12 July 1974, Volume 185, Number 4146 SCIENCE

The Long Search for Stable Transition Metal Alkyls

Geoffrey Wilkinson

Chemical compounds in which there is a single bond between a saturated carbon atom and a transition metal atom are of unusual importance. Quite aside from the significance and role in nature of the cobalt to carbon bonds in the vitamin B_{12} system and of the possible metal to carbon bonds in other biological systems, we need only consider that, during the time taken to deliver this lecture, many thousands, if not tens of thousands, of tons of chemical compounds are being transformed or synthesized industrially in processes which at some stage involve a transition metal to carbon bond. The nonchemist will probably be most familiar with polyethylene or polypropylene in the form of domestic utensils, packaging materials, children's toys, and so on. These materials are made by Ziegler-Natta or Phillips' catalysis, which utilize compounds of the metals titanium and chromium, respectively. However, transition metal compounds are used as catalysts in the synthesis of synthetic rubbers and other polymers, and of a variety of simple compounds used as industrial solvents or intermediates. For example, alcohols are made from olefins, carbon monoxide, and hydrogen by use of cobalt or rhodium catalysts; acetic acid is made by carbonylation of methanol using rhodium catalysts, and acrylonitrile is dimerized to adiponitrile (for nylon) by nickel catalysts. We should also not forget that the huge quantities of petroleum hydrocarbons processed by the oil and petrochemical industry are re-formed over platinum, platinum-rhenium, or platinum-germanium supported on alumina.

In all of these processes, every single molecule, at some point in the catalytic cycle, is involved in the formation of a metal to carbon single bond. Of course, catalytic processes require that the metal to carbon bond be unstable—or, more accurately, that it be labile and able readily to undergo chemical reactions such as

$$M\text{–}CR_3 + CO \rightarrow M\text{—}\overset{\overset{O}{\|}}{C}\text{—}CR_3$$

$$M\text{–}CR_3 + H_2 \rightarrow MH + HCR_3$$

where M is metal and R is alkyl.

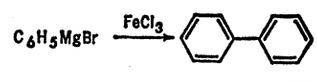
Today, however, I am concerned not with catalysis but with the synthesis of simple, stable metal compounds that have single bonds to saturated carbon. The synthesis of stable metal alkyls, and indeed the nature of the transition metal to carbon bond, is a problem that has been with us for a long time.

The first attempts to make such compounds took place shortly after Frankland's epoch-making discovery of diethylzinc. Thus, in 1859, Buckton wrote, "a rich harvest can scarcely fail to be reaped from submitting to the action of diethylzinc the metallic compounds of the other groups" (*1*). However, he failed with the transition metals silver, copper, and platinum, as indeed did other workers in the 1800's.

We must not forget, however, that a transition metal organo compound, although of a quite different type, had been made much earlier by the Danish pharmacist Zeise. By the interaction of alcohol and chloroplatinic acid he had made the salt $K[C_2H_4PtCl_3]$ known now as Zeise's salt. There followed much discussion of the exact constitution of this substance, but it was to be more than 125 years before the structure was determined and the way in which ethylene is bound to the metal was fully understood.

The first stable metal alkyls to be isolated were those of platinum (*2*) and gold (*3*) by William Pope and his co-workers Peachy and Gibson at the Municipal School of Technology in Manchester. The structure of the trimethylplatinum compound $[(CH_3)_3PtCl]_4$ was not to be determined by x-ray diffraction for another 40 years. At the meeting of the Chemical Society in London on 21 March 1907, at which the discovery was announced, the chairman, Sir Henry Roscoe, complimented the authors on opening out an entirely new branch of investigation "which might indeed be said to be a wonderful find." This promise took a very long time indeed to be fulfilled. Even in 1955 it could be written (*4*), "It will be apparent from this overall picture of alkyls and aryls of the transition metals that the often heard generalization that they are much less stable and accessible than those of nontransition metals is quite true."

