

THE TRANSITION METAL TO CARBON SIGMA BOND

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ABSTRACT

On account of the apparent instabilities or difficulties in isolating simple alkyls of transition metals it has commonly been assumed firstly that the bond strength is low and secondly that the presence of π -acid ligands such as CO, R_3P , $\pi-C_3H_5$, etc. on the metal are necessary for the existence of stable metal-carbon σ -bonds. Although only a few bond strengths have been estimated, and these in compounds with other ligands present, there is no sound reason for assuming that the metal to carbon bond strengths are low. The reason for the instability of simple transition metal alkyls, M^n-R_n , generally is to be sought in the available possible pathways for decomposition reactions of the alkyls such as hydrogen transfer from α or β -carbon atoms of the alkyl chain alkene and/or alkane elimination reactions, etc.

The synthesis of elimination-stabilized alkyls of transition metals in high oxidation states is discussed and illustrated primarily by consideration of trimethylsilylmethyl derivatives, from which alkene elimination is impossible due to the incapacity for forming silicon to carbon double bonds. The chemical properties and structures of compounds $M^n(CH_2SiMe_3)_n$ where $M = V^{IV}$, Cr^{IV} , Mo^{III} , W^{III} etc., and of other related species are described together with appropriate infrared, nuclear magnetic resonance and electron spin resonance data.

Despite the extraordinary rapid developments in the organometallic chemistry of the d-block transition elements during the last twenty years, such as the binding of delocalized aromatic or quasi-aromatic entities, alkenes, alkynes, carboranes, pyrazoboles, etc., to metals, as well as the classical σ -bonded alkyl and aryl groups and the synthesis of a multitude of different types of compounds with mixed ligands, there are some surprising gaps in our knowledge of the most simple class of compounds, namely those where organic groups only are bound to metals by σ -bonds.

The early efforts¹ to prepare alkyls or aryls of transition metals showed very clearly that simple 'binary' compounds, MR_n , R = alkyl or aryl, were generally unstable under ordinary conditions, although they might be present in solutions at low temperatures. Following the preparation of the first extensive series of σ -bonded alkyl compounds with other ligands present², it appeared that only in the presence of such stabilizing ligands as

CO , $h^5\text{-C}_5\text{H}_5$, R_3P etc., could stable compounds with transition metal to carbon σ -bonds be isolated.

It has often been stated that in the absence of such stabilizing ligands, the metal to carbon bond is weak, the implication sometimes being that the presence of stabilizing ligands substantially increases the actual $\text{M}-\text{C}$ bond strength. Thus Parshall and Mrowca³ say 'By any criterion, simple transition metal alkyls are very unstable' and 'In contrast to the simple alkyls, some metal complexes bearing other ligands in addition to alkyl or aryl groups are strikingly stable.' Similarly, Razuvaev and Latyaeva⁴ say, referring to mixed complexes of the type $(h^5\text{-C}_5\text{H}_5)_2\text{TiR}_2$, 'in these compounds the electronic energy levels of the metal are filled by π -electrons of the sandwich (C_5H_5) group leading to an increase in the stability of the compound as a whole, *and of the metal carbon bond in particular*' (present author's italic). Many other authors have made similar comments on the general instability of σ -bonds. The factors involved in the stability of metal to carbon single bonds, have been discussed in some detail by Green⁵, including the views originally put forward by Chatt and Shaw in connection with the supposed increased stability, of alkyls of the type $(\text{R}_3\text{P})_2\text{PtR}_2$. He too concludes 'that it seems unlikely that metal-carbon bonds are particularly strong.'

Now it is clear that arguments based on the chemical or thermal stability of compounds—*stable* is a much misused and misunderstood word, there often being confusion between thermodynamic and kinetic stability—or on the *apparent* non-existence of compounds (we should bear in mind the theoretical explanations for the non-existence of the now well-established perbromate ion), tell us nothing about bond strengths. Bond lengths obtained from x-ray data can, of course, in some cases such as $\text{C}-\text{C}$ bonds⁶ be correlated with bond strengths but there is clearly insufficient data for metal to carbon σ -bonds on both counts. Despite this there has been a tendency to claim that shortened metal to carbon bond distances (sometimes shortened relative to what?), especially in aryls and perfluoroalkyls indicate stronger bonds. Attempts to correlate only $\text{M}-\text{C}$ bond lengths with thermal stabilities are doomed to failure and it has been truly stated⁷ that 'arguments based on thermal stabilities of transition metal aryl compounds (relative to the analogous alkyl derivatives) or on shortened metal-carbon bond distances are without adequate support'. Quite apart from any other factors, direct comparisons, e.g. of a given alkyl *v.* an aryl may be difficult or impossible to make, and certainly, as was first recognised by Chatt and Shaw⁸, steric factors due to the associated ligands may be important, as well as the steric and electronic features of the alkyl or aryl group.

