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THE CHEMISTRY OF METAL CARBONYLS: "THE LIFE WORK OF WALTER HIEBER"*

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Professor Hieber, Ladies and Gentlemen!

It is a greater honour and a special pleasure for me to address this distinguished international audience of scientists at the beginning of this symposium on metal carbonyls, on the subject of the life work of my most respected teacher Walter Hieber.

When, a few months ago, Prof. E.O. Fischer and Prof. W. Beck asked me to give this lecture, I was at first hesitant because I was not sure that another colleague could not better do credit to the subject. In spite of this I am giving this talk** and the reason is that for 25 years of the more than 40 years of Walter Hieber's research on metal carbonyls I have had the personal pleasure of working in close contact with him at the Technische Hochschule München and of having personally experienced a large proportion of his most important scientific achievements from very close quarters.

In an earlier symposium on metal carbonyls, arranged by the American Chemical Society in 1964 in Philadelphia, our friend and colleague Professor Dahl described Professor Hieber as the "Father of Metal Carbonyl Chemistry". I do not believe that one can improve upon this description of the role of Walter Hieber in the development of the coordination chemistry of metal carbonyls which itself has played such a special part in the Renaissance of inorganic chemistry in general. This characterization of Walter Hieber rightly expresses the significant impulses which he has given to metal carbonyl chemistry, and therewith to the whole of organometallic chemistry, and how his work has formed a basis for so many later developments of which the chemistry of the so-called π-complexes is an important example.

When Walter Hieber began his first experiments on iron pentacarbonyl in 1927 the number of known carbon monoxide metal compounds was very small indeed as can be seen from Fig. 1. Knowledge of the structures, bonding and

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* Presented at the Symposium on Metal Carbonyl Chemistry, dedicated to Professor Walter Hieber, held at Ettal (West Germany), July 21st-July 27th, 1974.

** I should like to thank Dr. Malcolm Pilbrow for the translation of the text.

1871	$Pt(CO)_2Cl_2$	(P. Schützenberger)
1890	$Ni(CO)_4$	(L. Mond, C. Langer and F. Quincke)
1891	$Fe(CO)_5$	(L. Mond and F. Quincke; M. Berthelot)
1905	$Fe_2(CO)_9$	(J. Dewar and H.O. Jones)
1907	$[Fe(CO)_4]_n$ $(n = 20)$	(J. Dewar and H.O. Jones)
1910	$Co_2(CO)_8$ and $Co_4(CO)_{12}$	(L. Mond, H. Hirtz and M.D. Cowap)
1910	$Mo(CO)_6$	(L. Mond, H. Hirtz and M.D. Cowap)
1922	$Co(CO)_3NO$	(R.L. Mond and A.E. Wallis)
1924-26	$[Ru(CO)_2 Halg._2]_n$; $Ir(CO)_2Cl_2$; $Os(CO)_3Cl_2$	(W. Manchot and co-workers)
1927/28	$Cr(CO)_6$; $W(CO)_6$	(A. Job and co-workers)

Fig. 1. Metal carbonyl compounds 1871-1928.

chemical reactivity of this new class of compounds was at that time non-existent or at most minimal. Their unusual compositions and properties did not allow them to be classified with other known compounds, and in the literature of that time one finds strange formulations. Thus it was suggested that metal carbonyls were metal salts of organic pseudo-acids containing carbon chains with the metal bonded to oxygen atoms. As I began my own studies in 1933, textbooks assigned structures to $Ni(CO)_4$ and $Fe(CO)_5$ such as those shown in Fig. 2.

Thus, as Walter Hieber began his chemical research, the time was ripe for a systematic study of the metal carbonyls then known and for the initiation of the study of the coordination chemistry of metal carbonyls based on considerations of their structures.

Significant achievements in scientific research almost always result from a happy combination between scientific ability and imagination, together with the intuition to do the right experiment at the right time. We shall see in the course of this talk that with his very first experiments Prof. Hieber indeed began a series of the right experiments at the right time.

