

Aspects of the Transition Metal to Carbon σ -bond; Stable Binary Alkyls*

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Summary

The thermal instability of binary transition metal alkyls is a consequence of facile pathways for decomposition, notably the hydride transfer from a β -carbon atom followed by elimination of alkene. Where this reaction is not possible, as in compounds MR_n where $R = CH_3, CH_2C_6H_5, CH_2Si(CH_3)_3$ etc., stable alkyls may be synthesised. Examples of the new classes of alkyls, trimethylsilylmethyls and 1-norbornyls are noted and the properties of hexamethyltungsten outlined.

Quite soon after FRANKLAND's discovery in 1849 of the first organometallic compounds, the zinc alkyls, attempts were made to synthesise transition metal alkyls; however not until the isolation of the trimethylplatinum iodide tetramer, $[(CH_3)_3PtI]_4$, by POPE and PEACHY in 1907 was a stable product obtained.¹ During the next fifty years or so, repeated attempts to isolate alkyls or transition metals generally failed; coupling or other decomposition reactions were a common feature. Indeed, in 1955, COTTON wrote¹: "It will be apparent from this overall picture of alkyls and aryls of transition metals that the often heard generalisation that they are much less stable and accessible than those of non-transition metals is quite true." A basis of theoretical respectability to this statement was provided by overlap calculations, which purported to show the intrinsic low ability of transition elements to form σ -bonds to carbon in its usual sp_3 and sp_2 hybridization states.²

During the early 1950's a number of alkyl compound, with what are now termed π -bonding ligands, COs π - C_5H_5 , PR_3 , etc., also bound to the metal were prepared. Some examples are h^6 - $C_5H_5Fe(CO)_2CH_3$, $(Et_3P)_2PtICH_3$, h^5 - $(C_5H_5)_2Ti(C_6H_5)_2$ and $CH_3Mn(CO)_5$. It began to appear that only in the presence of such "stabilizing" ligands could σ -bonded alkyls and aryls generally be isolated. Thus in the latest extensive review on σ -bonded alkyls and aryls, PARSHALL and MROWCA^{3a} write, "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". Even GREEN,^{3b} in a detailed discussion of the stability of transition metal to carbon σ -bonds in which was clearly stated the important distinction which should be, but is not always, made between thermodynamic and kinetic stability, concluded that "it seems unlikely that metal-carbon bonds are particularly strong".

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¹ For reviews giving early references see F.A. COTTON, *Chem. Rev.* 55 (1955) 551; H.H. ZEISS, *Organometallic Chemistry*, Reinhold, 1960.

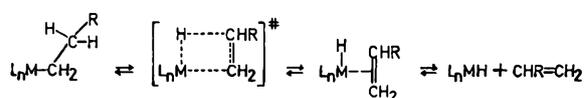
² H.H. JAFFE and G.O. DOAK, *J. Chem. Physics* 21 (1953) 196.

³ a) G.W. PARSHALL and J.J. MROWCA, *Adv. Organometal. Chem.* 7 (1968) 157. For structures of many such compounds see M.R. CHURCHILL, *Perspectives in Structural Chem.* 3 (1970) 91. b) M.L. H. GREEN, *Organometallic Compounds*, Vol. 2: *The Transition Elements*, Methuen, London 1968.

Now the bond strength data available is extremely meagre. For the Pt-C₆H₅ bond in *trans*-(Et₃P)₂Pt(C₆H₅)₃ a value of ca 250 kJ mol⁻¹ was obtained,⁴ which can be compared with *E*(Hg-C) in diphenylmercury of 136 kJ mol⁻¹. From the unimolecular gas phase decomposition of *h*⁵-C₅H₅Pt(CH₃)₃ a value of Pt-CH₃ of ca 164 kJ mol⁻¹ was estimated,⁵ while combustion data⁶ led to estimates of Ti-CH₃, ca 250 kJ mol⁻¹ and Ti-C₆H₅, ca 350 kJ mol⁻¹, for (*h*⁵-C₅H₅)₂TiR₂, R = CH₃ and C₆H₅. Other Ti-C bond energies, e.g., for Ti(C₂H₅)₃Cl, ca 130 kJ mol⁻¹, are said to be consistent with the activation energy of 85 to 125 kJ mol⁻¹ for the thermal decomposition of a different type of alkyl, namely (*h*⁵-C₅H₅)₂TiClR, R = CH₃, C₂H₅, C₆H₅, etc.⁷