Available thermodynamic data

As noted earlier, there are deficiencies in our knowledge of metal-carbon σ -bonds, and none is greater than that in thermodynamic data. The bond energies presently available are the following.

1. $\text{Pt}-\text{C}_6\text{H}_5$, *c.* 250 kJmol^{-1}

This was obtained by Calvet microcalorimetry of the reaction $\text{trans-(Et}_3\text{P)}_2\text{Pt(C}_6\text{H}_5)_2(\text{s}) + \text{HCl(g)} = \text{trans-(Et}_3\text{P)}_2\text{PtCl(C}_6\text{H}_5)(\text{s}) + \text{C}_6\text{H}_6(\text{g})$. From ΔH , with an estimate of $E(\text{Pt}-\text{Cl})$, a minimum value for the platinum-

phenyl bond energy of *c.* 250 kJmol⁻¹ per mole was obtained. This can be compared with *E*(Hg—C) in diphenylmercury of 136 kJmol⁻¹.

2. *Pt—CH₃*, *c.* 164 kJmol⁻¹

This was estimated¹⁰ from the rate of unimolecular gas phase decomposition of (*h*⁵-C₅H₅)Pt(CH₃)₃, with the assumption of a reasonable pre-exponential factor for the initial loss of CH₃.

3. *Ti—CH₃* *c.* 250 kJmol⁻¹; *Ti—C₆H₅* *c.* 350 kJmol⁻¹

These values were obtained from the heats of combustion of (*h*⁵-C₅H₅)₂-TiR₂, R=CH₃ and C₆H₅, with subsequent estimation of the bond dissociation energies¹¹.

In addition to the thermal data, there are force constant data derived from infrared measurements, some of it very indirect. Thus from a comparison of C—F force constants in CF₃I and CF₃Mn(CO)₅, the conclusion was drawn¹² that the Mn—CF₃ bond strength was high. For CH₃TiCl₃ there is a value of 1.85 × 10⁵ dyne cm⁻¹ for the Ti—C force constant¹³, which may be compared with the value for analogous Sn and Si compounds of 2.3 and 2.9 × 10⁵ dyne cm⁻¹ respectively.

In short we can say that at present there is insufficient data to sustain the view that transition metal to carbon σ-bonds are intrinsically weaker than bonds between carbon and non-transition elements. Indeed there seems no reason why the bond should be especially weak if we consider the fact that transition metals form quite thermally stable compounds with bonds to nitrogen in the dialkylamides, e.g. Ti(NR₂)₄ or Fe(NR₂)₃, etc., or the similar alkoxides such as Cr(OEt)₄¹⁴.

Furthermore, it is clear that the presence of so-called stabilizing ligands of the π-acid type is no guarantee of stability. Indeed the use of many such complexes in homogeneous catalytic reactions such as hydrogenation or hydroformylation and involving species such as RhCl(PPh₃)₃ or RhH(CO)(PPh₃)₃ depends on the instability of the metal to carbon bond. For example the equilibrium:



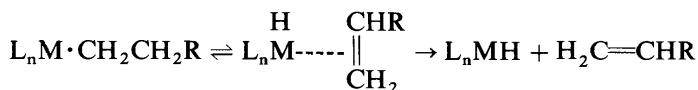
lies well to the left at 25°C/atm¹⁵.

Finally, we can note that even ethyl groups can be bound to transition metals in substitution-inert octahedral metal complexes^{16a}, of Cr^{III}, Co^{III} and Rh^{III} even with water and NH₃ as ligands, one example being [Rh(NH₃)₅C₂H₅]²⁺. The well-known vitamin B₁₂ coenzyme and its synthetic analogues such as the cobaloximes are other examples^{16b}.

