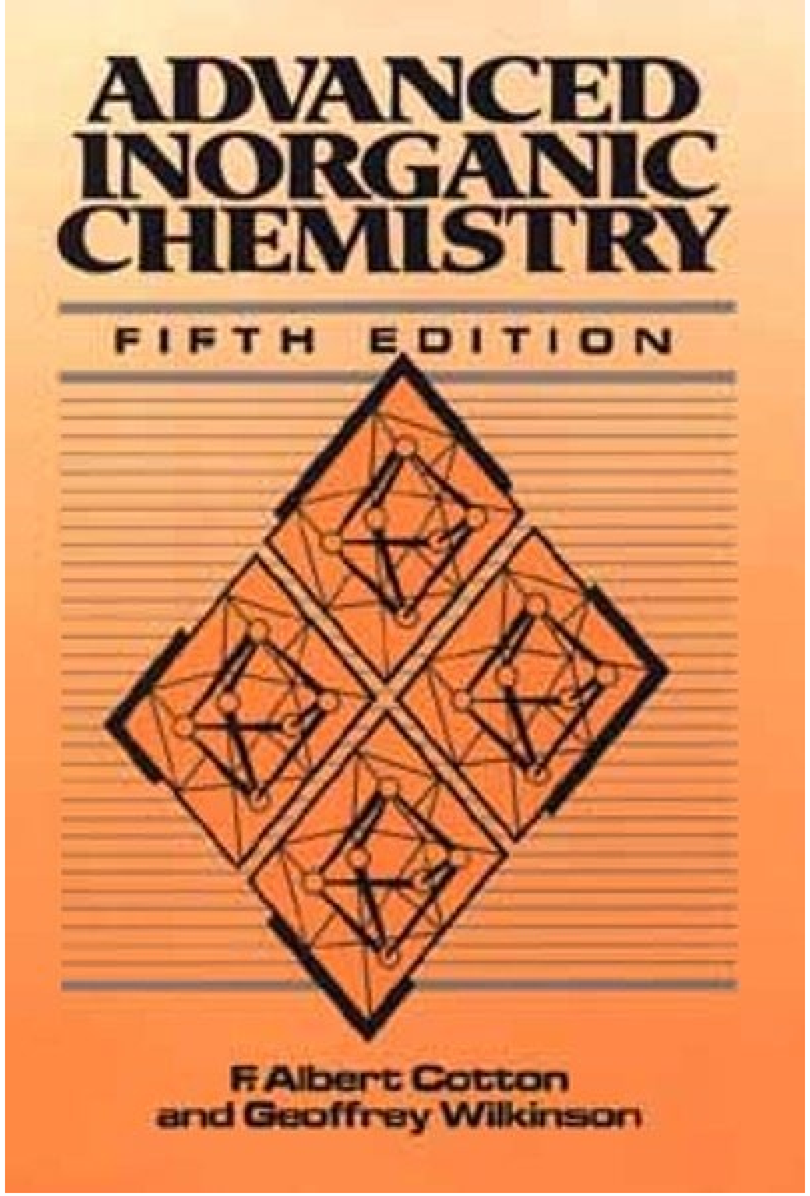

ADVANCED
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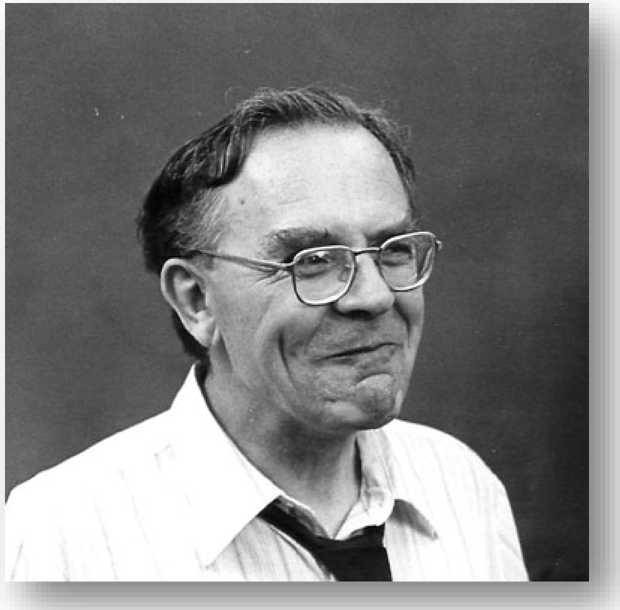
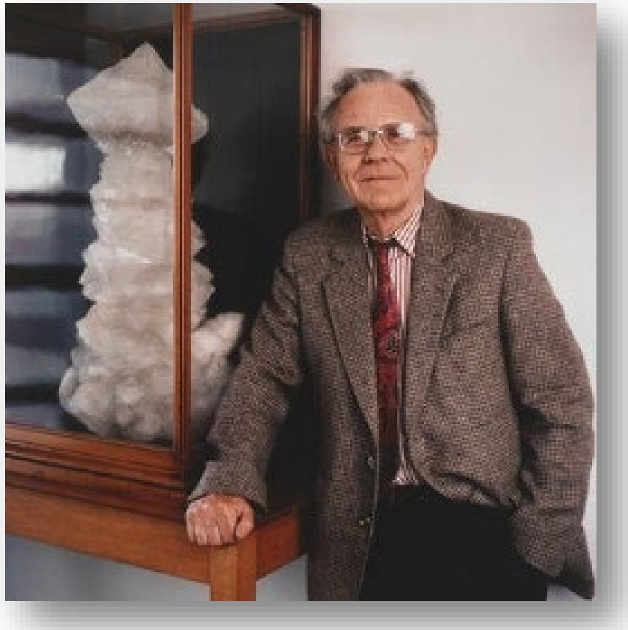
FIFTH EDITION