Although these estimates are for alkyls or aryls with other ligands present on the metal, they do not suggest that transition metal to carbon bonds are intrinsically weaker than those between carbon and non-transition metals. Arguments based on chemical or thermal stability of compounds—stable is a much misused and misapplied word—or on the *apparent* non-existence of compounds are clearly insupportable. Since oxygen and nitrogen (and of course halogens) may form “stable” compounds with transition metals in various oxidation states, e.g., Cr(OC₂H₅)₄ or Ti[N(SiMe₃)₂]₄, why not carbon?

We sought⁸ the answer to this question by considering that one of the major pathways for decomposition of transition metal alkyls is the hydride transfer-alkene elimination reaction. This reaction is the reverse of the synthesis reaction for metal to carbon bonds by attack of an alkene on a metal hydride species and which is involved at some point in many catalytic cycles such as those of homogeneous hydrogenation or hydroformylation of alkenes. The reaction is one involving transfer to the metal atom of a hydrogen from the β-carbon of an alkyl chain:

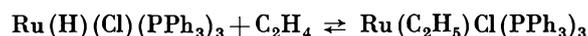


In the absence of “stabilizing” ligands i.e. for a binary alkyl, the metal hydride (probably solvated in solution) formed on elimination of alkene could decompose further to metal and hydrogen. This mechanism has been generally accepted and has been established in certain cases. A good example is the decomposition of *n*-CH₃CH₂CH₂CH₂CuP(*n*-Bu)₃. Here CuH is formed by H-transfer and alkene elimination; this then reduces the Cu-C in a second molecule resulting finally in the products but-1-ene, *n*-butane copper metal and hydrogen.^{9a} By contrast, the related neophyl, C₆H₅C(CH₃)₂CH₂CuP(*n*-Bu)₃, which has no hydrogen atoms on the β-carbon, decomposes largely by homolytic fission and a free radical pathway.^{9b}

It is important to note that the hydride transfer-alkene elimination pathway involves a *change in coordination*

number of the metal. In the alkyl, there is only a metal to carbon σ-bond, whereas in the hydride-alkene intermediate, two metal sites are involved. This means that if the required vacant coordination site on a metal alkyl species is unavailable, then decomposition by this particular pathway clearly cannot proceed. Of course, a site may be freed by thermal or photochemical dissociation of a ligand.

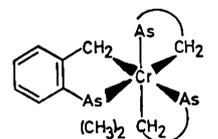
The corollary to this is that alkyls may not be stable even when so-called stabilizing ligands are present on a metal *provided* that one of the ligands is readily lost, or if the complex itself is coordinatively unsaturated. A good example of the instability of an alkyl even when π-bonding ligands are present is:



The equilibrium lies well to the left at 25°/1 atm pressure. Another example is RhH(CO)(PPh₃)₃. Such complexes quite often provide catalytic cycles for isomerisation or other reactions of alkenes;¹⁰ indeed, catalytic reactions depend on the lability of the metal-alkyl group.

The blocking of coordination sites by ligands may thus provide a rationale for the existence of some of the alkyls noted earlier. This concept is also illustrated by the stability of metal to carbon bonds in classical WERNER type octahedral complexes of metal ions whose electronic structure is such that they are substitution inert. Thus there are alkyls¹¹ of Cr^{III}, Co^{III} and Rh^{III} even with water or ammonia as ligands, one example being [RhC₂H₅(NH₃)₅]²⁺. The well known Vitamin B₁₂ coenzyme and the numerous synthetic analogues such as the dimethylglyoxime cobalts or cobaloximes are other examples; these have four nitrogen atoms in the plane with an alkyl group and another ligand in the *trans* positions.

The complex I is an especially good example;¹² the blocking of coordination sites is coupled with an alkyl which cannot readily undergo the H-transfer alkene elimination reaction and is coupled further with the chelate effect. This compound is stable to 350°C.



