Remarks on the Stability of Transition Metal–Carbon Bonds

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Evidence is compiled which suggests that σ bonds between transition metals and one-electron carbon donors are not weak. Lability of such bonds, in so far as it is a real phenomenon, cannot be explained in terms of the orthodox π-ligand stabilisation theory, although an electron promotion mechanism of a different type may operate in some cases. The importance for thermal decomposition of concerted mechanisms such as β-elimination, reductive elimination, and binuclear interactions is emphasised.

SOME years ago, Chatt and Shaw suggested that π-accepting ligands stabilise σ bonds between transition metals (in particular, square-planar Ni^{II}, Pd^{II}, and Pt^{II}) and ligand carbon by an electronic mechanism.[1] This 'supporting π-ligand theory' has been widely accepted and has passed into textbooks.[2] More recently it has been suggested that the sole function of the ligands is to block co-ordination sites on the metal, that the important feature of such ligands is their strong attachment to these sites, and that the role of any π bond is simply to increase the strength of attachment rather than to affect the nature or possible fragmentation of the metal–carbon bond as such.[3] Moreover, it has become plain that supporting ligands are not always necessary, and that the range of kinetically stable transition-metal–organic compounds is wider than had been expected.[3,4] An examination of evidence relating to the strength and stability of transition metal–alkyl and related bonds, and of the role of supporting ligands, therefore seems timely.

The Strength of Metal–Carbon Bonds.—Structural and spectroscopic evidence. The great diversity now found among supporting ligands,[2] and in some cases the absence of any such ligands, makes it unlikely that electronic properties of the ligands are responsible for the strength of the metal–carbon bonds. Methylplatinum(IV) complexes, for example, have been particularly well documented. The Pt–C bond lengths in $(Me_3PtOH)_4$,[5] $(Me_3PtCl)_4$,[5] $Me_3Pt(\pi\text{-}C_5H_5)$,[6] $[Me_3PtCH(COR)_2]_2$[5] [R = Pr or CH_2OEt], $(Et_3PtCl)_4$[7] and similar compounds are all *ca.* 210 pm, despite the diversity of the other ligands. The metal–carbon stretching frequencies in these compounds[5] and in related tertiary phosphine complexes of the type $(R_3P)_2PtMe_{4-n}X_n$[8,9] all have ν(Pt–C) in a narrow range (*ca.* 550 cm^{-1}), within the range of main-group methyls. Furthermore, the values are very similar to those of Pt^{II} derivatives such as $(R_3P)_2PtMeX$,[8] and the Pt–C bond distance in K[(acac)-$ClPt^{II}CHAc_2$],[10] while not directly comparable with those in the Pt^{IV} methyls because of the different hybridisation at carbon, is 211 pm.

At the other end of the Periodic Table there is a relative lack of evidence, presumably because of the higher lability of the compounds of interest. Recently, however, it has been reported[11] that the titanium–methyl force constant in $TiMe_4$ is 2·28 mdyn Å^{-1}. This is very similar to the Sn–C force constant in tetramethyltin (2·25 mdyn Å^{-1}), and there is ample thermodynamic evidence that the metal–carbon bonds in this and other main-group organometallic compounds are strong.[12]

Thus, although direct thermodynamic evidence on the strength of transition-metal–carbon bonds is scarce (some isolated examples have been reported,[13] but data on useful comparative series are lacking), spectroscopic and structural evidence from compounds over the entire transition-metal block suggest that these links are strong. Some comparative mass-spectrometric studies add tentative support to this.[12c,14] There is no reason to believe, therefore, that transition-metal–carbon bonds are in any way qualitatively different from metal–hydrogen, metal–metal, metal–nitrogen (*cf.* ref. 3) or main-group metal–carbon bonds.

Despite this, several transition-metal organometallics appear to have a higher lability than most main-group compounds. Whereas Me_4Sn is stable at room temperature, for example, tetramethyltitanium decomposes at 233 K in diethyl ether giving methane.[11] The problem in 1959[1] was to explain the existence and stability of transition-metal–organic compounds against a belief that the metal–carbon bonds were weak.[15] The converse appears to be true now. There is no reason to expect inherently weak M–C bonds, but the lability of many compounds requires explanation. We have therefore examined some plausible decomposition pathways.