A further important condition for scientific achievement is an ability to attract intelligent and promising young co-workers with whom research can be carried out. Prof. Hieber had the special ability to stimulate students' interest in new problems and ideas. I can still well remember the fascination for the

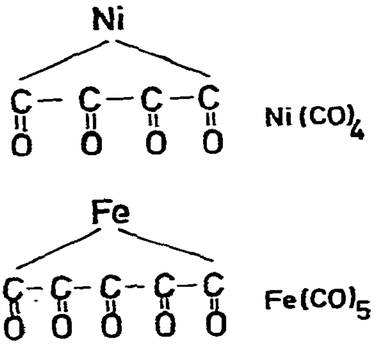


Fig. 2. Old formulations for $Ni(CO)_4$ and $Fe(CO)_5$.

I.) On Metal Carbonyls (1928 -1970)

Comprehensive Reviews: 7

"On Metal Carbonyls": Z. Elektrochem. 43, 390 (1937).
"The Present Status of the Chemistry of Metal Carbonyls": Angew. Chem. 55, 1 (1942).
"Metal Carbonyls": FIAT Review of German Science 1939-1946, Vol. 24/II.
"Recent Results of Research in the Field of Metal Carbonyls": Angew. Chem. 64, 465 (1952).
"Anionic Carbon Monoxide Complexes": Angew. Chem. 72, 795 (1960).
"Recent Views on the Reactivity of Metal Carbonyls": Angew. Chem. 73, 364 (1961).
"Metal Carbonyls. Forty Years of Research": Adv. Organometallic Chem. 8, 1 (1970).

Original Papers: 206

II.) On Nitrosyl Complexes (1939 -1971)

Original Papers: 39

III.) General Coordination Chemistry (1919 - 1956)

Original Papers: 32

Fig. 3. Publications of W. Hieber.

subject which Prof. Hieber generated in the lectures on complex chemistry which he gave in 1935 immediately following his appointment to the chair of inorganic chemistry at the Technische Hochschule München. All the students found that his presentation of the material brought a completely fresh approach to the subject. In subsequent discussions with a great many Hieber students I have been convinced that it was indeed his lectures which filled many talented young chemists with enthusiasm for inorganic chemistry and particularly for complex chemistry. It was these attributes of Walter Hieber which enabled him to build up a large and respected research school with which, in spite of the many problems associated with the times, he could begin and continue his life's research.

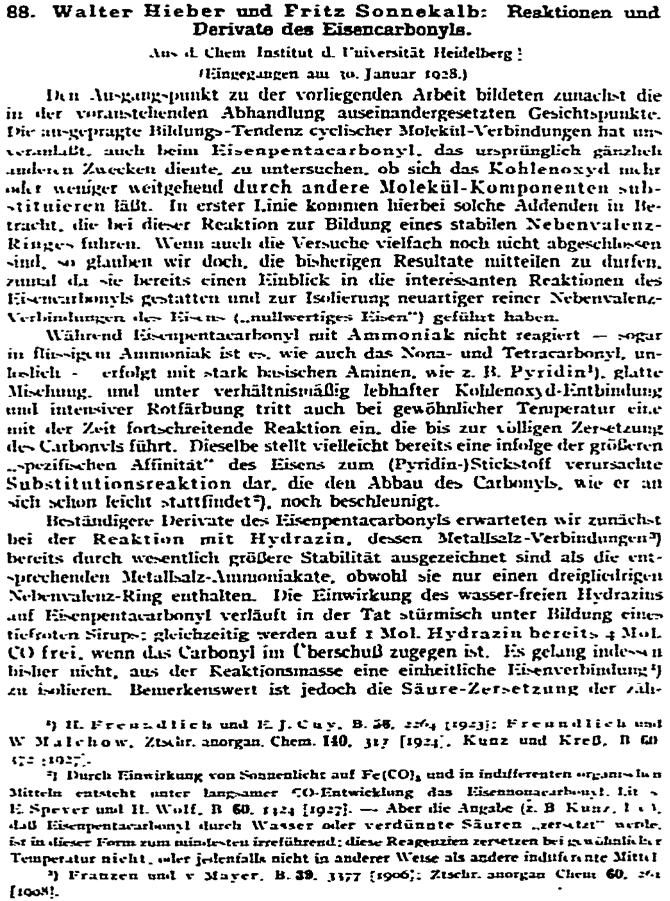
The extraordinary extent and success of this research is indicated by the impressive number of his publications. These are summarized in Fig. 3. In the years 1928 to 1970 Walter Hieber published a total of 213 reports on metal carbonyls. His review articles listed here and which appeared in 1937, 1942, 1946, 1952, 1960, 1961 and 1970 serve as milestones in his more than 40 years of pioneering work in metal carbonyl chemistry. In addition he has published 39 papers on nitrosyl compounds and a further 32 on general complex chemistry, including work as early as 1928 on silver(II) compounds. This research serves as an example of the broadness of Prof. Hieber's interests and of how the early experiments on coordination chemistry influenced and stimulated his metal carbonyl work.

