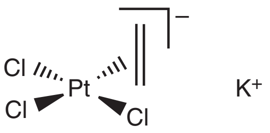
HISTORY OF ORGANOMETALLIC CHEMISTRY

1760-1900: THE FIRST COMPLEXES

The boom in organometallic chemistry occurred essentially in the United States, England and Germany during the 3rd quarter of the XXth century. It is in a military pharmacy in Paris, however, that the discipline was born in 1760. Cadet, who was working on cobalt-containing inks, used arsenic-containing cobalt salts for their preparation. In this way, he discovered the fuming and ill-smelling Cadet's liquid which comprises a mixture of cacadoyl oxide and tetramethyldiarsine by carrying out the following reaction:

$$\mathrm{As_2O_3} + 4\ \mathrm{MeCO_2K} \longrightarrow [(\mathrm{AsMe_2})_2\mathrm{O}] + [\mathrm{Me_2As\text{-}AsMe_2}] + \ldots$$

One of the key events of the XIXth century was the discovery of the first π complex, namely Zeise salt $\mathrm{K[PtCl_3(\eta^2\text{-}C_2H_4)]}$, in 1827, although the correct formula below was proposed much latter.

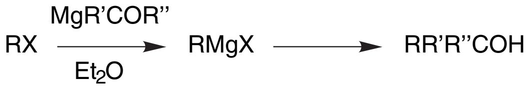


Zeise salt, 1827

In the mid-1850s, Frankland synthesized several air-sensitive metal-alkyl complexes such as $\mathrm{ZnEt_2}$ (1849), $\mathrm{HgEt_2}$ (1852), $\mathrm{SnEt_4}$ and $\mathrm{BMe_3}$ (1860), the mercury and zinc complexes being immediately used to synthesize many other main-group organometallic complexes. For instance, Friedel and Crafts prepared several organochlorosilanes $\mathrm{RnSiCl_{4-n}}$ from the reactions of $\mathrm{SiCl_4}$ with $\mathrm{ZnR_2}$ (1863). Shortly afterwards, Schützenberger, an Alsatian chemist, synthesized the first metal-carbonyl derivatives $\mathrm{[Pt(CO)_2Cl_2]}$ and $\mathrm{[Pt(CO)Cl_2]_2}$ (1868-1870). Twenty years later, the first binary metal-carbonyl compounds appeared: $\mathrm{[Ni(CO)_4]}$ (Mond, 1890) and $\mathrm{[Fe(CO)_5]}$ (Mond and Berthelot, 1891). From 1893 onwards and over a period of twenty years, Werner developed the modern ideas of inorganic chemistry in his proposal according to which the $\mathrm{Co^{3+}}$ ion is surrounded by six ligands in an octahedral complex $\mathrm{[CoL_6]^{3+}}$. These ideas were contrary to those proposed by the well-known chemists of that time such as Jorgensen, according to whom the ligands should be aligned in a chain with the metal at the terminus.

1900-1950: GRIGNARD, SABATIER, AND CATALYSIS IN GERMANY

It is at the turn of the XX^th^ century that the major French contribution came into fruition with the work of Barbier and especially of his student Victor Grignard. Grignard's name is forever engraved in the history of chemistry for the reaction of magnesium with organic halides RX leading, by oxidative addition, to Grignard reagent RMgX that can alkylate carbonyl derivatives.



$$RX \xrightarrow[Et_2O]{MgR'COR''} RMgX \longrightarrow RR'R''COH$$

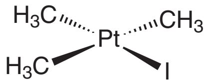
This discovery had an enormous impact, not only on organic chemistry, but also proved to be of considerable importance in transition-metal organometallic chemistry. For instance, in 1919, Hein synthesized what he believed to be a polyphenylchromium derivative $[(Cr(\sigma\text{-}Ph)_n]$:

$$CrCl_3 + PhMgBr \longrightarrow [Cr(\sigma\text{-}Ph)_n]^{0,+1} \qquad n = 2, 3 \text{ or } 4$$

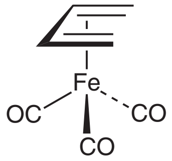
However, some 36 years later, it was revealed that the compound posseses a π sandwich-type structure.