F. Albert Cotton
and Geoffrey Wilkinson

Classic Paper Presentation

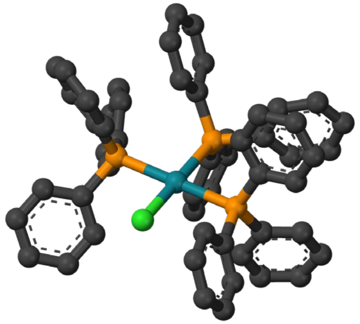




The long search for stable transitional metal alkyls

Sir Geoffrey Wilkinson

Noble prize in Chemistry, 1973



Presented by
Sinchan Mukherjee
24.02.2024

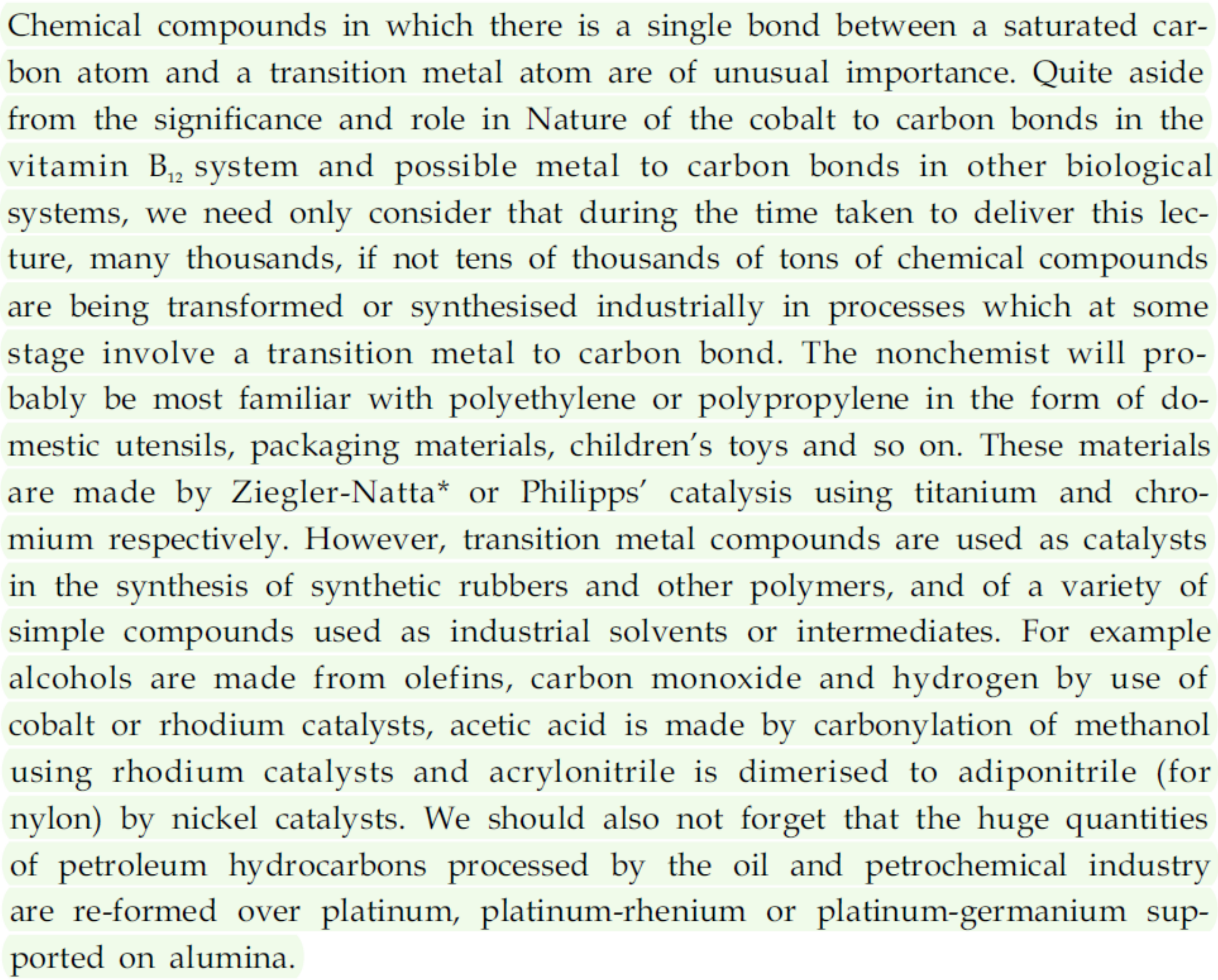
THE LONG SEARCH FOR STABLE TRANSITION METAL ALKYLS

Nobel Lecture, December 11, 1973

by

GEOFFREY WILKINSON

Imperial College of Science & Technology, London, England



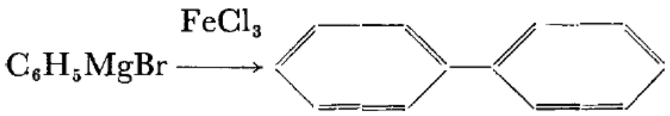
Chemical compounds in which there is a single bond between a saturated carbon atom and a transition metal atom are of unusual importance. Quite aside from the significance and role in Nature of the cobalt to carbon bonds in the vitamin B_{12} system and possible metal to carbon bonds in other biological 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 synthesised 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 Philipps' catalysis using 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 dimerised 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.

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.

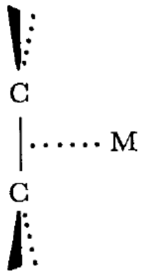
The first attempts to make such compounds were shortly after Frankland's epoch-making discovery of diethylzinc. Thus in 1859 Buckton wrote, "a rich harvest can scarcely fail to be reaped from submitting to the action of diethylzinc the metallic compounds of the other groups" (1). However, he failed with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

siton of coupled species. Typically, ferric chloride was used to make coupled products, e.g., diphenyl.

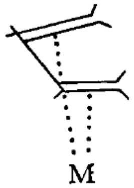


It was this coupling that Kealy and Pauson (5) were trying to utilize, to make dihydrofulvalene, which led to their synthesis of dicyclopentadienyl iron

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



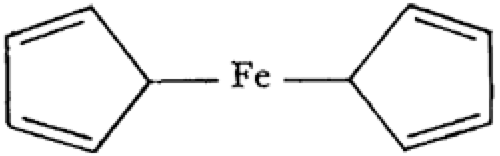
(I)