The main reason for the failure to isolate stable compounds, despite evidence that alkyls or aryls were present in solution at low temperatures, was that the interaction of transition metal halides with Grignard reagents or lithium alkyls usually gave either coupled products or products from decomposition of coupled species. Typically, ferric chloride was used to make coupled products, such as diphenyl.



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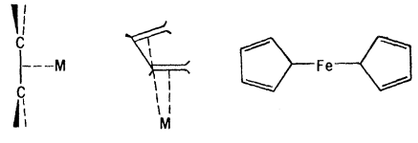
It was this coupling that Kealy and Pauson (*5*) were trying to utilize, to make dihydrofulvalene, which led to their synthesis of dicyclopentadienyl iron.

$$C_5H_5MgBr \xrightarrow{FeCl_3} (C_5H_5)_2Fe \text{ not } C_5H_5 - C_5H_5$$

It might be interesting to note in passing that my own conclusion about the structure of this iron compound was based on two points: first, my knowledge of the instability of transition metal alkyls and aryls, and second, my intuition concerning the nature, uncertain at that time, of the binding of ethylene in Zeise's salt and of butadiene in Reihlen's compound, $C_4H_6Fe(CO)_3$. I was convinced that ethylene was bound "sideways" (**1**) and that butadiene in its *cis* form could act as a chelate (**2**), both double bonds being bound to the metal. These structures were later confirmed by others. Thus I wanted to involve both double bonds of the cyclopentadienyl ring in the structure originally written (*5*) by Kealy and Pauson and Miller, Tebboth, and Tremaine (**3**), in a butadiene-like fashion (**4**) resulting in a "sandwich" structure.

Having read Linus Pauling's famous book, *The Nature of the Chemical Bond* (*6*), and heard about resonance, this meant that I could write various resonance forms of **4**, which directly led to the idea that all the carbon atoms were equivalent as in **5**; that is,



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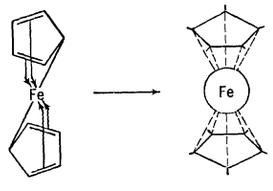
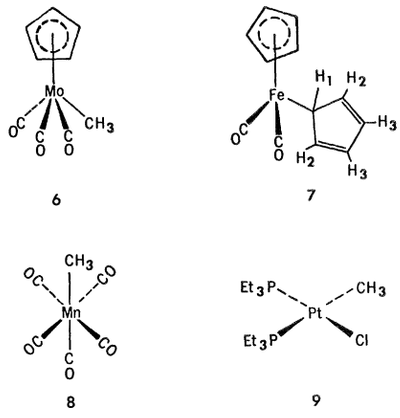


4 5

to the well-known structure of the molecule now known as ferrocene (*7*).

During the next few years a number of stable compounds in which alkyl or aryl groups were present were synthesized. The first was a phenyltitanium alkoxide $C_6H_5Ti(OC_3H_7)_3$ (*8*) and others soon followed. However, in essentially all of the compounds a special type of ligand was present. These ligands were what are referred to as π-acid or π-bonding ligands. Examples are π-C_5H_5, CO, and $P(C_2H_5)_3$. Representative types of these alkyls are **6** to **9**. The compound



6 7 8 9

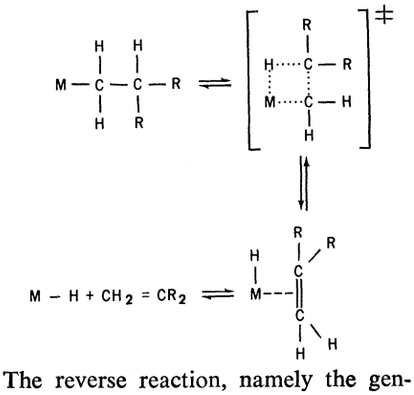
7 turned out to be especially interesting. We observed only two signals in the proton magnetic resonance spectrum, whereas the σ-C_5H_5 group alone should have had a complex spectrum; the infrared spectrum however was consistent with **7**. Because of the analogy with photography—where if one takes a picture of a moving wheel with a short exposure time (infrared), the picture is sharp, whereas if one uses a longer time (nuclear magnetic resonance, NMR), it is blurred—I had to draw the conclusion that the σ-C_5H_5 was actually quite slowly rotating via a 1 : 2 shift. This was the first recognition of what are now known as fluxional molecules, this particular type being called "ring whizzers."

