognized in the earlier work for the decomposition of some alkylmetal compounds.

More recently, consideration of the chemical properties of coordinated alkyl groups has been stimulated by both practical and theoretical developments. In the first place, although the role of transition metal compounds in effecting "abnormal" reactions of Grignard compounds has long been recognized [5, 6], such reagents are only now apparently being utilized in organic syntheses (particularly copper compounds [7].) This area of organometallic chemistry could well become very important.

Secondly, it has been suggested that transition metal–carbon σ bonds are not inherently weak, and that the purpose of stabilizing ligands is merely to block the coordination sites required for low energy routes to bond cleavage such as β-elimination. On this basis, there has been prepared a number of surprisingly stable binary metal compounds containing the neopentyl [8, 9] and trimethylsilylmethyl [9–11] groups, in which β-elimination is impossible. The metal bicyclo[2.2.1]hept-1-yls form a related series of compounds which are stable to β-elimination because the metal is bonded to a bridgehead carbon atom [12]. Possible theoretical implications of the high stability of these binary metal alkyl compounds have been discussed [13–15], albeit without knowledge of all possible decomposition pathways.

In spite of these advances, there is not yet available a clear understanding of the mode(s) of cleavage of the vast majority of transition metal–alkyl bonds, although data have now been reported on the modes and /or products of metal–carbon cleavage of compounds of titanium(IV) [16–19, 21–27], chromium(III) [28–37], manganese(II) [38], iron(II) [39–41], cobalt(II) and cobalt(III) [42–46], nickel(II) [47–53], platinum(II) [54–56], copper(I) and copper(II) [57–59, 62–64], silver(I) [59–61, 64, 65] and gold(III) [66]. In addition, there have been comparative studies of the products of decomposition of a variety of alkyl and aryl compounds of series of metal ions [59, 71, 72].

A critical examination of these references shows quite clearly that reactions involving cleavage of transition metal carbon bonds are much more complicated than has been thought. For instance, thermal decomposition of as simple a compound as $MeTiCl_3$ may proceed by four different routes [16–19], including autocatalysis by precipitated compounds of titanium in lower oxidation states [18]. The hydrocarbon products consist largely of methane and ethane, and reactions in the presence of saturated deuterated hydrocarbons yield methane which includes no deuterium [16]. Thus the hydrogen atom acquired by the methyl group to form methane must come from another methyl group by a process other than abstraction by a methyl radical. One likely route would involve α-elimination for form CH_2, CH or carbide complexes. Although there appears to be little evidence for the existence of such complexes of titanium, the process has also been proposed in the decomposition of chromium(III) methyl compounds (see below). In addition, reaction of Me_3SiCH_2MgCl with $MCl_5(M = Nb, Ta)$ gives $M_2(CSiMe_3)_2(CH_2SiMe_3)_4$ [20], an apparent case of α-elimination, although the fate of the lost hydrogens remains unknown.

Decomposition of $MeTiCl_3$ in the presence of deuterated ethers, which can coordinate to the metal, does result in partial incorporation of deuterium in the methane [17, 19]. It is not known, however, whether the mechanism of the formation of CH_3D involves transfer of a β-deuterium from the ether to the metal (as occurs with many alkoxide complexes [3]), followed by reductive elimination, or whether homolysis of the titanium–carbon bond generates a radical which can then abstract a deuterium atom from a coordinated ether (possibly before leaving the coordination sphere of the metal). Decomposition of $MeTiCl_3$ in the presence of deuterated toluene also yields CH_3D [17, 19], a process which may involve radicals, although exchange via coordination of the toluene has also been suggested as a possibility [19].

Coordination of a variety of neutral ligands to $MeTiCl_3$ can alter the apparent stability of the titanium–carbon bond [21], although comparative studies have not been carried out. Again the modes of decomposition have not been ascertained; the ratio of methane/ethane varies considerably in the series.

Decomposition reactions of Me_2TiCl_2 [18] and Me_4Ti [22] have also been studied, although little is known of the former; both compounds are less stable than is $MeTiCl_3$. The tetramethyl derivative gives mainly methane, while the perdeutero derivative in hexane gives CD_4 and smaller amounts of CD_3H [22]. It is suggested that the dominant mode of decomposition is an α-elimination, homolysis being a minor route. Decomposition is slower in donor solvents, amine adducts are more stable than is Me_4Ti [23], and adducts of chelating amines are more stable than are those of monodentate amines [23], possibly reflecting steric hindrance to the rearrangements which an α-elimination reaction might entail.