The first half of the XX^th^ century was especially noteworthy for the emergence of catalysis. The distinction between homogeneous and heterogeneous catalysis was first delineated by the French chemist Paul Sabatier (one of Berthelot's students). Sabatier and Senderens' work on the heterogeneous hydrogenation of olefins to saturated hydrocarbons using nickel eventually led to a Nobel Prize shared in 1912 between Sabatier and Grignard. Many seminal discoveries, however, were made in Germany during this first half of the XX^th^ century. In 1922, Fischer and Tropsch reported the heterogeneously catalyzed reaction between CO and H_2 (syngas) to form mixtures of linear alkanes and alkenes with few oxygenates as by-products (Fischer-Tropsch process, industrially developed in 1925). In 1938, Roelen discovered the catalysis by $[Co_2(CO)_8]$ of the hydroformylation of olefins by CO and H_2 (oxo process). From 1939 to the late 1940s, Reppe worked on the catalysis of transformation of alkynes (tetramerization to cyclo-octatetraene, 1948).

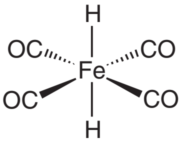
Curiously, there were only a few advances in the discovery of new complexes during this period. Besides iodotrimethylplatinum, $[PtMe_3I]$, synthesized by Pope at the beginning of the XX^th^ century, the list includes $[Fe(\eta^4\text{-butadiene})(CO)_3]$ made by Reilhen in 1930 and Hieber's work on metal carbonyls from 1928 onwards (e.g. the synthesis of $[Fe(H)_2(CO)_4]$, 1931).



First σ-alkyl-metal complex
Pope, 1909



First diene-complex
Reilhen, 1930



First metal-hydride complex
Hieber, 1931

1950-1960: THE DISCOVERY OF FERROCENE AND THE BOOM OF ORGANOMETALLIC CHEMISTRY

It is in the 1950s that inorganic and organometallic chemistry boomed, especially in the United States. Henry Taube classified the inorganic complexes as inert or labile towards substitution reactions, depending on the nature of the ligand and oxidation state of the metal (1951). This work laid the foundation of molecular engineering that allowed him to carry out a crucial series of experiments: the catalysis of substitution reactions by electron or atom transfer, and the distinction between outer-sphere electron transfer and that proceeding by the inner sphere which is considerably faster (1953).

Structural bio-organometallic chemistry has its origin with the English chemist Dorothy Crowfoot-Hodgkin who established the X-ray crystal structure of vitamin B_{12} coenzyme between 1953 and 1961 using a primitive computer, resulting in her awarding the Nobel Prize in 1964. Consecutively, the legendary Harvard University chemist Robert B. Woodward achieved the total synthesis of this coenzyme in 70 steps with 99 co-workers from 1961 to 1972.

In England too, several chemists had noted, at the beginning of the 1950s, this very stable orange powder that formed when cyclopentadiene is passed through iron tubings. Some chemists had even filled pots with it in their laboratory. Keally, Pauson and Miller first published the compound in 1951, and Pauson reported the structure $[Fe(\sigma\text{-}C_5H_5)_2]$ in the journal *Nature*. In doing so, he made the same mistake as Hein, 32 years earlier. In the meantime, however, Sidgwick had published the 18-electron rule for transition-metal complexes in his book "*The Electronic Theory of Valency*" (Cornell University, Ithaca, 1927). Pauson's proposed σ structure for bis-cyclopentadienyl-iron only had 10 valence electrons and was soon challenged. At Harvard University, Willkinson and Woodward recognizing Sidgwick's rule, immediately understood that the Pauson formulation was incorrect. A few months later, they published the first sandwich structure, just before Fischer: bis-cyclopentadienyl-iron is ferrocene, an 18-electron complex, in which the two rings are perfectly parallel, π-bound to the iron atom and having aromatic properties (1952).