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[1] J. Chatt and B. L. Shaw, (*a*) *J. Chem. Soc.*, 1959, 705; (*b*) 1960, 1718.

[2] M. L. H. Green, 'Organometallic Compounds,' Methuen, London, 1968, vol. II, pp. 220—224.

[3] G. Yagupsky, W. Mowat, A. Shortland, and G. Wilkinson, *Chem. Comm.*, 1970, 1369.

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[5] J. S. Thayer, *Organometallic Chem. Rev.* (*A*), 1970, **5**, 53.

[6] See K. W. Egger, *J. Organometallic Chem.*, 1970, **24**, 501.

[7] R. N. Hargreaves and M. R. Truter, *J. Chem. Soc.* (*A*), 1971, 90.

[8] R. J. Cross, *Organometallic Chem. Rev.*, 1967, **2**, 97.

[9] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2964.

[10] R. Mason, G. B. Robertson, and P. J. Pauling, *J. Chem. Soc.* (*A*), 1969, 485.

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[12] (*a*) A. L. Yergey and F. W. Lampe, *J. Amer. Chem. Soc.*, 1965, **87**, 4204; (*b*) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, 1961, **65**, 2186; (*c*) D. B. Chambers, F. Glockling, and J. R. C. Light, *Quart. Rev.*, 1968, **22**, 317; (*d*) M. F. Lappert, J. B. Pedley, J. Simpson, and T. R. Spalding, *J. Organometallic Chem.*, 1971, **29**, 195.

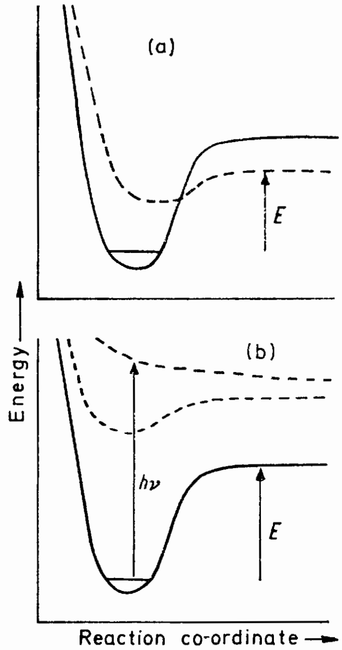
[13] *E.g.*, S. J. Ashcroft and C. T. Mortimer, *J. Chem. Soc.* (*A*), 1967, 930.

[14] M. I. Bruce, *Adv. Organometallic Chem.*, 1968, **6**, 273; M. Cais and M. S. Lupin, *Adv. Organometallic Chem.*, 1970, **8**, 211.

[15] F. A. Cotton, *Chem. Rev.*, 1955, **55**, 551.

It is inherent in the nature of the problem that least information is available about the compounds most in question, those which are most labile. It is not possible at present, therefore, to assign with certainty the decomposition pathway of many examples. Nevertheless, we believe there are sufficient data available to suggest a major shift in emphasis from the currently accepted explanations based on bond weakness.

Possible Pathways for Metal–Carbon Bond Cleavage.—We classify pathways for the cleavage of metal–carbon bonds as concerted or non-concerted, and we further sub-divide non-concerted pathways into promotional and non-promotional. By concerted pathways we mean here all those in which more than one co-ordination site at the carbon-bonded metal is involved. We shall suggest that it is the availability of such pathways which controls the lability of metal–carbon bonds, at least at the end of the transition series. By promotional pathways we mean those in the course of which the metal adopts an electronic configuration distinct from that assignable to it in the original complex. We shall suggest that these could play a major role at the beginning of the transition series. The mechanism suggested by Chatt and Shaw [1] is promotional. We argue below that such mechanisms are not likely to operate in the way suggested for thermal reactions at the end of the transition series (though they may well be implicated in photolysis).



(a) Role of excited state in promotional reactions, (b) excited state correlating with excited state of products. ——— Ground state, – – – – excited states, E thermal activation energy, $h\nu$ photochemical threshold

Non-concerted Pathways.—A promotional non-concerted bond cleavage is depicted in (a). Here the excited state of the starting compound corresponds to the ground state of the primary decomposition products, and the activation of thermal decomposition involves promotion to a low-lying electronically-excited state. (b) Depicts a non-promotional bond cleavage. In this case the excited states of the products correlate with excited states of the starting material.