A more unusual way of inhibiting or preventing the hydride transfer reaction proceeding is to use an alkyl group whose nature is such that there is either no β-hydrogen or the β-carbon is replaced by another element which cannot form a double bond to carbon, and hence cannot form an alkene.⁸

Some such binary alkyls were known for some time for certain transition metals, notably the benzyls of Ti, Zr and Hf¹³ and the methyl, Ti(CH₃)₄, although the latter is thermally most unstable as discussed later. The

Table 1. Representative binary alkyls of transition metals

Compound	Form, m.p.	Properties; structure	
<i>Trimethylsilylmethyls R^a</i>			
VOR ₃	Lemon yellow needles	m.p. 75	Diamagnetic, $V=O$ stretch
R ₂ N ₆ (CSiMe ₃) ₂ N ₆ R ₂	Red-brown prisms	m.p. 152	Has (CSiMe ₃) bridge groups ^b
CrR ₄	Purple-red needles	m.p. 40	d^2 tetrahedral
W ₂ R ₆	Orange plates		Isomorphous Mo ₂ R ₆ with MM bond ^c
ReOR ₃	Red needles	m.p. 138	Has Re = O stretch
<i>Neopentyls; tritylmethyls^a</i>			
Ti(CH ₂ CMe ₃) ₄	Pale yellow prisms	m.p. 99	Diamagnetic
Mo ₃ (CH ₂ CMe ₃) ₆	Pale yellow prisms	m.p. 135	Diamagnetic, Mo-Mo bond
Cr(CH ₂ CPh ₃) ₄	Purple prisms	m.p. 130 ^o	
<i>Norbornyls (R')^d</i>			
CoR' ₄	Brown		Paramagnetic $\mu = 2.0$
FeR' ₄	Purple		diamagnetic
MnR' ₄	Green		Paramagnetic $\mu = 3.78$
CrR' ₄	Red-brown		Paramagnetic $\mu = 2.84$

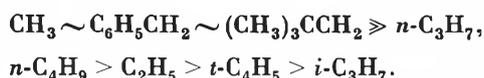
^a G. WILKINSON *et al.*, *J. Chem. Soc. (Dalton)* 1972, 533; *J. Organometal. Chem.* 38 (1972) C35 and in press.

^b F. HUG, W. MOWAT, A. C. SKAPSKI and G. WILKINSON, *Chem. Comm.* 1971, 1477.

^c F. HUG, W. MOWAT, A. C. SKAPSKI, A. SHORTLAND and G. WILKINSON, *Chem. Comm.* 1971, 1079.

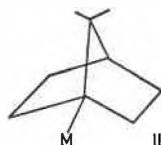
^d B. K. BOWER and H. G. TENNANT, *J. Amer. Chem. Soc.* 94 (1972) 2512.

applicability of this concept to binary alkyls of other metals is well demonstrated by studies on the relative stabilities of dialkylmanganese compounds made *in situ* in ether solutions.¹⁴ These show that the most stable species are those that do not readily eliminate alkene, the order being



Of course the phenyl group is also in this category and it has long been known that phenyl compounds are often more stable than the corresponding alkyls. This does not necessarily mean that they can be easily isolated however, as other decomposition pathways are possible.¹⁵

The concept of the prevention of H-transfer alkene elimination led us to the synthesis of *trimethylsilylmethyl compounds*, generally $\text{M}(\text{CH}_2\text{SiMe}_3)_n$, and later to the corresponding neopentyl and related species.^{8,16} Some representative examples are given in Table 1. More recently, a second major new class of alkyls which also fit the required criteria have been described by BOWYER and TENNANT.¹⁷ These are the *1-norbornyl and related compounds*, in which the metal is bound to the bridge head carbon as in II



Some examples of this class are also given in Table 1.

For both norbornyls and trimethylsilylmethyls, the thermal and chemical stability may be quite high; it is of course quite reasonable to assume that with these

rather bulky ligands, especially the norbornyls, steric factors and the shielding of the metal from attacking reagents may be of considerable importance. It is also noteworthy that both alkyls give tetrahedral compounds of metals in the IV oxidation state. For Mn, Fe and Co it is quite remarkable to find compounds in the IV oxidation state with carbon as a ligand since this oxidation state with other ligand atoms is exceedingly rare.¹⁰

⁴ S. J. ASHCROFT and C. T. MORTIMER, *J. Chem. Soc. A* 1967, 930.