Decomposition reactions of compounds in the series Cp_2TiRCl [24] also appear to be very complex. Kinetic studies show that decomposition is first order, and it has been suggested that titanium–carbon bond scission occurs to give a radical which remains within the coordination sphere of the metal. The principal products were reported to be those of disproportionation (i.e. olefin plus alkane) where R contains a β-hydrogen, or of hydrogen abstraction where R contains no α- or β-hydrogen atoms, although another report claims that the relative amounts of hydrocarbon products from the decomposition of $Cp_2TiEtCl$ depend on the extent of the reaction [25]. Again more than one mode of decomposition seems likely.

In related systems, it has been shown that thermal decomposition of Cp_2TiR_2 (R = Ph [26], $PhCH_2$ [27]) gives only RH; in both cases, decomposition in C_6D_6 gave no deuterated products. The latter observation has been taken as evidence against radical formation, a possibly questionable conclusion as benzene is a relatively poor hydrogen donor. Interestingly, reaction of $Cp_2Ti(CH_2Ph)_2$ with carbon monoxide yields $(PhCH_2)_2CO$ and divalent $Cp_2Ti(CO)_2$ [27], an apparent case of reductive elimination.

One of the most thoroughly studied alkyl–metal systems is that of chromium(III). A number of papers have appeared, notably concerning decomposition reactions of compounds of the types $RCrCl_2 \cdot 3S$ and $R_3Cr \cdot 3S$ (S = solvent), and again several mechanisms apply [28–37]. In general, based on temperatures at which fragmentation occurs, monoalkyl compounds are more stable than are the corresponding trialkyl derivatives, while the alkyl stability sequence is normal > secondary > tertiary [36].

In the case of monoalkyl compounds, most decompositions have been carried out in situ on freshly prepared solutions in tetrahydrofuran (THF), yielding solvated chromium(II) chloride. The compounds, which are almost certainly to be formulated as $RCrCl_2 \cdot 3THF$ [37], give predominantly the alkane, RH, with lesser amounts of terminal olefin (in those cases where R contains a β-hydrogen atom) and, in varying quantities, depending on the nature of R and experimental conditions, the coupling product, R_2 [29, 30, 33, 36, 37]. Free radicals are apparently not involved, as methane-d_0 is the main product from the decomposition of $MeCrCl_2 \cdot 3THF$ in chloroform-d_1 [37]. The coordinated THF is regarded as being an important source of hydrogen in these systems [36, 37], although no investigation using deuterated THF has been reported and, as with the above-mentioned titanium systems, the postulated mode of abstraction of hydrogen is not known.

Studies with the specifically-labelled compound $PhCH_2CH_2CD_2CH_2CrCl_2 \cdot 3THF$ showed that decomposition is entirely homolytic [33] (in the sense that a reduced chromium(II) species is formed; the authors do not imply homolytic fission to yield a radical) i.e.

$$PhCH_2CH_2CD_2CH_2CrCl_2 \cdot 3THF \xrightarrow[THF]{30^\circ C} PhCH_2CH_2CD_2CH_3\ (51\%)$$

$$+\ PhCH_2CH_2CD_2CH_2D\ (22.5\%) + PhCH_2CH_2CD{=}CH_2\ (22\%) + CrCl_2 \cdot n THF$$

The terminal olefin is probably formed by β-elimination; the trideuteroalkane may result from combination of the migrating deuterium atom with an alkyl group from a second chromium atom. No evidence for a chromium hydride (or deuteride) could be found in this and similar systems [37], however, and any postulated mechanism must be consistent with the fact that decomposition is first order in metal complex in a variety of solvents [37]. Substitution of the coordinated THF by the much better ligand, pyridine, stabilizes the alkyl compounds considerably [37], perhaps by occupying the coordination sites necessary for hydrogen transfer reactions to occur.

Decomposition reactions of trialkylchromium(III) complexes also occur by several routes, although again free radicals appear not to be involved. Thus reactions of $(PhCH_2)_3Cr\cdot 3THF$ in ethyl ether in the presence of dihydroanthracene, an excellent source of hydrogen for free radicals, or anthracene, which readily combines in ether with free radicals, lead to neither change in product distribution nor to products expected from attack of a benzyl radical on anthracene [28].