An example of non-promotional cleavage is the (hypothetical) fragmentation of tetramethyltin to give methyl and trimethylstannyl radicals. Here the unpaired electron of the Me_3Sn fragment will be in an orbital derived from $5s,p$ and of the same symmetry as was each of the electrons in the tin–carbon bond before its cleavage. Excited states in which the metal–carbon bond is weakened may exist, but will not facilitate thermal cleavage.

Promotional cleavage may be illustrated, for the sake of concreteness, by the homolytic cleavage of a metal–carbon bond in tetramethyltitanium (though whether such a unimolecular homolysis is, in fact, responsible for the observed breakdown of this compound is at present unknown). Non-promotional cleavage of such a bond would leave trimethyltitanium in an excited state, with the unpaired electron in an orbital of $4s,p$ character, whereas in the ground state it would be in a $3d$ orbital. Thus the ground state of the products correlates with an excited state, which we can most plausibly write as $[\sigma(a_1)^2[\sigma(t_2)]^5[d(e)]^1$, of the starting material. This excited state will resemble the cation Me_4Sn^+, $[\sigma(a_1)]^2[\sigma(t_2)]^5$, rather than neutral tetramethyltin, in its metal–carbon bonding. It is relevant that [12] while $D(Me_3Sn{-}CH_3)$ is *ca.* 70 kcal mol^{-1}, $D(Me_3Sn^+{-}CH_3)$ is *ca.* 20 kcal mol^{-1}. Presumably the odd electron in the trimethylstannyl radical is either antibonding with respect to the remaining tin–carbon bonds, or else is raised in energy to occupy a pure p orbital.* In the trimethyltitanium fragment, on the other hand, the odd electron will be in an orbital at once non-bonding with respect to the remaining metal–carbon linkages, and of lower energy (in the fragment) than that involved in the broken metal–carbon bond.

Promotional cleavage of the type suggested here is an oxidation of the ligand from (formal) R^- to $R^{\cdot}$ with correlative reduction of the metal. The decomposition of $(CD_3)_3Cr(THF)_3$, to give CD_3H,[16] may well be of this type. There is no reason why the mechanism should not operate for other metal–ligand reactions, not involving co-ordinated carbon, such as those responsible for the production of Nb^{IV} complexes [17] from Nb^{V} and amines.

Reactions by this mechanism will be inhibited by π-donating ligands, which will reduce the electron demand of the metal, and this may be the situation in

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* Such an increase in energy would not make the bond cleavage promotional, in our sense, since this p orbital correlates directly with the (sp^3) hybrid orbital involved in the original bond.

[16] J. R. C. Light and H. H. Zeiss, *J. Organometallic Chem.*, 1970, **21**, 391.

[17] M. Albrutt, K. Feenan, and G. W. A. Fowles, *J. Less-Common Metals*, 1964, **6**, 299.

$(\pi\text{-}C_5H_5)_2TiMe_2$[18] [the low ν(CO) frequencies of $(\pi\text{-}C_5H_5)_2Ti(CO)_2$[19] suggest that π-cyclopentadienyl is strongly donating to Ti], $NbMe_3Cl_2$,[20] and $[(CH_3)_3SiCH_2]_3VO$.[3] If such ligands as phosphines and arsines inhibit the reaction at all, it will be because they are good σ donors; their π-acceptor properties will be largely ineffectual in the situation under discussion.

For compounds in which the metal has six or more d electrons the situation is rather different. A promotional process here is more likely to involve excitation of a non-bonding electron to anti-bonding levels, the process discussed by Chatt and Shaw[1] for d^8 complexes. We shall examine in detail the situation for d^6 and d^8 complexes.

A reaction closely akin to anion loss from a d^6 system is carbonyl loss from the hexacarbonyls of chromium, molybdenum, and tungsten, as in their S_N1 substitution reactions. Under thermal reaction conditions, the $M(CO)_5$ intermediates cannot be isolated; they can, however, be generated photochemically[21] and examined in matrices,[22,23] in which they are square pyramidal. (Although it was, at one time, thought[22] that in the case of molybdenum, at least, the square pyramidal species was metastable with respect to a trigonal bipyramidal species, this has been shown not to be the case, the observed species being almost certainly binuclear, and of unknown composition.[24]) Such species would be expected to have a d-orbital configuration directly correlating with that of the starting material, and in view of their long life at 90 K[22,23] and the transient local lattice softening associated with their production[24] may be presumed to have reverted to their ground states and equilibrium geometries. Their generation by a thermal mechanism is thus expected to be non-promotional.