It is obvious that in the space of time available today I can only concentrate attention on the most important aspects of this vast area of research and on those experiments which have been most significant in the general development of metal carbonyl chemistry. Since its beginning just about 50 years ago, and particularly since the early 1950's with Kealy and Pauson's discovery of "Ferrocene" and Fischer and Hafner's preparation of "Dibenzenechromium", research in the chemistry of metal carbonyls has developed explosively. Thus at present more than 1500 papers on carbonyl complexes are published yearly.

There is no doubt that the foundations for this unexpected development have been the examplary works of Walter Hieber. This is the more impressive when one remembers that the modern spectroscopic methods of compound characterization were only available to Hieber in the last years of his research career. It is amazing that Hieber gave exact analytical data and proposed structures for often very complicated compounds, many of which in recent years have been proved correct by X-ray structure determinations.

Of course, even in the earlier years, various physical-chemical methods of compound characterization were available such as magnetic and dipole moment measurements; UV spectroscopy and since 1957 IR spectroscopy have had broad application in the clarification of structural problems.

In current times, when the area of the chemistry of metal carbonyls and their derivatives has become so vast and explosively growing that one can hardly keep up with all the developments and when the most modern and rational methods of structure determination are available, it is still most interesting to ask about the first steps which Walter Hieber made into the then "terra incognita" of metal carbonyl chemistry.



88. Walter Hieber und Fritz Sonnekalb: Reaktionen und Derivate des Eisencarbonyls.

(Aus d. Chem. Institut d. Universität Heidelberg.)

(Eingegangen am 10. Januar 1928.)

Den Ausgangspunkt zu der vorliegenden Arbeit bildeten zunächst die in der voranstehenden Abhandlung auseinandergesetzten Gesichtspunkte. Die ausgeprägte Bildungs-Tendenz cyclischer Molekül-Verbindungen hat uns veranlaßt, auch beim Eisenpentacarbonyl, das ursprünglich gänzlich anderen Zwecken diente, zu untersuchen, ob sich das Kohlenoxyd mehr oder weniger weitgehend durch andere Molekül-Komponenten substituieren läßt. In erster Linie kommen hierbei solche Addenden in Betracht, die bei dieser Reaktion zur Bildung eines stabilen Nebenvalenz-Ringes führen. Wenn auch die Versuche vielfach noch nicht abgeschlossen sind, so glauben wir doch, die bisherigen Resultate mitteilen zu dürfen, zumal da sie bereits einen Einblick in die interessanten Reaktionen des Eisencarbonyls gestatten und zur Isolierung neuartiger reiner Nebenvalenz-Verbindungen des Eisens („nullwertiges Eisen") geführt haben.

Während Eisenpentacarbonyl mit Ammoniak nicht reagiert — sogar in flüssigem Ammoniak ist es, wie auch das Nona- und Tetracarbonyl, unlöslich — erfolgt mit stark basischen Aminen, wie z. B. Pyridin[1]), glatte Mischung, und unter verhältnismäßig lebhafter Kohlenoxyd-Entbindung und intensiver Rotfärbung tritt auch bei gewöhnlicher Temperatur eine mit der Zeit fortschreitende Reaktion ein, die bis zur völligen Zersetzung des Carbonyls führt. Dieselbe stellt vielleicht bereits eine infolge der größeren „spezifischen Affinität" des Eisens zum (Pyridin-)Stickstoff verursachte Substitutionsreaktion dar, die den Abbau des Carbonyls, wie er an sich schon leicht stattfindet[2]), noch beschleunigt.