⁵ K. W. EGGAR, *J. Organometal. Chem.* 24 (1970) 501.

⁶ V. I. TELNOI *et al.*, *Doklady Akad. Nauk.* 174 (1967) 1374.

⁷ N. M. CHIRKOV, *Kinetics and Catalysis (Kinet. i. Katal)* 11 (1970) 269.

⁸ G. YAGUPSKY, W. MOWAT, A. SHORTLAND and G. WILKINSON, *Chem. Comm.* 1970, 1369.

⁹ (a) G. M. WHITESIDES *et al.*, *J. Amer. Chem. Soc.* 92 (1970) 1426.

(b) G. M. WHITESIDES, E. J. PANEK and E. R. STEDRONSKY, *J. Amer. Chem. Soc.* 94 (1972) 232.

¹⁰ See F. A. COTTON and G. WILKINSON, *Advanced Inorganic Chemistry*, 3rd edition, Wiley, 1972, Chapter 24.

¹¹ M. D. JOHNSON and N. WINTERTON, *J. Chem. Soc. A* 1970, 50;

G. WILKINSON *et al.*, *J. Chem. Soc. A* 1968, 1801; M. ARDON *et al.*, *Inorg. Chem.* 10 (1971) 2812; C. T. LOO *et al.*, *J. Chem. Soc. (Dalton)* 1972, 585.

¹² A. TZSCHACH and H. NINDEL, *J. Organometal. Chem.* 24 (1970) 159.

¹³ U. ZUCCHINI *et al.*, *J. Organometal. Chem.* 26 (1971) 357; J. J. FEL-

TEN and W. P. ANDERSON, *J. Organometal. Chem.* 36 (1972) 87;

W. BRÜSER *et al.*, *J. Organometal. Chem.* 32 (1971) 335. - For X-ray

structural studies G. R. DAVIES *et al.*, *Chem. Comm.* 1971, 677, and

I. W. BASSI *et al.*, *J. Amer. Chem. Soc.* 93 (1971) 3787.

¹⁴ M. TAMURA and J. K. KOCHI, *J. Organometal. Chem.* 29 (1971) 111.

¹⁵ See e.g. W. HERWIG and H. H. ZEISS, *J. Amer. Chem. Soc.* 81

(1959) 4798; G. M. WHITESIDES and W. J. EHMANN, *J. Amer. Chem.*

Soc. 92 (1970) 5625; numerous papers by H. H. ZEISS in *J. Organometal.*

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¹⁶ W. MOWAT, A. SHORTLAND, G. YAGUPSKY, N. J. HILL and G. WIL-

KINSON, *J. Chem. Soc. (Dalton)* 1972, 533; *J. Chem. Soc. (Dal-*

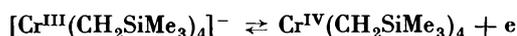
ton) 1973, in press.

¹⁷ B. K. BOWER and H. G. TENNANT, *J. Amer. Chem. Soc.* 94 (1972)

2512.

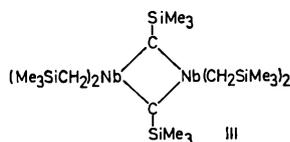
For Cr^{IV} species, which have been studied in detail,¹⁶ the electronic absorption and electron spin resonance spectra can be interpreted on the basis of an essentially tetrahedral *d*² structure. The blue or red-purple species are petroleum soluble and volatile; they can be compared with the corresponding well known alkoxides and dialkylamides.

So far, the mechanisms of the formation of these alkyls have not been studied. In one case, Cr^{IV}, it is clear that in the reaction of the lithium alkyl with CrCl₃(tetrahydrofuran)₃, an anionic Cr^{III} species is first formed and that this can be readily oxidised to the Cr^{IV} complex:



E = -1.28 vs S. C. E. in ethanol

However, in other situations disproportionation reactions may be involved and how the binuclear species with a metal-metal bond, e. g., (Me₃SiCH₂)₃Mo≡Mo(CH₂SiMe₃)₃ and the niobium and tantalum bridged «carbene» complexes III are formed is not at all understood.