We must hence in discussing the thermal stabilities of transition metal alkyls, take into consideration the pathways by which decomposition reactions can proceed, i.e. the kinetic stability of the compounds. Homolytic dissociation of the M—C bond will of course depend on the M—C bond strength, but other ways of decomposition by the hydride transfer-alkene elimination reaction or by other transfer processes, e.g. from hydrogens on the α-carbon of an alkyl, will depend in addition on other factors, such as the possible oxidation states of the metal and especially of the availability of coordination sites in intermediates or transition states. It is not our intention to discuss the decomposition reactions of alkyls, as the literature is extensive and the modes various, depending on the nature of the metal and the alkyl

groups, but as examples, attention can be drawn to recent work on alkyls of chromium¹⁷, copper¹⁸, titanium¹⁹ and manganese²⁰.

Since it has been evident that one of the main pathways for decomposition is the hydride transfer-alkene elimination reaction



we made the suggestion²¹ that binary alkyls should be thermally stable *provided that* either (i) there is a group of the type $M-CH_2-XHR_n$, where X is any atom that can form a single but *not* a multiple bond to carbon, or (ii) the β -carbon atom of an alkyl chain bears atoms or groups of atoms which cannot be as readily transferred to the metal as is hydrogen. The H-transfer-alkene elimination reaction *cannot then proceed*, although of course, other decomposition pathways could.

Whilst there are many groupings of the type $M-CH_2Y$, e.g. $Y = NR_2$, NC , OR , SnR_3 , HgR , PR_2 , $Mn(CO)_5$, etc., which could serve, the model chosen, for ease of accessibility and preparative convenience, was the trimethylsilylmethyl group, $CH_2Si(CH_3)_3^\dagger$.

We must note at this point that there are already in the literature numbers of known thermally stable binary alkyls and aryls which meet the above criteria. These are mainly the following:

(a) The benzyls²³ of Ti and Zr, $M(CH_2Ph)_4$. The x-ray structure of the zirconium analogue, recently published²⁴ confirms the view based on spectroscopic and preliminary x-ray data²³, that there are normal σ -bonds.

(b) The chelated biscarborane derivatives made from 2,2'-dithiocarboranes and metal halides²⁵, one example of which is the anion $\{Ni[(B_{10}C_2H_{10})_2]_2\}^{2-}$.

(c) Phenyl and perfluorophenyl compounds, some of which, like $(C_6H_5)_3Cr(C_4H_8O)_3$ ²⁶ have been known for some time. Examples are the cluster coppers $[CuC_6F_5]_8$ ²⁷, AgC_6H_5 ²⁸, $Au(C_6H_5)_3$ ²⁹ and $Ti(C_6F_5)_4$ ³⁰. There are also perfluoro silvers³¹ such as $Ag(CF_3CF=CCF_3)$ which may well be cluster compounds.

(d) The methyl group of course cannot undergo alkene elimination although other modes of decomposition of metal methyls are possible. Nevertheless some simple methyls such as $Ti(CH_3)_4$ or $Mn(CH_3)_2$ although unstable are considerably more stable than their ethyl analogues. (This is, incidentally true also for $CH_3Mn(CO)_5$ *v.* $C_2H_5Mn(CO)_5$) and the compounds $(CH_3)_3MCl_2$, $M = Nb$, Ta ³², are stable for some time even at room temperature.

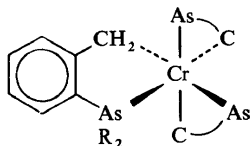
There are also several anionic methyls of transition metals, some of which, notably those of chromium such as $Li_4[Cr_2Me_8]$ have been studied crystallographically³³.

(e) We can also note, that since the alkene elimination reaction involves two coordination sites, increased stability of an alkyl may result if such sites are blocked, as in the substitution-inert complexes noted above. Other

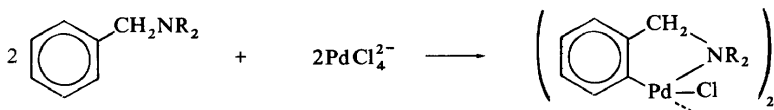
[†] Numerous trimethylsilylmethyl derivatives with π -bonding ligands present have been made²².

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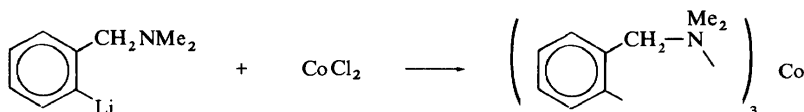
examples of thermally stable adducts are TiMe_4I_2 , and $\text{TiMeCl}_3\text{I}_2$ ³⁴. A particular stable complex (to 350°C) is the chelate benzyl tris[ω -dimethylarsino-*o*-tolyl]chromium(III)^{35a}.