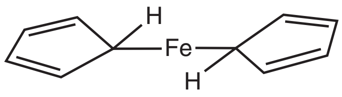
R.B. Woodward and Ferrocene

Robert Burns Woodward (1917-1979), who was a genious and had been a child prodigy, receiving his Ph.D. from MIT at age 20, has played a key role in the discovery of the sandwich structure of ferrocene. Ernst Otto Fischer (1918-) and Geoffrey Wilkinson (1921-1997) received the 1973 Nobel Prize for their pioneering work on the chemistry of the organometallic sandwich compounds. Although this Award is well recognized as being fully justified, the fact that Woodward was not included has been questionned. Woodward, a full Professor in the chemistry department at Harvard and Wilkinson, a first-year assistant Professor in the same department, joined their efforts in the beginning of 1952, after reading Peter Pauson's paper in *Nature* (published in England on December 15, 1951, and arrived in the U.S. about a month later) to carry out a series of experiments with Myron Rosemblum, a graduate student, and Mark Whittig, a post-doc, in order to show the sandwich structure. This, shortly thereafter led to the *JACS* communication of 1952. The proof for the sandwich structure was the dipole moment that was zero and the infrared spectrum showing only one type of C-H bond. It was Woodward, however, who recognized that ferrocene would behave like a typical aromatic compound, and Wilkinson later acknowledged that he had not considered this possibility. Later in 1952, another article from Woodward, Rosenblum and Whiting in *JACS* confirmed the aromatic properties of di-cyclopentadienyl-iron and proposed the name ferrocene.

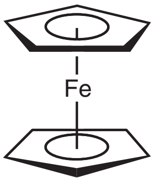
On October 26, 1973, two days after the announcement of the Nobel Prize, Woodward mailed a letter from London to the Nobel Committee in which he stated: "*The notice in the Times (October 24, p. 5) of the award of this year's Nobel Prize in Chemistry leaves me no choice but to let you know, most respectfully, that you have – inadvertently, I am sure – committed a grave injustice… Indeed, when I, as a gesture to a friend and junior colleague interested in organometallic chemistry, invited Professor Wilkinson to join me and my colleagues in the simple experiments which verified my structural proposal, his reaction to my views was close to derision… But in the event, he had second thoughts about his initial scoffing view to my structural proposal and its consequences, and altogether we published the initial seminal communication that was written by me*."According to Wilkinson, however, it was when he read the Pauson paper that he said to himself: "*Jesus-Christ it can't be that. It's a sandwich!*"

Indeed, there was room for another person in this Nobel Prize, but it is possible, as stated by Roald Hoffmann, that a strategic error of Woodward was not to expand his organometallic research to include other transition metals and instead concentrate on the aromatic chemistry of ferrocene. Actually, before Woodward and Wilkinson's work, William E. Doering at Columbia suggested in September 1951 the sandwich structure to Peter Pauson whose paper with the wrong structure had been sent to *Nature* on August 7, 1951. An article with the same wrong structure was submitted to the *Journal of the Chemical Society* by Miller, Tebboth and Tremaine from the British Oxygen Company on July 11, 1951 and published in England on March 24, 1952. Independently, Pfab and Fisher reported the first resolution of the X-ray crystal structure of ferrrocene in the beginning of 1952.

For a full account of the story, see: T. Zydowsky, *The Chemical Intelligencer*, Springer-Verlag, New York, 2000, p. 29. The author is grateful to Helmut Werner, a pioneer *inter alia* of π complexes including the first triple-sandwich compound, for bringing this article to his attention.