In general, trialkylchromium(III) compounds containing β-hydrogen atoms yield large amounts of alkanes, smaller but irregular amounts of terminal olefins, and an olefin isomerization catalyst, presumably a chromium hydride [30–33, 35], which catalyzes the isomerization of the terminal olefins initially produced. Experiments with the deuterated compounds $(PhCH_2CH_2CD_2CH_2)_3Cr\cdot 3THF$ and $(PhCH_2CH_2CH_2CD_2)_3Cr\cdot 3THF$ have been very useful in elucidating the routes of chromium–carbon scission in this series [32]. Besides $Ph(CH_2)_2CD_2CH_3$, the former yields significant amounts of the trideuterated alkane, $Ph(CH_2)_2CD_2CH_2D$. The manner in which the third deuterium atom is acquired is not known, but may result from direct attack of one alkyl group on another, or it may result via the β-elimination of $Ph(CH_2)_2CD{=}CH_2$ from a chromium deuteride. This monodeuterated olefin is also obtained, while hydrolysis of the resulting reaction mixture yields H_2 and HD, suggesting the presence of chromium hydrides and deuterides. Evidence for α-elimination from this compound is inferred from the presence of $Ph(CH_2)_2CD{=}CHD$ among the products. The nature of the hydrocarbon products from the 1,1-dideutero compound leads to similar conclusions concerning the routes to decomposition; the presence of HD on hydrolysis is further evidence for an α-elimination process.

The presence of CH_2CD_2 and, after hydrolysis, of HD from the decomposition of $(CD_3)_3Cr\cdot 3THF$ also suggests the importance of α-elimination; a transitory carbene complex has been suggested as an intermediate [34].

The series of dialkylmanganese(II) compounds (alkyl = Me, Et, n-Pr, i-Pr, n-Bu, t-Bu, neopentyl, benzyl) has been studied in some detail [38], and has been found to yield manganese metal and varying relative amounts of olefin and alkane, but no coupling products. Those containing a β-hydrogen appear to first eliminate olefin to yield hydridoalkyl compounds. The latter may then eliminate a second olefin to yield MnH_2, eliminate alkane directly or interact with a second alkylmanganese molecule to eliminate alkane. The presence of the hydride, suggested by the ease of hydrogenation of added olefin, was confirmed by the evolution of HD on deuterolysis of the reaction mixture.

Based on the relative rates of decomposition, the relative stabilities are Me, $PhCH_2$, $Me_3CCH_2 \gg$ n-Pr, n-Bu $>$ Et $>$ t-Bu $>$ i-Pr. The high stabilities of the first three probably reflect the lack of β-hydrogen atoms. The absence of methylcyclopentane in the decomposition products of a 5-hexenyl complex was taken as evidence that the system does not generate the 5-hexenyl radical [38].

The compound $Me_2FeBipy_2$(Bipy = bipyridyl) decomposes to give mainly CH_4 [39], while the diethyl and di-n-propyl analogues give varying amounts of alkane and olefin plus a "black pyrophoric residue" [39–41]. In the presence of excess bipyridyl, the iron(0) complex $FeBipy_3$ is formed [27], along with some of the coupling product [39]. On the other hand, treatment of the diethyl compound with sulphuric acid or iodine yields much larger amounts of n-butane. for reasons unknown.

The related complex, $Et_2CoBipy_2$, gives equimolar amounts of ethane and ethylene, as well as traces of butanes [42]. Reactions of Grignard reagents in the presence of cobalt(II) chloride and anthracene gave products expected from the attack of radicals on anthracene [43].

A series of alkylcobaloxime complexes has been studied: pyrolysis of the methyl, cyanomethyl and chloromethyl derivatives gives CH_4, CH_3CN and CH_3Cl, respectively, while complexes with β-hydrogen atoms give only the olefins [44–46]. In general, the products from photochemical decomposition are very similar, although the distribution of the hydrocarbon products depends greatly on both the nature of the other ligands in the complex and on the solvent [46]. The similarities in hydrocarbon products from both the thermal and photolytic decompositions, as well as the formation of toluene in the decomposition of a methylcobaloxime complex in benzene, have been taken as evidence for radical formation [44–46].

The complexes $R_2NiBipy$ (R = Et, n-Pr) decompose to give, apparently, equal amounts of alkane (RH) and olefin (R – H) [47, 48], while coordination of an electronegative olefin to give bipyridyl(olefin)dialkylnickel results in generation of the coupling product, R_2, and bipyridyl(olefin)nickel. Addition of triphenylphosphine to bis[tris(2-biphenylylphosphito)]-dimethylnickel yields ethane and a nickel(0) complex [49] as does heating $Me_2Ni(PMe_3)_3$ [50], although the complexes $R_2Ni(PPh_3)_2$(R = n-Pr, n-Bu) eliminate predominantly the 1-olefins [51].