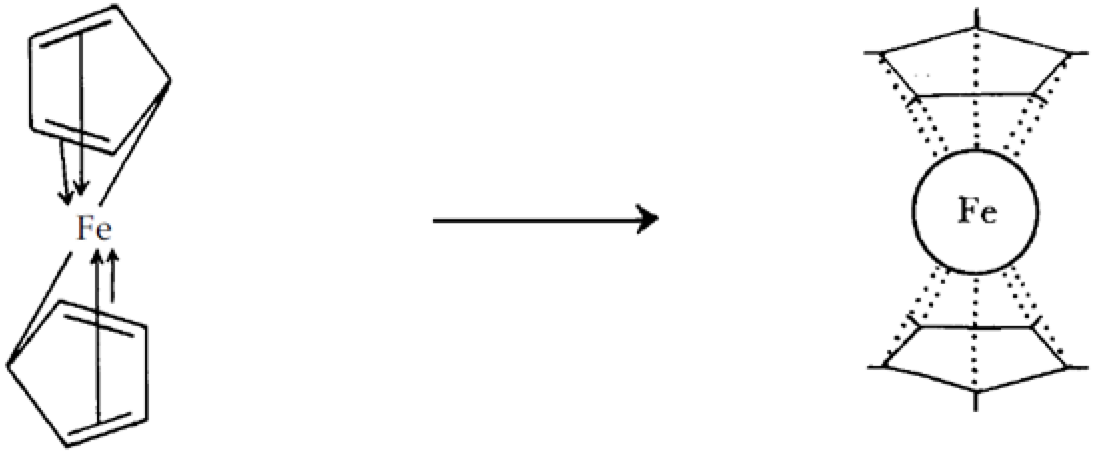
(II)

It might be interesting to note in passing that my own conclusion about the structure of this iron compound was based on two points. Firstly, my knowledge of the instability of transition metal alkyls and aryls, secondly 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" (I) and that butadiene in its *cis* form could act as a chelate (II), both double bonds being bound to the metal.

"sandwich" structure.



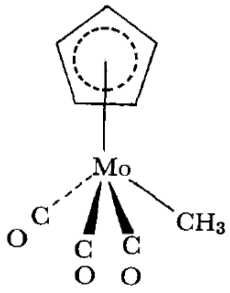
(III)



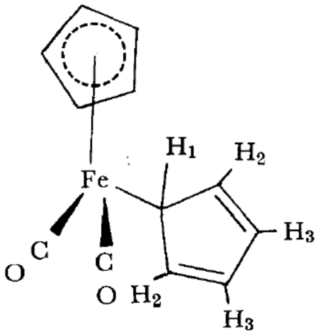
(IV) (V)

Having read Linus Pauling's* famous book, *The Nature of the Chemical Bond*, and heard about resonance, this meant that I could write various resonance forms of IV, which directly led to the idea that all the carbon atoms were equivalent as in V, that is to the well known structure of the molecule now known as ferrocene*.

During the next few years a number of stable compunds in which alkyl or aryl groups were present were synthesised. The first was a phenyltitanium alkoxide $C_6H_5Ti(OC_3H_7)_3$ (6) 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, PEt_3, etc. Representative types of these alkyls are (VI-IX).



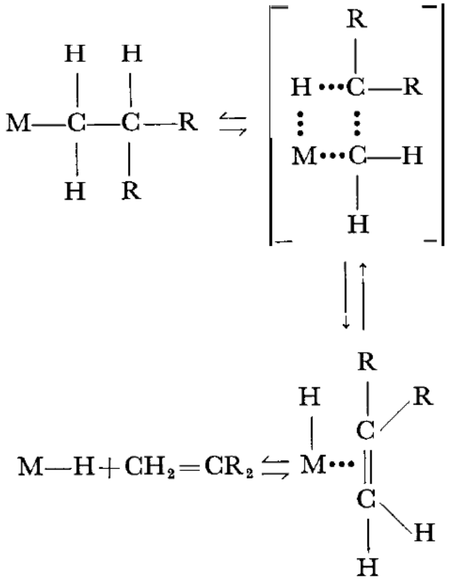
(VI)