Beständigere Derivate des Eisenpentacarbonyls erwarteten wir zunächst bei der Reaktion mit Hydrazin, dessen Metallsalz-Verbindungen[3]) bereits durch wesentlich größere Stabilität ausgezeichnet sind als die entsprechenden Metallsalz-Ammoniakate, obwohl sie nur einen dreigliedrigen Nebenvalenz-Ring enthalten. Die Einwirkung des wasser-freien Hydrazins auf Eisenpentacarbonyl verläuft in der Tat stürmisch unter Bildung eines tiefroten Sirups; gleichzeitig werden auf 1 Mol. Hydrazin bereits 4 Mol. CO frei, wenn das Carbonyl im Überschuß zugegen ist. Es gelang indessen bisher nicht, aus der Reaktionsmasse eine einheitliche Eisenverbindung[4]) zu isolieren. Bemerkenswert ist jedoch die Säure-Zersetzung der zäh-

[1]) H. Freundlich und E. J. Cuy, B. 56, 2264 [1923]; Freundlich und W. Malchow, Ztschr. anorgan. Chem. 140, 317 [1924]. Kunz und Kreß, B. 60, [illegible] [1927].

[2]) Durch Einwirkung von Sonnenlicht auf $Fe(CO)_5$ und in indifferenten organischen Mitteln entsteht unter langsamer CO-Entwicklung das Eisennonacarbonyl. Lit. s. E. Speyer und H. Wolf, B. 60, 1424 [1927]. — Aber die Angabe (z. B. Kunz, l. c.), daß Eisenpentacarbonyl durch Wasser oder verdünnte Säuren „zersetzt" werde, ist in dieser Form zum mindesten irreführend; diese Reagenzien zersetzen bei gewöhnlicher Temperatur nicht, oder jedenfalls nicht in anderer Weise als andere indifferente Mittel.

[3]) Franzen und v. Mayer, B. 39, 3377 [1906]; Ztschr. anorgan. Chem. 60, [illegible] [1908].

[4]) Über die spurenweise Bildung von Semicarbazid s. exper. Teil, S. 562.

Fig. 4. Reprinted from Ber. Deutsch. Chem. Ges., 61 (1928) 558.

As is shown in Fig. 4, Prof. Hieber's first publication from 1928 was in collaboration with F. Sonnekalb and had the title "Reactions and Derivatives of Iron Carbonyl". In this and in the work which immediately followed dealing with the reactivity of iron pentacarbonyl and triiron dodecacarbonyl towards various amines and alcohols, several new problems presented themselves. These problems and their solutions were to be of fundamental importance for the subsequent advances to be made in the chemistry of metal carbonyls. These reactions with amines result in the expulsion of carbon monoxide with the production of deep-red amine-containing iron carbonyls. They were described as amine-substituted iron carbonyls although at the time the unusual stoichiometry was difficult to comprehend completely. As we shall see in detail later these compounds are complex salts of polynuclear carbonylferrate anions and hexacoordinated iron(II) cations. Although the description of these compounds was incorrect at the time the finding that carbon monoxide could be displaced by other neutral ligands was to be of great significance. Hieber's report, also from 1928, of the reactions of iron pentacarbonyl with chlorine, bromine and iodine which lead to dihalogeno-tetracarbonyl complexes clearly showed the coordinative bonding of the carbon monoxide thus indicating that in metal carbonyls and their derivatives the carbon monoxide is present as a neutral molecule. With these important results the carbonyl complexes could definitely be described as coordination compounds for which the "Inert Gas Rule" holds. This, of course, meant a considerable simplification of the formulation of these complexes. At the same time this initial work set the scene for further research and achievements for Prof. Hieber, namely for: (1) the preparation of anionic carbonyl complexes, (2) the discovery of carbonyl hydrides of iron and cobalt, and (3) the systematic study of substitution and disproportionation reactions of metal carbonyls.

Between 1953 and 1960 Prof. Hieber and his group fully explained the reactions of mono- and polynuclear metal carbonyls of the 3*d*-metals with nitrogen and oxygen bases. As early as 1935 the hexacarbonyls of the Group VIa metals had been shown to react with such nitrogen Lewis bases as pyridine, 1,10-phenanthroline or 2,2'-bipyridyl to give substitution products. In contrast, the mono- and poly-nuclear carbonyls of the other 3*d*-metals gave valency disproportionation of the particular metal. With this knowledge came the explanation of the reactions of iron carbonyls with various amines and alcohols which had been performed between 1928 and 1931.

In the top part of Fig. 5 can be seen the formulations from 1928 of complexes formed by the reactions of iron carbonyls with ethylenediamine, pyridine and methanol. These are in fact ionic compounds. All these reactions occur by disproportionation of iron(0) with the formation of hexacoordinated iron(II) cations and the mono- or poly-nuclear carbonylferrate anions:

$[Fe(CO)_4]^{2-}$, $[Fe_2(CO)_8]^{2-}$, $[Fe_3(CO)_{11}]^{2-}$ or $[Fe_4(CO)_{13}]^{2-}$.