Decomposition of the compounds $CpNiPPh_3R$ (R = alkyl) containing a β-hydrogen atom proceeds mainly via β-elimination in the melt [52, 53] and in solution [53], although relatively small amounts of alkane are also formed. A hydrido complex is presumably formed and exists long enough to isomerize olefins, but is too unstable to be detected and apparently decomposes by reductive elimination to cyclopentadiene and nickel metal. Decomposition of the trimethylsilylmethyl compound, which does not contain a β-hydrogen atom, to tetramethylsilane is first order in benzene. On the basis of the temperatures at which fragmentation occurs, stabilities in solution decrease in the order $CF_3 > Ph$, Me_3SiCH_2, $PhCH_2$, Me > Et, n-Bu > n-Pr > sec-Bu > iso-Pr > t-Bu [53]. This order is similar to those discussed above for chromium(III) and manganese(II), i.e. alkyl groups containing no β-hydrogens > n-alkyl compounds > branched alkyl compounds.

The mechanism of the thermal decomposition of $n\text{-}Bu_2Pt(PPh_3)_2$ has been studied in detail [54]. The reaction appears to involve dissociation of a phosphine and elimination of 1-butene from one of the butyl groups to form an olefinhydridobutyl complex, followed by loss of olefin and reductive elimination of butane to give a complex of platinum(0). Free radicals were ruled out on the basis of product distribution.

Pyrolysis of selectively deuterated isomers of $PtMe_3I(PMe_2Ph)_2$ has been shown to proceed by a first order intramolecular mechanism to give ethane and *trans*-$PtMeI(PMe_2Ph)_2$ [55]. In contrast, the compounds bipyridyltrimethylplatinum iodide [55] and $CpPtMe_3$ [56] decompose to give methane, the latter apparently via the formation of radicals in the gas phase.

The thermal decomposition reactions of alkylcopper compounds have received considerable attention. Diethylcopper(II), generated by reacting $CuCl_2$ with EtMgBr, yields n-butane and ethylcopper(I) [57]. Alkylcopper(I) compounds containing β-hydrogen atoms generally appear to yield equimolar amounts of alkane (RH) and alkene (R – H) [57, 58]; the reaction is believed to proceed initially by a β-elimination to yield a copper(I) hydride [58], although the mechanism of formation of alkane is not known. Decomposition of vinylcopper(I) complexes gives only the coupling products [59] as do a number of silver(I) complexes [59–61].

Decomposition of a 5-hexenyl complex of copper(I) does not yield methylcyclopentane, showing that the 5-hexenyl radical was not formed [58], while the retention of configuration of the dienes formed from the decomposition of vinylcopper(I) [59] and silver(I) [59] compounds shows as well that vinyl radicals are not formed. Similarly, aryl radicals are not formed in the decomposition of fluoroarylcopper(I) octamers [62] and tetramers [63]. In contrast, the product distributions from the decomposition of neophyl(tri-n-butylphosphine)-copper(I) and -silver(I) suggest that these compounds do decompose via homolytic fission [64], while the decomposition of Me_3SiCH_2Ag in ethyl ether in the presence of cumene yields products which are characteristic of radical attack on both the solvent and the cumene [65].

Tertiary phosphine–gold(III) complexes containing two methyl or two ethyl groups yield either ethane or n-butane, respectively, and gold(I) complexes on decomposition [66]. No hydrogen abstraction reactions occur, and the reaction appears to involve a reductive elimination mechanism.

The above summary shows quite clearly that the formation of hydrocarbons from the thermal decomposition of transition metal-alkyl compounds cannot be taken as evidence for homolytic cleavage of metal–carbon bonds, although homolysis does apparently occur in some systems and is undoubtedly very important in the thermal decomposition reactions of many alkyl compounds of the main group metals and metalloids [67].

The large differences in the proportions of alkanes, olefins and coupling products from different systems suggest that cleavage of metal–carbon bonds can proceed by several routes. The work on the titanium(IV) and chromium(III) systems, for instance, shows that both α- and β-elimination mechanisms can occur, and it seems possible that homolytic cleavage to generate short-lived radicals (to be, perhaps, distinguished from "free" radicals) which react with other coordinated ligands is a third possibility.