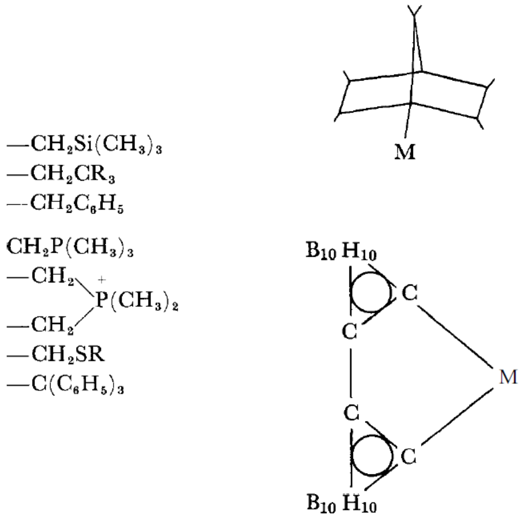
(VII)

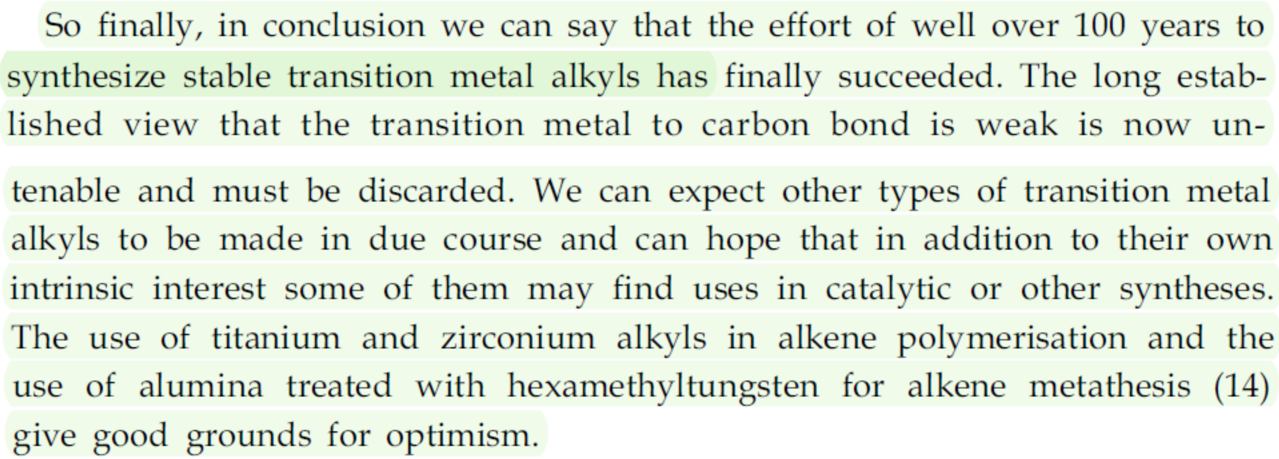
The compound (VII) turned out to be especially interesting. We observed only two signals in the proton magnetic resonance spectrum whereas the **σ-C_5H_5** group alone should have had a complex spectrum; the infrared spectrum however was consistant with (VII). Because of the analogy with photography 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 (n.m.r.) 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”.

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 decompose further e.g., to metal and hydrogen.