The stoichiometries of these anions obey the Sidgwick—Bailey rule. It is not always predictable, however, which of the possible mono-, di-, tri- or tetranuclear anions will be formed in any particular reaction. This depends on the carbonyl, the Lewis base and also on the reaction conditions, particularly temperature. These carbonylferrate anions are isoelectronic with the respective

1928 – 1932: $Fe_2(CO)_5en_2$, $Fe_4(CO)_{12}en_3$, $Fe_2(CO)_4en_3$, $Fe(CO)_3en$
$Fe_2(CO)_4pyr_3$, $Fe(CO)_3pyr$
$Fe(CO)_3 \cdot CH_3OH$, $Fe_2(CO)_6 \cdot CH_3OH$

1957 – 1959: $nFe^{0} \longrightarrow Fe^{2+} + [Fe_{n-1}]^{2-}$ $(n = 2, 3, 4, 5)$
$Fe^{2+} + 6B \longrightarrow [FeB_6]^{2+}$

Uncharged carbonyl	Carbonylferrate anion
$Fe(CO)_5$	$[Fe(CO)_4]^{2-}$
$Fe_2(CO)_9$	$[Fe_2(CO)_8]^{2-}$
$Fe_3(CO)_{12}$	$[Fe_3(CO)_{11}]^{2-}$
$(Fe_4(CO)_{14})^{*)}$	$[Fe_4(CO)_{13}]^{2-}$

*) unknown

Fig. 5. Reactions of iron carbonyls with nitrogen and oxygen bases.

neutral iron carbonyls if one considers that 2 electrons replace one carbonyl group.

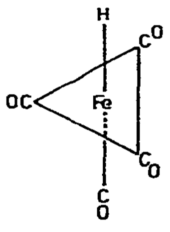
Mono- or poly-nuclear carbonylferrate anions can also be obtained by the so-called "Base Reactions", i.e. by the reaction of iron pentacarbonyl, diiron enneacarbonyl and triiron dodecacarbonyl with alkali, as shown in Fig. 6. The existence of these anions was proved by their precipitation with complex cations, by which reactions hydrido carbonylferrate ions can also be produced depending upon the acidity.

The structures of most of these various carbonylferrates has since been

1931: $Fe(CO)_5 + 4OH^- \longrightarrow [Fe(CO)_4]^{2-} + CO_3^{2-} + 2H_2O$

1957: $Fe_2(CO)_9 + 4OH^- \longrightarrow [Fe_2(CO)_8]^{2-} + CO_3^{2-} + 2H_2O$
$Fe_3(CO)_{12} + 4OH^- \longrightarrow [Fe_3(CO)_{11}]^{2-} + CO_3^{2-} + 2H_2O$

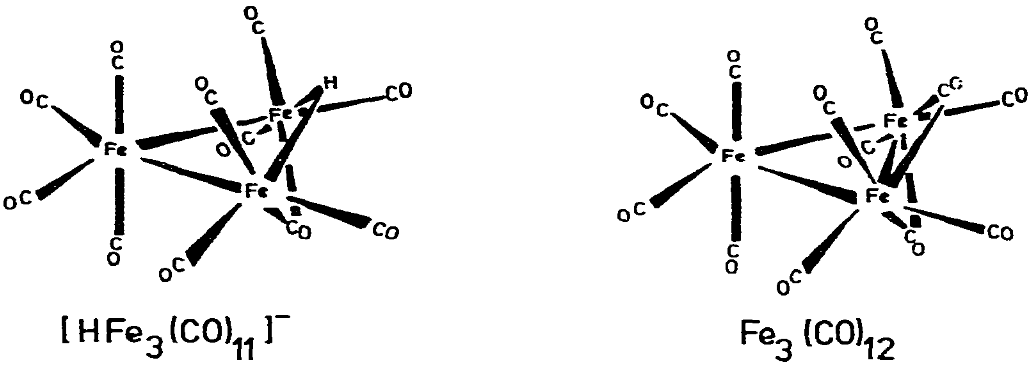
$[Fe(CO)_4]^{2-} + H_2O \rightleftharpoons [HFe(CO)_4]^- + OH^-$
$[Fe_3(CO)_{11}]^{2-} + H_2O \rightleftharpoons [HFe_3(CO)_{11}]^- + OH^-$



M.B. Smith and B. Bau 1973

$[HFe(CO)_4]^-$

Fig. 6. The "base-reactions" of iron carbonyls.