Radical or cation loss would generate d^7 or d^8 systems. These might be expected to be square pyramidal or alternatively (in the latter case) trigonal bipyramidal. Square pyramidal species would have the extra one or two electrons in a d orbital belonging to a_1 in the point group C_{4v}; this correlates with the orbitals of the original bond, and hence with the ground state of the octahedral parent. The trigonal bipyramidal species also correlates with the ground state of the parent; the three-fold axis correlates with an original four-fold axis so that the vacant d_{z^2} orbital correlates with a vacant e_g orbital of the parent, while the four occupied d orbitals correlate with the original t_{2g} set to which is added that d orbital involved in the original metal–carbon bond. Thus, in both these cases also, non-concerted bond cleavage is predicted to be a pure ground-state process.

Non-concerted cleavage in a square planar d^8 system can be considered in a similar manner. Here loss of a ligand will give rise to a state of symmetry D_{3h} or lower, by way of a transition state of C_{2v} symmetry. (If the departing ligand is not in the same plane as the other three in the transition state, the symmetry will be lower, but such a departure path is rendered unfavourable by the repulsion between the electrons in $d_{xz,yz}$ orbitals and those of the original bond.) Anion loss could produce either a diamagnetic T-shaped species correlating with the ground state (analogous to the observed square pyramidal species generated by ligand loss from octahedral complexes, in which case the bond cleavage is non-promotional), or else a trigonal species with a triplet ground state, correlating with a $d_{xy\rightarrow x^2-y^2}$ excited state of the parent.

This last possibility corresponds to one of the promotional mechanisms discussed by Chatt and Shaw;[1] it must, however, be rejected on two counts. Firstly, there is the analogy with the non-existence of trigonal bipyramidal $M(CO)_5$; and indeed of paramagnetic octahedral Pd^{II} and Pt^{II} complexes of normal ligands, showing that metals of the second and third transition series, at least, generally undergo distortions to remove such orbital degeneracies as can give rise to triplet states. Secondly, the promotion in question will be highly energy absorbing as long as the crystal field of the departing R^- anion is appreciable; thus the promotion can only occur when the bond is already broken and can not be invoked to explain the bond-breaking process itself. (This last argument ignores electron–electron repulsion terms, which will clearly stabilise the promoted state, but these can here be assumed to be far smaller than ligand-field effects.)

The d^9 and d^{10} species generated by radical and cation loss also correlate with the ground state of the parent complex; indeed, the arguments are simpler and there is no alternative to be considered. It follows that non-concerted thermal ligand loss from square-planar d^8 systems is a non-promotional process.

Thus thermal decomposition by a non-concerted mechanism is comparable in d^6—d^9 complexes to the same process in main-group derivatives. In view of the similar strengths of the metal–carbon bonds, it is unrealistic to propose this mechanism in order to explain any lability greater than that normally found in main-group organometallics. We suggest, therefore, that in the case of the d^6—d^9 complexes at least, greater importance must be attached to concerted decomposition mechanisms. Several such mechanisms are well documented and may operate in a wider range of compounds than has hitherto been suspected.

Pathways for Concerted Bond Cleavage.—We would emphasise the importance of three types of concerted bond cleavage process; there may be others. These

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[19] J. G. Murray, *J. Amer. Chem. Soc.*, 1959, **81**, 752.

[20] G. L. Juvinall, *J. Amer. Chem. Soc.*, 1964, **86**, 4202.

[21] See, *e.g.*, W. Strohmeier, *Fortschr. Chem. Forsch.*, 1968, **10**, 306, and references therein.

[22] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, 1962, **84**, 3589; 1963, **85**, 1013.

[23] M. A. Graham, A. J. Rest, and J. J. Turner, *J. Organometallic Chem.*, 1970, **24**, C54.