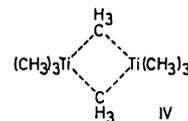
Although not all of the transition metals have as yet been obtained as binary alkyls, there seems no good reason to doubt that in due course such compounds will be synthesized. The myth of the instability of the transition metal to carbon bond has now been finally destroyed.

Table 2. Force constants for tetravalent methyls

Data by H. H. EYSEL, H. SIEBERT, G. GROH and H. J. BERTHOLD, *Spectrochim. Acta* 26A (1970) 1595

M (CH ₃) ₄	Si	Ge	Sn	Pb	Ti
mdyne A ⁻¹	2.93	2.72	2.25	1.90	2.28

The methyl group is of especial interest since not only is it the simplest alkyl, but it cannot undergo the H-transfer alkene elimination reaction. Until recently the only known binary methyl was Ti(CH₃)₄, although trimethyldichlorides of Nb and Ta, and methylpentachlorotungsten were known. Purely on the basis of the force constant data, Table II, it is difficult to understand why Ti(CH₃)₄ decomposes above -40°C whereas tetramethyl lead can be distilled at 110°/1 atm without decomposition. Clearly however, as a transition metal compound TiMe₄ is coordinatively unsaturated and decomposition pathways may be possible through intermediates or transition states with bridging methyl groups as in IV.



Such pathways involving expansion of the coordination shell are impossible for the Group IV methyls.

The effect of blocking the vacant coordination sites in Ti(CH₃)₄ or TiCl₃CH₃ by two ligands or a chelate ligand such as 2,2'-dipyridyl is clearly shown by the substantially increased thermal stability of such octahedral adducts.¹⁸

This idea suggested to us that if an octahedral methyl could be synthesised, there should be a good chance for thermal stability. The obvious candidate was hexamethyltungsten since hexachlorotungsten is readily available, and the obvious route is the interaction of WCl₆ with methyl lithium in ether. It is possible that this reaction has been studied previously without success, since for success it is necessary that only half of the stoichiometric quantity of CH₃Li be used. If greater quantities are used no (CH₃)₆W is obtained, probably due to the formation of anionic species. The reaction is a complex one and has not been studied in detail. At -20° in ether, red solutions are initially formed followed by the formation of yellow crystals which turn green and redissolve to give a greenish brown solution. Electron spin resonance spectra show that this solution contains W^V. On removal of solvent, yields close to 50% based on WCl₆ of W(CH₃)₆ can be obtained.¹⁹ The final step presumably involves a disproportionation: 2W^V ⇌ W^{VI} + W^{IV}. Since essentially all of the CH₃Li finishes up as W(CH₃)₆ presumably diethylether is acting as the reductant. Hexamethyltungsten is a red crystalline, extremely volatile solid, m. p. ca 30°. Its spectroscopic properties are quite straightforward and those expected for an octahedral species, e. g., a single W-C stretch at 482 cm⁻¹ and a single proton resonance line at τ = 8.38 with *J*(H-¹⁸³W) = 3.0 Hz.

The formation of this compound clearly does dispose of the idea that transition metals in high oxidation states cannot form stable alkyls. There seems now no reason to doubt that other transition metal methyls in high oxidation states can be prepared, provided that the appropriate synthetic procedure is discovered. Preliminary experiments show that a petroleum soluble, volatile species, possibly U(CH₃)₈ is obtained by the interaction of UCl₆ and CH₃Li.