$[HFe_3(CO)_{11}]^-$ $Fe_3(CO)_{12}$

Fig. 7. Structures of $[HFe_3(CO)_{11}]^-$ and $Fe_3(CO)_{12}$ (L.F. Dahl and coworkers 1965/1966).

shown by X-ray methods. Thus Smith and Bau have recently shown that the $[HFe(CO)_4]^-$ anion exists as a distorted trigonal bipyramid with three equatorial carbon monoxide ligands. This structure is of considerable importance with respect to the structure of the isoelectronic hydrido tetracarbonylcobalt since the thermal instability of this latter compound, which was discovered by Hieber in 1934, has precluded its X-ray structure analysis.

The X-ray results of Dahl and his co-workers on the neutral complexes $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, and on the anions $[HFe_3(CO)_{11}]^-$ and $[Fe_3(CO)_{11}]^{2-}$ are especially interesting since they clearly indicate the structural relationships between these systems, as shown in Fig. 7. The structure of triiron dodecacarbonyl can readily be related to that of diiron enneacarbonyl by replacement of one of the three CO bridges in the latter by a *cis*-$Fe(CO)_4$ group. The difference between $[HFe_3(CO)_{11}]^-$ and $Fe_3(CO)_{12}$ lies in the presence of a hydride bridge in place of a CO bridge whilst in $[Fe_3(CO)_{11}]^{2-}$ the Fe—H—Fe bridge is apparently replaced by a direct Fe—Fe bond.

In the $[Fe_4(CO)_{13}]^{2-}$ anion shown in Fig. 8 the four iron atoms form a

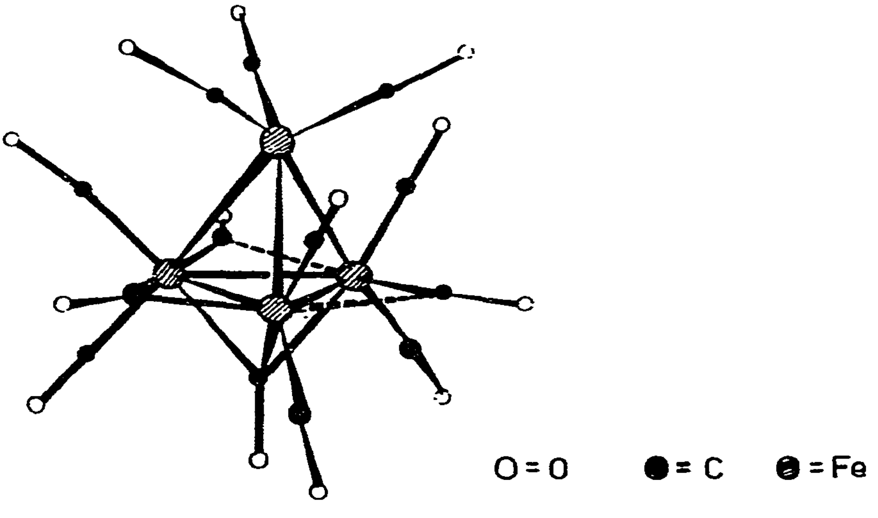


Fig. 8. Structure of the $[Fe_4(CO)_{13}]^{2-}$ anion (R.J. Doedens and L.F. Dahl, 1966).

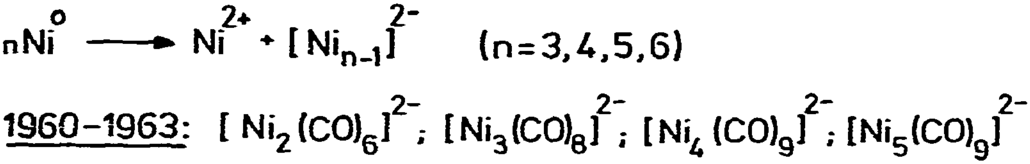


Fig. 9. Reactions of $Ni(CO)_4$ with nitrogen Lewis bases.

tetrahedron with an $Fe(CO)_3$ group as an apex. This is bonded by Fe—Fe bonds to the three $Fe(CO)_3$ groups which form the base of the tetrahedron. The thirteenth CO molecule bridges these three iron atoms of the base.