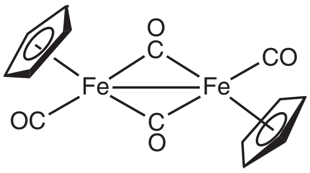


$FeCp_2$: erroneous σ structure
Pauson, 1951

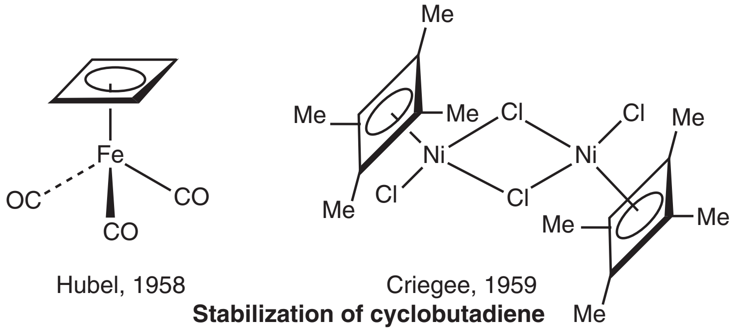


π-sandwich structure of ferrocene
Wilkinson and Fischer, 1952

Wilkinson did not make tenure in Harvard, and he moved back to London at Imperial College, fortunately for British inorganic chemistry. This structure awarded Wilkinson and Fischer the Nobel Prize in 1973. Cobaltocenium, isoelectronic with ferrocene, was also synthesized in 1952. Sandwich complexes with other metals shortly followed, opening the route to an organometallic chemistry of π complexes with poly-hapto ligands developed particularly in Oxford by Wilkinson's bright student, Malcolm L.H. Green. Some of these complexes such as $[FeCp(CO)_2]_2$ have a metal-metal bond and a non-rigid structure, carbonyls jumping rapidly from one metal to another: these are the fluxional complexes (Cotton and Wilkinson, 1955). Longuet-Higgins and Orgel predicted in 1956 that it would be possible to isolate 18-electron complexes of cyclobutadienyl, a highly instable anti-aromatic compound. Their prediction turned into reality only two years later with syntheses of such complexes using several transition metals.



Cotton and Wilkinson, 1955
Fluxional molecule



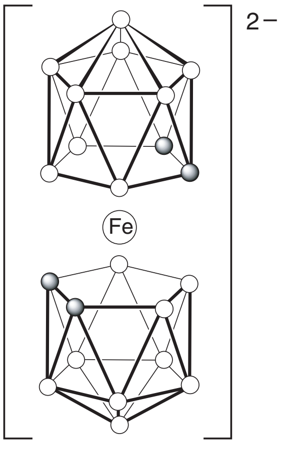
Hubel, 1958 Criegee, 1959
Stabilization of cyclobutadiene

Another very important discovery, in 1955, was that of olefin polymerization catalyzed by soluble titanium and aluminum compounds by Ziegler and Natta. These authors were awarded the Nobel Prize for chemistry in 1963. The stereospecific polymerization of propylene, which was also discovered by Ziegler and Natta, was attributed initially to the surface effect of the heterogeneous initiator, but this interpretation did not survive. Ziegler also discovered the hydroalumination of olefins, leading to tris-alkyl-aluminum, which is a very important industrial chemical. It was also during this period that Georg Wittig found the reaction that now bears his name (1953) and that Herbert C. Brown discovered the hydroboration of olefins (1956). They were jointly awarded the 1979 Nobel Prize. This decade ended with the report of the first oxidative addition reaction in transition-metal chemistry by Shaw and Chatt in 1959.

1961-1981: THE DISCOVERY OF MULTIPLE METAL-CARBON BONDS AND THE GOLDEN AGE OF CATALYSIS

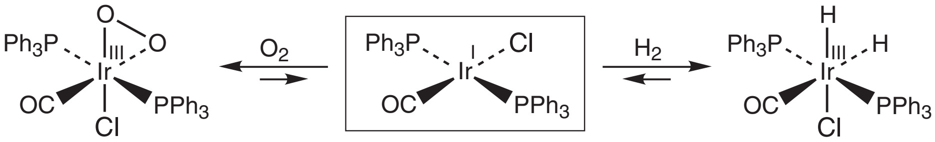
Molecular compounds with metal-metal bonds had been known for a long time. Gold nanoparticles were known *inter alia* in Ancient Egypt for their decorative and therapeutic properties, and calomel was used by chemists in India in the XIIth century. The Hg-Hg bond in the mercurous ion was recognized at the beginning of the XXth century. It was in the 1960s, however, that a more complete development of metal clusters appeared, particularly for the metal-carbonyl clusters by Paolo Chini in Italy, Earl Muetterties and Lawrence Dahl in the United States and Lord Jack Lewis in England. At the same time, the syntheses, structures and properties of multiple metal-metal bonded compounds, including those with up to the quadruple bonds were studied, in particular by F. Albert Cotton.