There are other examples of chelate alkyls, where, in addition to excluding the possibility of β -elimination of hydride, resistance to homolytic fission of the $\text{M}-\text{C}$ bond is enhanced by chelation^{35b,c}. In some cases such compounds are formed by attack of the metal atom on an *ortho* $\text{C}-\text{H}$ bond, viz.



but in others prior lithiation is employed, e.g.



The best indication of relative stabilities for binary alkyls has come from the very elegant studies²⁰ by Tamura and Kochi on the decomposition of manganese dialkyls, prepared *in situ*, which shows that the stability order is: $\text{CH}_3 \sim \text{C}_6\text{H}_5\text{CH}_2 \sim (\text{CH}_3)_3\text{CCH}_2 \gg n\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9 > \text{C}_2\text{H}_5 > t\text{-C}_4\text{H}_9 > i\text{-C}_3\text{H}_7$.

The most stable are clearly those which do not readily eliminate alkene. In connection with this finding it may be noted that in addition to trimethylsilylmethyl compounds we have also isolated several of their neopentyl analogues. We may note also that the tertiary butyl group has not been found in transition metal alkyls until recently, when $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(t\text{-butyl})$ was obtained indirectly (not by a Grignard route) and proved to be remarkably stable. The authors³⁶ comment wisely that 'the failure to prepare transition metal tertiary butyls may be less a consequence of inherent instability, thermodynamic or kinetic, than of methods chosen to synthesize them'.

In summary therefore, despite the present lack of $\text{M}-\text{C}$ bond energy data, it is clear (i) that the transition metal to carbon bond is probably no weaker than bonds between carbon and other metallic elements, and (ii) that the main purpose of additional ligands, π -acid or otherwise, in 'stabilizing' compounds with metal to carbon σ -bonds is merely to firmly block off the coordination sites required for decomposition reactions to proceed.

Trimethylsilylmethyl and neopentyl compounds

We now consider some of the binary alkyls containing Me_3SiCH_2 and Me_3CCH_2 groups and which can be obtained by conventional reactions of the metal chloride with the lithium or Grignard reagent (*Table 1*). Although

Table 1

Compound	Form	m.p.°C	Comment
$\text{Me}_3\text{SiCH}_2\cdot$ (R)			
VR_4	dark-green needles	43	paramagnetic
VOR_3	lemon-yellow needles	75	
$\text{NbR}_2\text{CSiMe}_3$	wine-red prisms	81	} dimers
$\text{TaR}_2\text{CSiMe}_3$	orange prisms	50	
$[\text{CrR}_4]^-$	blue-green anion	—	paramagnetic
CrR_4	purple-red needles	40	paramagnetic
Mo_2R_6	yellow plates	99	} isomorphous
W_2R_6	orange-brown plates	110	
Me_3CCH_2 (R')			
$[\text{CrR}'_4]^-$	dark-blue anion	—	paramagnetic
CrR'_4	red-purple needles	100	paramagnetic
$\text{Mo}_2\text{R}'_6$	yellow prisms	d 135	dimeric

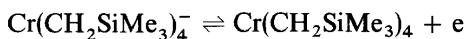
moderately air-sensitive they are thermally stable, can be handled under nitrogen and purified by chromatography, sublimation or crystallization by conventional methods.

Chromium

Both $(\text{CH}_3)_3\text{SiCH}_2$ and $(\text{CH}_3)_3\text{CCH}_2$ form both Cr^{III} and Cr^{IV} complexes. The chromium(III) species are anionic and have been obtained only in solution by interaction of $\text{CrCl}_3\cdot 3\text{THF}$ with the lithium alkyl, or by reduction, e.g. by Na/Hg or electrolytically in tetrahydrofuran, of the Cr^{IV} compound.

The coloured anions are paramagnetic and both the electronic spectra and electron spin resonance spectra can be readily interpreted in terms of a *tetrahedral* structure.

The ions are readily oxidized, commonly by traces of air to the deep blue-purple, neutral chromium(IV) compounds. The ions can be oxidized electrochemically and the chromium(IV) species reduced to the anions, e.g. by sodium amalgam in tetrahydrofuran, so that there is the reversible reaction



In 10^{-4}M solution in ethanol with tetra *n*-butyl ammonium iodide as supporting electrolyte, the half-wave potential for polarographic reduction of $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ is -1.28 V *v.* the saturated calomel electrode.