Some reactions of W(CH₃)₆ are shown in Figure 1. One of the important reactions of W(CH₃)₆ is that with tertiary phosphines such as P(CH₃)(C₆H₅)₂, since it shows that hexamethyltungsten can expand its coordination shell and can form 7-coordinate adducts. Since the presence of phosphines (or alkenes, which presumably also coordinate) inhibits the reaction of CO with W(CH₃)₆, this suggests that this and other reactions

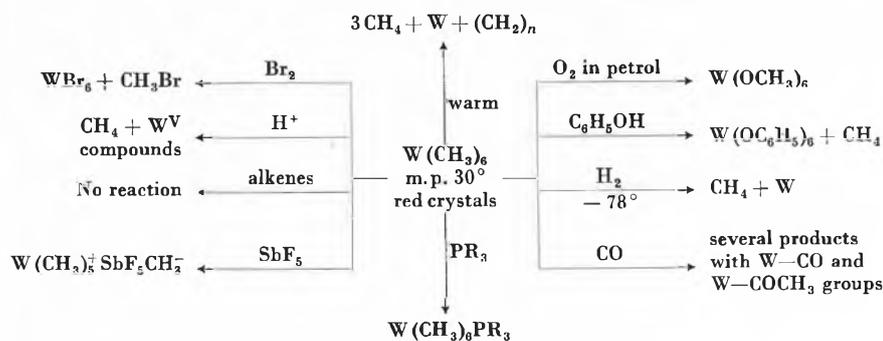
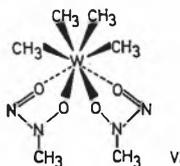


Fig. 1. Some reactions of hexamethyltungsten

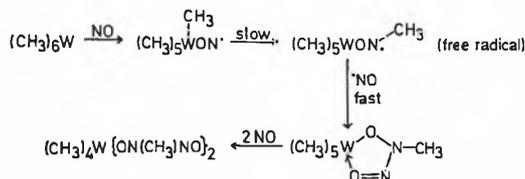
probably proceed *via* initial formation of a 7-coordinate species:



One of the few well defined quantitative reactions is that with nitric oxide. This gives the compound VI which has a distorted 8-coordinate W^{VI} structure²⁰ with four



CH_3 groups bound to tungsten and two N-methyl-N-nitrosylaminate chelate rings. This molecule is stereochemically non-rigid since on cooling the proton resonance of the methyl groups bound to tungsten shows a single line at 30°C broadens and below -50° shows a well defined doublet. We have been able to show by *in situ* reaction in an n.m.r. tube that the two chelate rings are formed successively. The mechanism may well involve steps of the following kind



Only few NO reactions of this type have been characterised;²¹ the derivative obtained from $(h^5-C_5H_5)_2Zr(CH_3)_2$ probably has a chelate ring rather than a unidentate $-ON(CH_3)NO$ group as proposed.²¹ The formation of a 9-coordinate Zr complex then clearly explains why only *one* of the Zr- CH_3 groups reacts.

In conclusion we can say that:

- (i) the transition metal to carbon bond is *not* especially weak;
- (ii) thermally stable binary alkyls can be synthesised provided the nature of the alkyl group is chosen so that the hydride-transfer alkene elimination pathway for decomposition is prevented;
- (iii) stable complex alkyls can be obtained when vacant coordination sites on the metal are blocked by suitable ligands, often π -bonding ones, except in octahedral substitution inert complexes of Cr^{III} , Co^{III} and Rh^{III} where even H_2O or NH_3 can suffice;
- (iv) the isolation of hexamethyltungsten dispels the myth that transition metals in high oxidation states cannot form binary alkyls and gives hope that methyls or other alkyls in the highest known oxidation states of transition metals can be prepared.

¹⁸ K. J. THIELE and J. MÜLLER, *Z. anorg. Chem.* 362 (1968) 113, 120; R. J. M. CLARK and A. J. MCALESS, *J. Chem. Soc. A* 1970, 2026; G. W. A. FOWLES *et al.*, *J. Chem. Soc. A* 1971, 1920; R. TABACCHI and A. JACOT-GUILLARD, *Chimia* 24 (1970) 271.

¹⁹ A. SHORTLAND and G. WILKINSON, *Chem. Comm.* 1972, 318; *J. Chem. Soc. (Dalton)* 1973, in press

²⁰ S. F. FLECHTER, A. SHORTLAND, A. C. SKAPSKI and G. WILKINSON, *Chem. Comm.* 1972, 922.

²¹ For references see P. C. WAILES, H. WEIGOLD and A. P. BELL, *J. Organometal. Chem.* 34 (1972) 155.