So the view developed that in order to have stable compounds with alkyl or aryl groups bound to a metal, some "stabilizing" group also had to be present. As recently as 1968, it was written (*9*), "By any criterion, simple transition metal alkyls are unstable" and "In contrast to the simple alkyls, some metal complexes bearing other ligands in addition to alkyl or aryl groups are strikingly stable."

However, it was not too well recognized that the presence of such "stabilizing" ligands is no guarantee of stability because other factors are involved. Indeed, the activity of many metal complexes with π-bonding ligands present in catalytic reactions depends on the lability of the metal to carbon bonds.

Despite all the intense study of metal-carbon bonds and the arguments about their stability, it is remarkable that only few bond energies are known. The available thermodynamic data show that M–C bonds are not exceptionally weak and the bond energies are quite comparable to those of nontransition metal to carbon bonds. It could be argued that, since the compounds for which bond energies have been determined have "stabilizing" π-bonding ligands present, the M–C bond energies are abnormally high; but this view cannot be sustained. There is no reason to assume this to be so, nor is there any reason to assume that carbon would differ appreciably in its capability to bond to transition metals compared to other first row elements such as oxygen and nitrogen or to the halogens. For both oxygen and nitrogen, metal compounds in high oxidation states are well known, for example, the alkoxides such as $V(OR)_4$ and dialkylamides such as $W(NR_2)_6$. So, accepting that there is no thermodynamic reason for the instability of simple alkyls, the conclusion was that they are kinetically unstable.

There are several ways by which a metal alkyl can decompose, but for transition metal compounds one of the best established is the so-called hydride transfer–alkene elimination reaction. Here, a hydrogen atom is transferred from the second or β-carbon of the alkyl chain to the metal. The intermediate hydrido-alkene complex can then lose alkene and the resulting metal hydride decomposes further, for example, to metal and hydrogen.

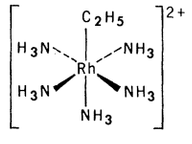


The reverse reaction, namely the generation of a metal alkyl from a metal hydride plus alkene, is the key reaction in many catalytic cycles involving alkenes, hydrogen, and metal species. It is involved, for example, in homogeneous hydrogenation of unsaturated organic compounds and in the hydroformylation reaction in which

aldehydes or alcohols are synthesized from alkenes, carbon monoxide, and hydrogen.

Two relevant studies on this decomposition reaction are illustrative. First, a comparison of the relative stabilities of dialkylmanganese compounds made in situ shows that those alkyls, for example, $Mn(CH_3)_2$ or $Mn(CH_2C_6H_5)_2$, that cannot readily undergo this reaction are most stable (*10*). Second, a comparison (*11*) of the decomposition products of two similar alkyls, one that has a β-hydrogen, $Bu_3PCuCH_2CH_2$-CH_2CH_3, and one that has not, Bu_3-$PCuCH_2C(CH_3)_2C_6H_5$, shows that the former decomposes via hydrogen transfer alkene elimination, whereas the other decomposes by homolytic fission and a free radical pathway.

It will be observed that the hydrogen transfer scheme involves a change in coordination number of the metal. Thus the alkyl group occupies only one coordination site, whereas in the intermediate hydrido-alkene two sites are involved, one for M–H and one for olefin coordination. Thus, one way in which an alkyl could be stabilized against decomposition is by coordinative saturation of the metal. If the sites required for the reaction to proceed are occupied by firmly bound ligands, then there is no possible pathway for decomposition. The stability of the alkyls with π-bonded ligands referred to above are prime examples of this situation. Other examples are the alkyls of the substitution-inert octahedral metal ions Cr^{III}, Co^{III}, and Rh^{III}, such as the Werner-type complex ion (*10*). A different type is on the chelated, coordinatively saturated alkyl (**11**) which is thermally stable to 350°C.