The birth of an extraordinary family, the carboranes and metallocarboranes, whose father is Frederic Hawthorne, also occurred during this decade in the United States. Later, W.N. Liscomb obtained a Nobel Prize (1976) for the clarification of the structures of boranes.



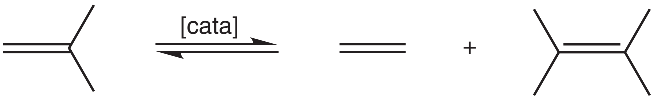
Dicarbolyl iron(II) analog of ferrocene
M.F. Hawthorne, 1965

In 1962, Vaska published the famous 16-electron complex [Ir(CO)(Cl)(PPh_3)] that bears his name. It is well known for the reversible addition of dioxygen and for the series of other oxidative addition reactions that it undergoes with a large number of substrates, including H_2 at 25°C.

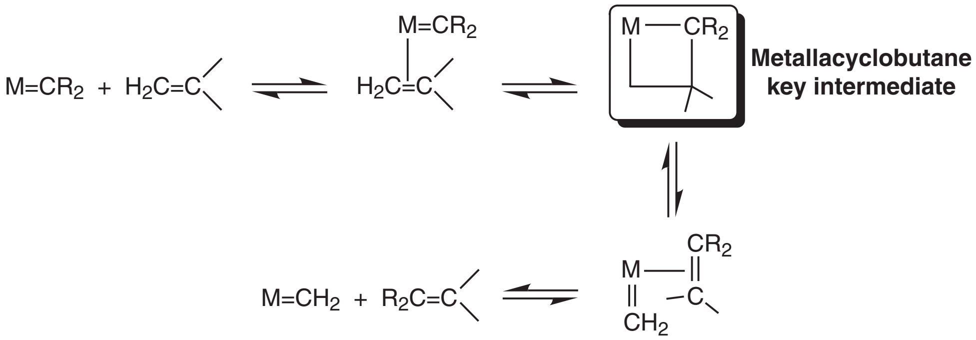


Vaska's complex and the oxidative addition of O_2 and H_2, 1965

In 1964, the first metal-carbene complex was published by E.O. Fischer and the catalyzed metathesis of olefins (below) was reported by Banks.

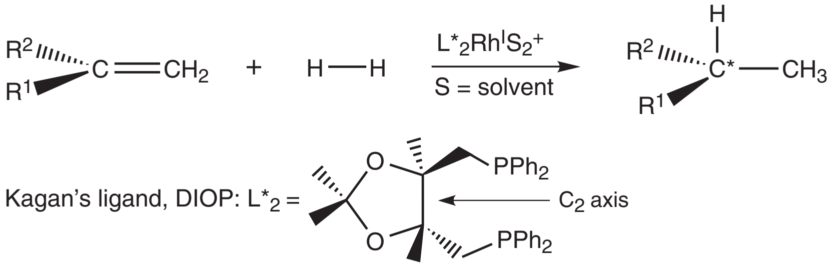


Although these two events were not connected at this time, several years later it turned out that they had a considerable mutual impact. Indeed, in 1971, Yves Chauvin, from the Institut Français du Pétrole near Paris, proposed that the mechanism of olefin metathesis proceeds by coordination of an olefin onto the metal center of a transition-metal alkylidene complex to form a metallacyclobutane that can decompose to a new metal-alkylidene and a new olefin. Subsequently, this mechanism was shown by Chauvin and others to be correct, and metal-alkylidene complexes, discovered three years later by Richard R. Schrock, now occupy a central place in organometallic chemistry and catalysis (*vide infra*).