Serious complications which have not been considered by either structural or kinetic studies are the possiblities of redistribution reactions and aggregation of alkylmetal compounds in solution. Redistribution of $MeTiCl_3$ to Me_2TiCl_2 and $TiCl_4$ has been demonstrated and does affect the nature of the decomposition products [18]. The effects of aggregation are rather unpredictable, but the increase in stability of vinyl(tri-n-butylphosphine)copper(I) complexes [59] on the addition of excess tri-n-butylphosphine or a triphosphine has been attributed to a lower degree of aggregation. Some hydride [68] and fluoraryl [62, 63] complexes of copper(I) are known to be tetrameric or octameric, and alkylhyridocopper(I) clusters have been considered as intermediates in the reactions of copper(I) hydride with alkylcopper(I) complexes [69]. Thus, aside from the well-recognized differences in stabilities, it is apparent that binary alkyl compounds can have properties which are very different from those of alkyl complexes which are "diluted" by other ligands.

Both redistribution and aggregation could result in alkyl groups being in unexpectedly close proximity to each other, leading to concerted abstraction and combination reactions which would not take place if the alkyl groups were further apart. In this connection, it is worth noting that many of the alkylmetal systems discussed above were generated by treating metal halides with alkylating reagent and then decomposed in situ. Problems of handling the compounds have in many cases precluded even a most elementary study of their structures.

Reductive elimination of alkane (RH) from alkylhydrido complexes or coupling products (R_2) from dialkyl complexes may proceed via concerted reactions, and could provide low energy pathways, following redistribution, to decomposition of the supposed monoalkyl complexes. In this context, it is interesting to note that decarbonylation of (–)-(*R*)-2-methyl-2-phenylbutanal by $RhCl(PPh_3)_3$ proceeds with retention of configuration to (+)-(*S*)-2-phenylbutane [70]. The reaction proceeds in two stages involving the asymmetric carbon atom, alkyl migration from CO to the metal, and reductive elimination of the hydrocarbon. As the former is believed to proceed with retention of configuration, the latter must also, suggesting that reductive elimination of hydrocarbons can be a concerted process.

Reductive eliminations should be facilitated by the presence of an easily attained lower oxidation state, a hypothesis for which there is some evidence. For instance, decomposition of the complexes $Et_2FeBipy_2$ [39–41] and $Et_2NiBipy_2$ [47, 48] in the presence of strongly electronegative olefins, which can stabilize the zerovalent states of these metals, leads to increased proportions of n-butane as compared with the product distribution in the absence of electronegative olefins. Considerably larger amounts of n-butane are also obtained from the reactions of ethyl Grignard reagents with $CuCl_2$ [57, 58, 71] and $FeCl_3$ [71, 72] than with CuCl and $FeCl_2$, while silver(I) salts, which are very easily reduced, give large yields of coupling products [71]. High yields of coupling products are also obtained from palladium(II) systems in the presence of triphenylphosphine [71], which can stabilize palladium(0) complexes [73], and from $Cp_2Ti(CH_2Ph)_2$ in the presence of carbon monoxide [27].

TABLE 1

DISSOCIATION ENERGIES OF CARBON–HYDROGEN BONDS (R–H) AND CARBON–MERCURY (R–HgCl, R_2Hg) BONDS (kcal/mole)

R	D(R–H)	D(R–HgCl)	$\bar{D}$(R_2Hg)
Me	102	64 ± 3	29 ± 2
Et	97	58 ± 4	24 ± 3
n-Pr	99	60 ± 4	27 ± 4.5
iso-Pr	94	56 ± 6	20 ± 3.5
n-Bu	101	–	–
t-Bu	89.5	–	–
$PhCh_2$	77	–	–
Ph	103	64 ± 6	33 ± 5
CF_3	103	–	–

In conclusion, it may be instructive to compare the relative stabilities of some of the alkylmetal complexes studied here, i.e. (for $CpNiPPh_3R$) CF_3 > Ph, Me, $PhCH_2$ > Et, n-Bu > n-Pr > iso-Pr > t-Bu [53], with the dissociation energies of the purely σ-bonds formed by the same alkyl groups with hydrogen and mercury (Table 1) [74]. As is shown, the order of decreasing carbon–hydrogen bond strengths is CF_3, Ph > Me > n-Bu > n-Pr > Et > iso-Pr > t-Bu while the orders of decreasing carbon–mercury bond strengths are Ph, Me > n-Pr > Et > iso-Pr and Ph > Me > n-Pr > Et > iso-Pr.