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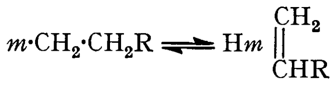
are β-elimination, reductive elimination, and binuclear elimination. The β-elimination process, *e.g.*



$$m\cdot CH_2\cdot CH_2R \rightleftharpoons Hm \begin{array}{l} CH_2 \\ \| \\ CHR \end{array}$$

is well documented,[2] and its relevance to thermal lability has been emphasised.[3,4] Recent examples of bond cleavage by β-elimination are the loss of but-1-ene from tributylphosphine–butylcopper [25]

$$LCuCH_2CD_2C_2H_5 \longrightarrow LCuD + CH_2{:}CD\cdot C_2H_5$$

and the presumed formation of bis(cyclopentadienyl)-phenylenetitanium by thermal decomposition of bis-(cyclopentadienyl)diphenyltitanium: [26]

$$(C_5H_5)_2Ti(C_6D_5)_2 \longrightarrow [(C_5H_5)_2TiC_6D_4] + C_6D_6$$

Reductive elimination is the reverse process to oxidative addition; it provides a pathway to the cleavage of metal–carbon and other metal–ligand bonds without β-migration, the formation of such high-energy species as alkyl cations, radicals or anions, or electron promotion:

$$Me_3AuPPh_3 \longrightarrow MeAuPPh_3 + C_2H_6 \quad \text{(ref. 27)}$$

$$(Me_2PhP)_2PtMeCl_3 \longrightarrow (Me_2PhP)_2PtCl_2 + MeCl \quad \text{(ref. 28)}$$

$$(Me_2PhAs)_2PtBrMe_2(COCH_3) \longrightarrow (Me_2PhAs)_2PtMeBr + CH_3COCH_3 \quad \text{(ref. 28)}$$

$$(Ph_3P)_2Ir(CO)H_3 \longrightarrow (Ph_3P)_2Ir(CO)H + H_2 \quad \text{(ref. 29)}$$

Reductive elimination following oxidative addition provides a pathway for acid cleavage of metal–carbon bonds [30]

$$(Et_3P)_2PtMeCl + HCl \longrightarrow [(Et_3P)_2PtMeHCl_2] \longrightarrow (Et_3P)_2PtCl_2 + CH_4$$

The third type of process, binuclear elimination, is an intermolecular process involving the formation of metal–metal bonds and/or of metal alkyl bridges. Such bridges are present in the ground state of beryllium and magnesium alkyls, and account for the ready exchange of alkyl groups in compounds of zinc, cadmium, and mercury.[31] Dative metal–metal bond formation, followed by binuclear elimination, is presumably implicated in the decomposition with hydrogen loss of $HCo(CO)_4$, where the slow step, which involves no appreciable cobalt–hydrogen bond breaking,[32] may be written

$$HCo(CO)_4 + HCo(CO)_3 \longrightarrow [H_2Co(CO)_7]$$

This stage is followed by reductive elimination of H_2, possibly preceded by hydrogen migration. [Similarly, a binuclear elimination process has been postulated to account for the formation of dialkyl ketones by the thermal decomposition of $RCo(CO)_4$ [33]]. Concerted elimination with or without prior migration is also clearly involved in the reactions

$$2Ph_3PAuMe \longrightarrow 2Ph_3P + 2Au + C_2H_6$$

(no methane being formed, even in xylene,[34] so that radical pathways may be excluded *), and

$$Bu_3PCuD + Bu_3PCuCH_2CD_2C_2H_5 \longrightarrow 2Bu_3P + 2Cu + CH_2D\cdot CD_2\cdot C_2H_5 \quad \text{(ref. 25)}$$

It is also relevant that metal–metal bonding could be expected to occur in any interaction between co-ordinatively unsaturated transition-metal complexes, and that the thermal fragmentation of transition-metal complexes has been shown in some cases to involve transference of organic groups across a metal–metal bond, *e.g.*[35]

$$(Et_3P)_2Pt(PbPh_3)Cl \longrightarrow (Et_3P)_2PtPhCl + [PbPh_2]$$

Effect of the Organic and Other Ligands.—Multiple bonding may be expected to stabilise metal–carbon bonds irrespective of the precise breakdown mechanism. This accounts for the relatively high stability of ethynyl, aryl, and perfluoroalkyl complexes; the multiple bonding may be independently demonstrated by a comparison of metal–carbon bond lengths.[36,37] It is reasonable to compare ethynyl complexes with those of CN^- and CO.