Mechanism proposed by Chauvin for olefin metathesis

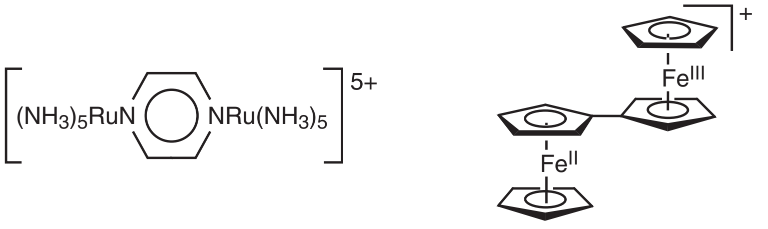
In 1965, Wilkinson (together with his former Ph.D. student John Osborn), and Coffey independently discovered the first homogeneous olefin hydrogenation catalyst, Wilkinson's catalyst, [RhCl($(PPh_3)_3$)]. In 1970, Henri Kagan reported in a patent the first efficient enantioselective asymmetric Rh^I hydrogenation catalyst bearing his chelating chiral ligand DIOP of C_2-symmetry, and his work became widely known with his famous articles in *Chem. Commun.* and *J. Am. Chem. Soc.* in 1971 and 1972, respectively.



An important application of the Kagan ideas and type of chelate complexes permitted the synthesis of *L*-DOPA, the Parkinson disease drug, which was carried out five years later by Knowles at the Monsanto company.

It is also during this decade (1973-1980) that Sharpless reported the asymmetric epoxidation of allylic alcohols, a useful reaction in organic chemistry. The Nobel Prize in Chemistry was awarded to Knowles, Sharpless and Noyori in 2001 for asymmetric catalysis.

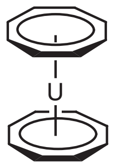
At the end of the 1960s, the concept of mixed valence appeared. H. Taube, on the experimental side, and N.S. Hush, with the theoretical aspects, made seminal decisive contributions. Taube characterized the first mixed-valence and average-valence complexes by varying the nature of the ligand L in the series $[(NH_3)_5RuLRu(NH_3)_5]^{5+}$. In organometallic chemistry, the first mixed-valence complex, biferrocenium monocation was published in 1970.



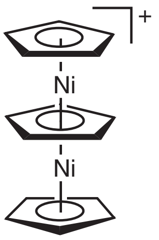
The Creutz-Taube complex, 1969 Biferrocenium, Cowan (1970)

First inorganic (Ru) and organometallic (Fe) mixed-valence complexes

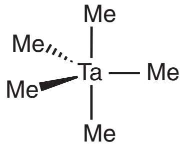
A. Streitweiser and U. Mueller-Westerhoff reported uranocene, the first f-block sandwich complex, in 1968, and in 1970, Wilkinson found that metal-alkyl complexes that have less than 18 valence electrons are stable provided that they do not have β-hydrogen atoms. H. Werner and A. Salzer reported the first triple-decker sandwich complex in 1971.



Uranocene
Mueller-Westerhoff
and Sreitweiser, 1968

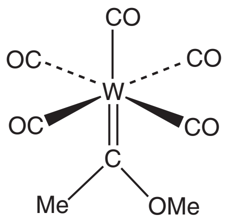


First triple-decker sandwich complex
Werner and Salzer, 1971

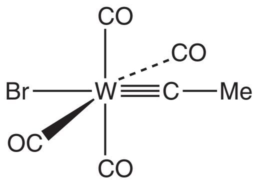


Stable metal-alkyl complexes (no βH)
Wilkinson, 1970

During this same year, 1971, E.O. Fischer synthesized the first metal-carbyne complex and the Monsanto Company developed the rhodium-catalyzed carbonylation of methanol to acetic acid. In 1975, the DuPont de Nemours Company produced adiponitrile using the Ni^0-catalyzed hydrocyanation of butadiene.