These three series are not very dissimilar to each other or, with the exception of the benzyl group, to the order to stabilities of the $CpNiPPh_3R$ (and other) series. Although the differences between some pairs of compounds in the four series are barly significant, the very similar trends may indicate that the relative stabilities of the alkylnickel complexes depend in part on the metal–carbon bond dissociation energies, a thermodynamic parameter.

In partial support of this hypothesis, it is now widely accepted that the relatively high stabilities of metal–perfluoroalkyl complexes are a result of increased metal–carbon bond strengths [3, 75]. In accord with this conclusion, metal–carbon bond lengths in perfluoroalkyl compounds are invariably shorter than those of the simple alkyl analogues [75]. On the other hand, there is little evidence for similar bond shortenings in, for instance, trimethylsilylmethyl compounds, which are also regarded as being "unusually" stable. The chromium–carbon bond lengths in [$Cr(CH_2SiMe_3)_2Bipy_2$]I are not significantly different from those of some aryl analogues [76], nor is the platinum–carbon bond length in *trans*-$PtCl(CH_2SiMe_3)(PMe_2Ph)_2$ [77] significantly different from the bond lengths in a variety of other alkylplatinum compounds [75].

Although bond length data on similar systems of these types of compounds are not generally available, as they are for perfluoroalkyl compounds [75], it seems unlikely, however, that significant stability - bond length correlations will be made. As pointed out elsewhere [9, 10], and substantiated in this article, although metal–alkyl bond strengths do vary, the controlling factors in the decomposition of the majority of complexes are not homolytic cleavage of the metal–carbon bonds to give radicals, but rather are kinetic in nature and depend on the availability of low energy routes such as β-elimination.

In the case of branched alkyl compounds, the metal–carbon bond strengths may be decreased by steric interactions between the alkyl groups and other ligands. Coordination of tertiary phosphines has been reported to force the isomerization of coordinated secondary alkyl groups to the less sterically demanding normal isomers [78], while steric factors have also been invoked [45] to explain the relatively low stabilities of many secondary alkylcobaloxime complexes.

Low kinetic stabilities may especially be a factor in cases where the elimination yields a complex of a highly branched olefin (eqn. 2). Stabilities of complexes of branched olefins are generally relatively low [79], and dissociation of a heavily branched olefin from an olefinhydrido complex such as the intermediate in eqn. (2) could be a factor which would tend to destabilize branched alkyl complexes [80].

On the other hand, the t-butyl complexes $CpFe(CO)_2$-t-Bu [81] and Cr-t-Bu_4 [82] are believed to be stable because they are too crowded to allow the rearrangement necessary for a β-elimination. The former is particularly interesting, as previous attempts to prepare it by reaction of the carbonylate anion, $[CpFe(CO)_2]^-$, with t-butyl chloride yielded isobutene and the hydride $CpFe(CO)_2H$ [83], in high yield.

Finally three recent notes may be mentioned as "food for thought". The oxidative addition of alkyl halides to d_8 and d_{10} systems has been on occasion considered as S_N2 processes, in which the metal acts as a nucleophile, as concerted three-centre additions, and as free radical processes [84]. Evidence for the last-mentioned seems convincing and suggests, invoking the principle of microscopic reversibility, that the reverse process of reductive elimination (a likely mode of decomposition) may indeed in some systems generate radicals.

It has also been noted that oxidative cleavage of the metal–carbon bonds in some systems proceeds stereospecifically with retention of configuration at the α-carbon atom [85]. It has now been shown [85] that the reactions involve initial oxidation of the metal followed by nucleophilic attack at the α-carbon atom by, say, halide ion to cause displacement of the metal, a rather novel mechanism for metal–carbon bond cleavage.

It has also been shown that tertiary aryl phosphines can play a rather unusual role in facilitating metal–carbon bond scission. The compounds $MMe(PPh_3)_3$ (M = Rh [86], Ir [87]) release methane to yield the *ortho*-metallated compounds $M(C_6H_4PPh_2)(PPh_3)_2$. The reactions apparently involve oxidative addition of an *ortho*-aryl–hydrogen bond to the monovalent metal to give the trivalent derivatives $MMe(C_6H_4PPh_2)H(PPh_3)_2$; the latter then eliminate methane. Both steps are probably concerted, although the hydrocarbon product is of the type which has often been taken as evidence for radical dissociation.

The above three examples emphasize the point that has already been made, that metal–carbon bond scission reactions can occur in an often bewildering number of ways. Great care must be taken in the analysis of reaction products and in the acquisition of kinetic and thermodynamic data before mechanisms can be deduced and, thus, before the factors affecting the stabilities of transition metal–alkyl bonds will be understood.

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