The blue-purple petroleum soluble chromium(IV) compounds are very similar to the corresponding Cr^{IV} dialkylamides or alkoxides. Again they are paramagnetic and the e.s.r., electronic and infrared spectra can be interpreted in terms of a distorted tetrahedral structure.

The chemical inertness of $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ is quite remarkable. It is

unaffected by carbon monoxide at 200 psi and 100°C, by solvents, amines, tertiary phosphines, etc. It will, of course, undergo reduction and with hydrogen chloride at low temperatures gives a red unstable solid (probably CrCl_4) together with tetramethylsilane. Nitric oxide gives petroleum soluble products not yet characterized.

Vanadium

The vanadium(IV) compound closely resembles the chromium(IV) compound in structure (distorted tetrahedral) and in its chemical properties. The major difference is that on oxidation (e.g. by passing a tetrahydrofuran solution through a cellulose column) it forms an oxovanadium(V) complex $\text{O}=\text{V}(\text{CH}_2\text{SiMe}_3)_3$. The latter is quite stable in air, soluble in organic solvents and does not react with CO, phosphines or primary amines.

Molybdenum and Tungsten

For these elements yellow isomorphous compounds of stoichiometry $\text{M}_2(\text{CH}_2\text{SiMe}_3)_6$ are formed; although the interacting solutions of the halide and Grignard reagent undergo a variety of colour changes, the final solutions and the final products are the same. The compounds are more reactive than $\text{Cr}(\text{CH}_2\text{SiMe}_3)_4$ and will undergo a series of reactions with CO, not yet fully investigated. On refluxing the Mo compound with acetic acid, molybdenum(II) acetate, $\text{Mo}_2(\text{OCOCH}_3)_6$ is formed, while with 12M HCl, and RbCl, the salt $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ can be isolated, both reactions showing the persistence of the metal-metal bond. The x-ray structure of the molybdenum compound³⁷ shows a very short Mo—Mo distance, 2.167 Å only slightly longer than that in $\text{Mo}_2(\text{OCOCH}_3)_6$; the alkyl groups are staggered. The Mo—CH₂—Si angle of 121.1° and possibly the Mo—Mo—CH₂ angle of 100.6° is probably a consequence of the mutual repulsion of the bulky trimethylsilyl groups, rather than of any electronic factors. As in the structure of $\text{Zr}(\text{CH}_2\text{C}_6\text{H}_5)_4$, there is evidently a normal metal to carbon σ-bond (Mo—CH₂ = 2.131 Å; Zr—CH₂ = 2.27 Å).

The Mo—Mo bond is best regarded as a triple bond and a rough M.O. treatment can be made along the lines of those used by Cotton for other binuclear metal-metal bonded species. Thus the six available electrons can be anodated in the d_{z^2} orbitals to form the Mo—Mo σ-bond and in π-bonds formed by overlap of two sets of d_{xz} and d_{yz} orbitals. Since the d_{xy} , $d_{x^2-y^2}$ pair, which have δ-symmetry, are unused, there would appear to be no restriction of rotation about the Mo—Mo bond, and hence unlike say $\text{Re}_2\text{Cl}_8^{2-}$, where the δ-orbitals are involved and the configuration is eclipsed in $\text{Mo}_2(\text{CH}_2\text{SiMe}_3)_6$ the observed staggered form is that expected for minimum electrostatic repulsions.

Niobium and Tantalum

At the present time the precise structure of these virtually identical and isomorphous compounds is not fully resolved. Analytical data suggests the stoichiometry $\text{M}(\text{CH}_2\text{SiMe}_3)_2(\text{CSiMe}_3)$ and further the nuclear magnetic resonance spectra show three peaks; the CH₂ resonance and one CH₃ resonance evidently being due to CH_2SiMe_3 , and a second CH₃ resonance presumably attributable to an SiMe_3 group. Why the apparent stoichiometry

is found is a puzzle. The loss of a CH_2 group from a CH_2SiMe_3 group bound to a metal has been previously observed³⁹ in the reaction of $h^5\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}$ (or W) Na with $(\text{CH}_3)_3\text{SiCH}_2\text{I}$ but here the isolated product, $h^5\text{-C}_5\text{H}_5(\text{CO})_3\text{MoCH}_3$ contained a methyl group.

In conclusion, we can now say that there is no longer reason to doubt that provided the right conditions are met, thermally stable and isolatable binary alkyls of transition metals can be made and that one can look forward to new series of different types being produced in the future.

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