Carbon ions within which charge delocalisation can occur will be less prone to oxidation. This might account in part for the stability of $(PhCH_2)_4Ti$ as compared with Me_4Ti,[38] and of pyridylmethyl complexes of a

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* The converse is not true. Methane could be produced by binuclear processes, perhaps involving hydrogen-atom migration from a bridging carbon. Thus labelling experiments would be needed to elucidate the mechanism.

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[29] L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 1965, 6974.

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[31] D. S. Matteson, *Organometallic Chem. Rev.* (*A*), 1969, **4**, 263.

[32] F. Ungvary and L. Marko, *J. Organometallic Chem.*, 1969, **20**, 205.

[33] R. F. Heck, *Adv. Organometallic Chem.*, 1966, **4**, 243.

[34] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, 421.

[35] E. H. Brooks and R. J. Cross, *Organometallic Chem. Rev.* (*A*), 1970, **6**, 227.

[36] (*a*) M. R. Churchill and T. A. O'Brien, *J. Chem. Soc.* (*A*), 1970, 161; (*b*) 1969, 266; (*c*) 1968, 2970; (*d*) M. R. Churchill and M. V. Veidis, *Chem. Comm.*, 1970, 1099; (*e*) W. A. Spofford, P. D. Carfagna, and E. L. Amma, *Inorg. Chem.*, 1967, **6**, 1553; G. R. Davies, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc.* (*A*), 1967, 1750.

[37] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 1967, **6**, 1213.

[38] U. Giannini and U. Zucchini, *Chem. Comm.*, 1968, 940.

variety of metals.[39] A recent crystal-structure analysis on tetrabenzyltitanium [40] indicates that further stabilisation might be achieved by an interaction between the ring π electrons and titanium. Organic ligands that lack a β-atom with readily transferable groups are not likely to be lost by β-migration.[3,4] Bulky ligands will prevent attack on the metal–carbon bond; hence the stability of Ni(CPh$_3$)$_2$ [41] and Ni(CPh$_2$SiMe$_3$)$_2$.[4] Such steric factors may also explain the stability of the square planar complexes (Pr$^i_3$P)$_2$NiHX, (Pr$^i_3$P)$_2$NiMeX, and their cyclohexylphosphine analogues, while the tri-n-alkyl-phosphine analogues are unstable.[42] The ' ortho effect ' observed in nickel aryls [1b] may also be explained as an effect of steric protection.

Trimethylsilylmethyl ligands are bulky (though not so bulky as Bu^t or neopentyl) [43] and this factor, as well as the lack of transferable β-groups,[3] might block some concerted decomposition routes. The stability of trimethylsilylmethyl derivatives of Ti^{IV}, V^V, *etc.* against homolysis (if indeed such decomposition routes are operative) might be accounted for by unusual bonding properties of this ligand. The Mo–C–Si bond angles [44] in Mo$_2$(CH$_2$SiMe$_2$)$_6$ are *ca.* 120°, and e.s.r. measurements on silylalkyl radicals indicate an interaction between Si and its β-atoms.[45] Dimerisation and metal–metal bonding in these complexes may also inhibit promotional processes of the type discussed for Me$_4$Ti by giving some anti-bonding character to the vacant metal orbitals (*cf.* also Li$_4$Cr$_2$Me$_8$,4THF [46]).

On the view presented here, the role of ' supporting ligands ' is secondary; by blocking co-ordination sites they prevent some kinds of concerted process, and it is possible that, in addition, π-donating ligands may stabilise complexes against homolysis.

CONCLUSIONS

Transition-metal–carbon bonds are not inherently weak. Any lability of these bonds could in some cases be ascribed to ready non-concerted cleavage, but this is not always so. At least of comparable importance are: the high nucleophilicity of the ligand, and the associated possibility of concerted rearrangements; the existence of a large number of potential co-ordination sites at transition-metal centres; and the possibilities both of varying oxidation states and of metal–metal bonding. The assumption of non-concerted cleavage runs counter to what little evidence there is, at least at the end of the transition series; the traditionally invoked [1,2] promotional non-concerted cleavage mechanism is here demonstrably incorrect; and the role of supporting ligands secondary.

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