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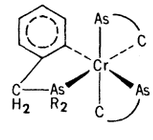

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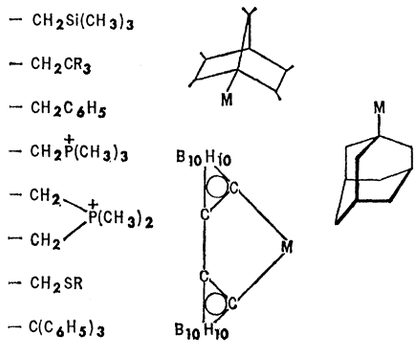
There seemed to be another way, however, by which stable alkyls could be obtained, namely by making the hydrogen transfer reaction impossible. Thus if the β-carbon atom were to be replaced by silicon or some other element that could *not* form a double bond to carbon, the formation of alkene becomes impossible, even if there were a hydrogen atom on silicon; the alternative is to have no hydrogen on the β atom. We illustrated this concept by use of the trimethylsilylmethyl [$-CH_2Si(CH_3)_3$] group as the alkyl and were able to isolate for the first time a number of kinetically stable alkyls such as $Cr[CH_2Si(CH_3)_3]_4$ (*12*).

A number of other groups, including of course the carbon analog neopentyl [$CH_2C(CH_3)_3$], fit the required criteria of having no β-hydrogen, and at present alkyls are known with the following groups:

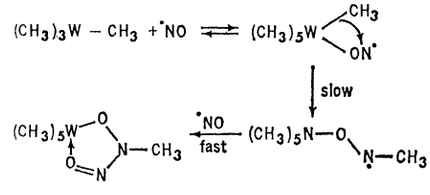


It may be noted that some of these alkyls, notably those of titanium, have been recognized as Ziegler-Natta type catalysts for the polymerization of alkenes (*13*).

The simplest of all alkyl groups is, of course, the methyl group. Although tetramethyltitanium has been known for some years, it decomposes above −70°C very readily. However, by blocking the remaining two vacant coordination sites of the tetrahedral alkyl, for example, by dipyridyl, the thermal stability can be substantially increased. Despite its instability, vibrational spectroscopic studies (*14*) of $Ti(CH_3)_4$ suggest that the Ti–C bond strength, as measured by its force constant, is quite comparable to those of the tetramethyls of Si, Ge, Sn, and Pb. By contrast, the least stable of these, tetramethyllead, can be distilled at its boiling point (110°C) without decomposition. The instability of $Ti(CH_3)_4$ is thus clearly kinetic, there being readily accessible pathways for decomposition possible because of its coordinative unsaturation. Although the chloride methyls of niobium and tantalum, $(CH_3)_3MCl_2$, have been known for some time and are reasonably stable and although we succeeded in characterizing a rather unstable tetramethyl of chromium, it appeared that, if a coordinatively saturated methyl could be synthesized, there was good reason to expect it to be stable. The obvious candidate was tungsten, for which the hexaalkoxides and dialkylamides as well as the halides are known. We succeeded in synthesizing hexamethyltungsten by the classical reaction of methyllithium with tungsten hexachloride (*15*). The reaction sequence is a very complex one, and in order to obtain any $W(CH_3)_6$ it is necessary to use only half of the theoretical quantity of methyllithium, probably to avoid the formation of a methyl anion of the type known for other metals, for example, $Li_4Mo_2(CH_3)_8$. The final step probably also involves the disproportionation of a reduced species:

$$W^{V} \rightarrow W^{IV} + W^{VI}$$

Once obtained, hexamethyltungsten is reasonably stable and can readily be characterized spectroscopically. It also has a number of interesting chemical reactions. It soon became evident that the compound, although octahedral, is not coordination saturated and that some of the reactions are very facile because coordinative unsaturation allows initial coordination of the reagent. Using teritary phosphines, we were able to isolate seven-coordinate adducts, $W(CH_3)_6PR_3$. One of the unusual reactions was that with nitric oxide—which quantitatively gives a compound $(CH_3)_4W[ON(CH_3)NO]_2$ which contains two *N*-nitroso-*N*-methyl hydroxylaminato rings. These are probably generated by initial coordination of nitric oxide followed by methyl transfer as in the sequence:



This sequence can happen only twice as the coordination number then reaches eight, which appears to be the maximum for tungsten in the VI oxidation state. Although the synthesis of other methyls is in principle possible, there is more art to it than science. The only other methyl in a very high oxidation state we have yet made is oxotetramethylrhenium(VI), $ReO(CH_3)_4$ but oxo or similar methyls of tungsten, molybdenum, osmium, and the like may well be stable if suitable synthetic methods are found (see *16*).

In conclusion we can say that the effort of well over 100 years to synthesize stable transition metal alkyls has

finally succeeded. The long-established view that the transition metal to carbon bond is weak is now untenable and must be discarded. We can expect other types of transition metal alkyls to be made in due course and can hope that in addition to their own intrinsic interest some of them may find uses in catalytic or other syntheses. The use of titanium and zirconium alkyls in alkene polymerization (*13*) and the use of alumina treated with hexamethyltungsten for alkene metathesis (*17*) give good grounds for optimism.

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Physicochemical Correlates of Olfactory Quality

A series of physicochemical variables are weighted mathematically to predict olfactory quality.

Susan S. Schiffman

A model does not exist in olfaction which strictly relates quantitative measures of olfactory quality with quantitative physicochemical measures. Although each of the more notable olfactory theories makes useful suggestions, none provides a basis for developing a complete model which could accurately order all olfactory stimuli.

Olfactory Theories

Amoore (*1*) suggested that the shape and size of a molecule are the crucial physicochemical parameters for stimulation in olfaction. He proposed receptor sites which relate to molecular stimuli in a "lock and key" fashion. Molecules of similar size and shape are expected to have similar odor quality. In testing this hypothesis, Amoore and Venstrom (*2*) found significant correlations between odor quality and a hand-calculated index of molecular size and shape for five classes of odors (ethereal, camphoraceous, musky, floral, and minty). Amoore (*3*) found a correlation of 0.90 between odor quality and a computer-generated molecular shape index when 25 substances were compared with benzaldehyde (almond odor).

Wright (*4*) has challenged Amoore's results, indicating that it is inappropriate to represent anything as complicated as a three-dimensional molecular shape by an index consisting of a single number. Many different three-dimensional profiles could share the same molecular shape index. Wright's theory (*5*) is that the mechanism for stimulation of olfactory receptors is low energy molecular vibrations. Molecules with similar vibrational frequency patterns are expected to have similar odor quality. In testing this hypothesis Wright and Robson (*6*) determined that a pattern of frequencies in the far infrared spectra correlated highly with the bitter almond odor. Wright and Brand (*7*) found a relationship between pheromone activity and molecular vibration in insects.

Dravnieks and Laffort (*8*) have related four factors concerned with intermolecular interaction forces (an apolar factor, a proton receptor factor, an electron factor, and a proton donor factor) to both quantitative and qualitative odor discrimination in human beings. Dravnieks (*9*) has also devised a chemical building block model which relates the hedonic qualities of olfactory stimuli to a series of physicochemical variables.

Other theories concerning the process of olfactory stimulation have also been proposed: Beets' theory of profile functional groups (*10*); Henning's emphasis on the position of functional groups in relation to the rest of the molecule (*11*); and Mozell's suggestion that the olfactory epithelium is similar to a gas chromatograph (*12*).

In spite of these efforts, the ability to predict olfactory quality from quantitative physicochemical measures for a wide range of olfactory stimuli has yet to be achieved. The purpose of this article is to demonstrate a procedure which, when extended to a wide range of stimuli, can provide us with means for predicting olfactory quality from physicochemical parameters.

Multidimensional Scaling

The recently developed methodology of multidimensional scaling can aid in deepening our understanding of the relationship between psychological dimensions in olfaction and physicochemical variables. Multidimensional scaling procedures can order olfactory sensations in spaces to reveal relationships and distances among the olfactory stimuli based on experimental mea-

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