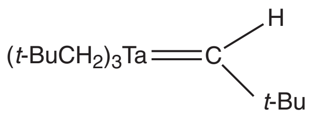


Stabilized carbene complex
Fischer, 1964

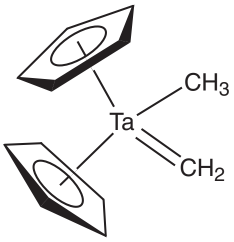


Carbyne complex
Fischer, 1973

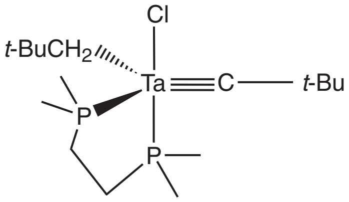
It is also in the early 1970s that Richard R. Schrock, a former student of John Osborn at Harvard, then at the DuPont de Nemours Company in Delaware, made the very important discoveries of the first stable, isolable methylene-, alkylidene- and nucleophilic alkylidyne complexes of transition metals. These classes of compounds later brought a new dimension to the field of the metathesis reactions. Thus, in 1974, Schrock reported the isolation and X-ray crystal structure of the neopentylidene complex $[Ta(CH_2CMe_3)_3(=CH\text{-}CMe_3)]$, the first transition metal carbene complex that is not stabilized by an heteroatom on the carbene. This complex also represented the discovery of the α-elimination reaction. In 1975, Schrock published the isolation and X-ray crystal structure of $[TaCp_2Me(=CH_2)]$, the first methylene complex and a transition-metal cousin of Wittig's reagent. Indeed, Schrock's "ylid" was shown to react by methylene transfer with aldehydes, ketones and esters. Other similar methylene transfer reagents followed, for instance, Tebbe's complex $[TiCp_2(\mu\text{-}Cl)(\mu\text{-}CH_2)AlMe_2]$ and later the species "$[TiCp_2(=CH_2)]$", which is now used and generated by heating $[TiCp_2Me_2]$. In 1976, Schrock reported the first synthesis of an alkylidyne complex $[Ta(CH_2CMe_3)(Me_2PCH_2CH_2PMe_2)(C\text{-}t\text{-}Bu)]$ in which the alkylidyne ligand possesses nucleophilic character.



First alkylidene complex
Schrock, 1974



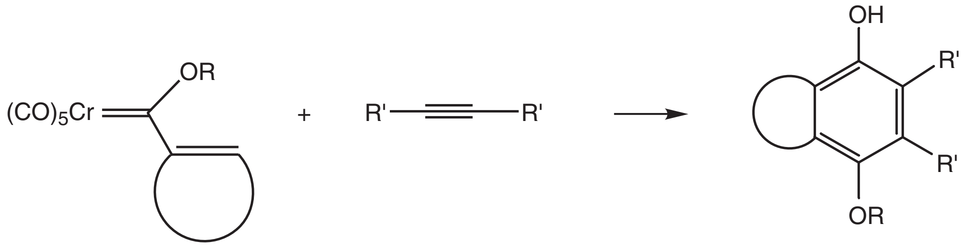
First methylene complex
Schrock, 1975



First nucleophilic alkylidyne complex
Schrock, 1976

Schrock also showed in 1980 that, importantly, some alkylidene complexes of tantalum and tungsten can metathesize olefins if they contain alkoxy ligands, and, in 1990, he reported a whole family of very active tungsten metathesis catalysts including chiral ones, which led him to disclose, in collaboration with Hoveyda, the first examples of enantioselective metathesis reactions.

The first application of Fischer-type metal-carbene complexes in organic synthesis also appeared in 1975 with the Dötz reaction:



Other applications of the stoichiometric reactions of transition-metal complexes in organic synthesis, such as the Pauson-Khand reaction, were reported in the same year.

In 1977, H. Kagan published a practical synthesis of an excellent reducing agent, SmI_2, which found many applications in organic synthesis such as the pseudo-Barbier reaction, the Reformatsky reaction, the formation of pinacols, and the deoxygenation of epoxides and sulfoxides. Various reactions involving the formation of C-C bonds by treatment of SmI_2 with unsaturated substrates were subsequently developed by Kagan's group and many other research groups.