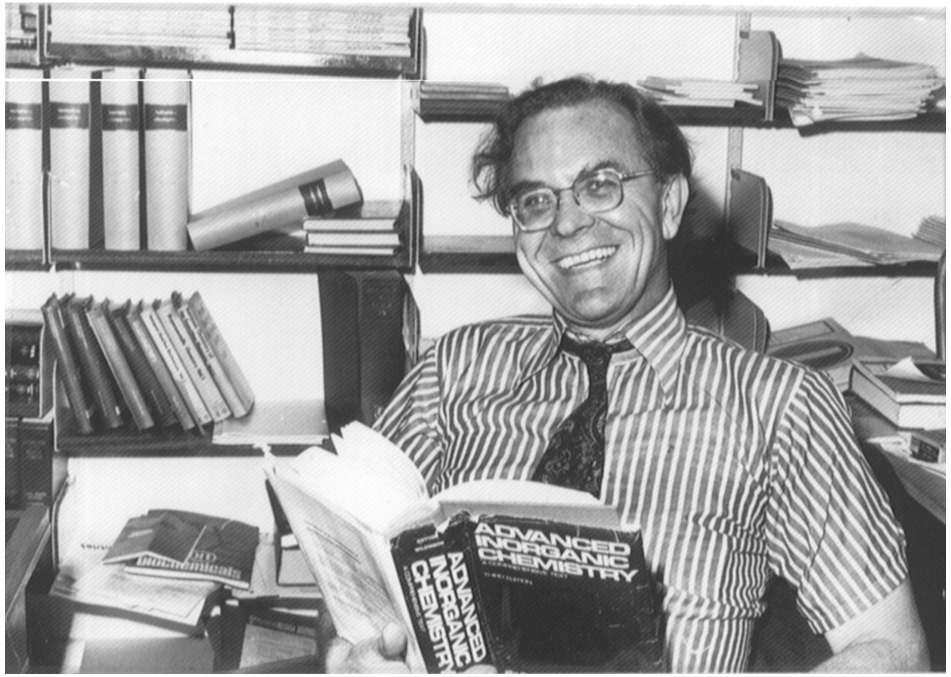


There seemed, to be another way, however, by which stable alkyls could be obtained, namely by making the H-transfer reaction impossible. Thus if the β-carbon atom were to be replaced by silicon or some other element that could not form a double bond to carbon the formation of alkene becomes impossible, even if there were a hydrogen atom on silicon; alternatively to have no hydrogen on the β atom. We illustrated this concept (10) by use of

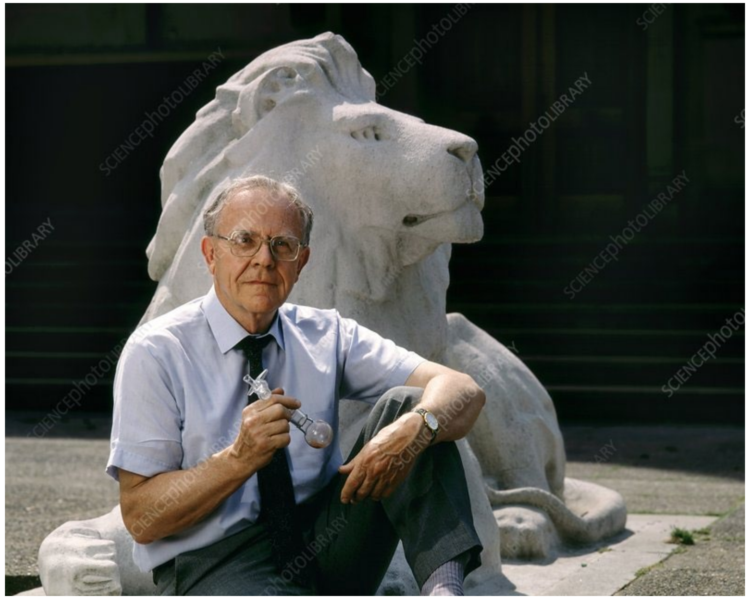

$-CH_2Si(CH_3)_3$
$-CH_2CR_3$
$-CH_2C_6H_5$
$CH_2P(CH_3)_3$
$-CH_2$, $\overset{+}{P}(CH_3)_2$, $-CH_2$
$-CH_2SR$
$-C(C_6H_5)_3$



So finally, 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 polymerisation and the use of alumina treated with hexamethyltungsten for alkene metathesis (14) give good grounds for optimism.



Born	14 July 1921 Todmorden, West Riding of Yorkshire, England
Died	26 September 1996 (aged 75) London, England
Nationality	British
Alma mater	Imperial College London (PhD)
Known for	Homogeneous transition metal catalysis
Awards	FRS (1965)[1] Nobel Prize in Chemistry (1973) Royal Medal (1981) Ludwig Mond Award (1981) Davy Medal (1996)



Scientific career	
Fields	Inorganic chemistry
Institutions	University of California, Berkeley Harvard University Imperial College London
Thesis	*Some physico-chemical observations on hydrolysis in the homogeneous vapour phase* (1946)
Doctoral advisor	Henry Vincent Aird Briscoe[2]
Other academic advisors	Glenn T. Seaborg (post doctoral advisor)
Doctoral students	Andrew R. Barron Martin A. Bennett F. Albert Cotton Alan Davison[3][4] Malcolm Green[5] John A. Osborn
Other notable students	Richard A. Andersen (postdoc)

Thank You