I have made a special point of dealing with these polynuclear carbonylferrate anions in some detail, because, as a result of earlier discussions with Prof. Hieber, I well know how the extremely difficult chemistry involved in this area had long fascinated him and for how important he considered this particular work within his general research programme. I think that you, Prof. Hieber, will be especially pleased and satisfied that your excellent conclusions have found such an impressive proof. There is no doubt that this work represents a great fulfillment of your first experiments aimed at revealing the secrets of metal carbonyl chemistry and which you carried out 47 years ago in Heidelberg. Before I begin to discuss the history of the discovery and development of hydrido metal carbonyls I should like to conclude this section on anionic carbonyl complexes with a short summary of the most important results associated with the other 3*d*-metals.

Similar to the iron carbonyls, nickel tetracarbonyl undergoes valency disproportionation with nitrogen Lewis bases (Fig. 9) to give polynuclear carbonylnickelate anions; these also obey the Sidgwick—Bailey rule, but they have been less well studied because of their ready decomposition.

In contrast to these reactions of metals with even atomic numbers dicobalt

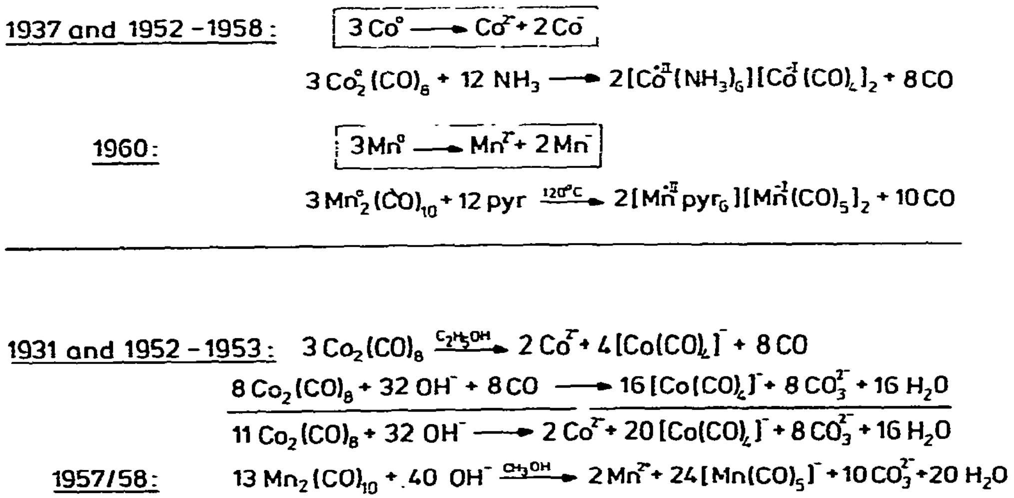


Fig. 10. Reactions of $Co_2(CO)_8$ and $Mn_2(CO)_{10}$ with nitrogen Lewis bases, and "base reactions" of $Co_2(CO)_8$ and $Mn_2(CO)_{10}$.

octacarbonyl and dimanganese decacarbonyl disproportionate with nitrogen and oxygen Lewis bases to give only the mononuclear carbonylmetallate anions $[Co(CO)_4]^-$ and $[Mn(CO)_5]^-$ with the elimination of carbon monoxide, as shown in Fig. 10. This work, especially that on dicobalt octacarbonyl, was carried out between 1952 and 1958 by Prof. Hieber and his research team and represents an extraordinarily thorough investigation involving reactions with a vast number of different nitrogen and oxygen Lewis bases. Tetracobalt dodecacarbonyl reacts in the same way with Lewis bases as the dicobalt complex.

In contrast, the reaction of dicobalt octacarbonyl with alcoholic alkali follows a completely different course since the carbon monoxide set free in the valency disproportionation causes the real base reaction with formation of carbonate and the tetracarbonylcobaltate anion (Fig. 10). Thus this reaction differs from the "base reactions" of the three iron carbonyls mentioned earlier in that in the cobalt system the number of CO groups in the cobalt carbonyl and in the tetracarbonylcobaltate anion is the same.

The "base reaction" of dimanganese decacarbonyl with alkali is analogous and is also shown in Fig. 10 in an overall equation.

In Fig. 11 it is shown that if instead of treating dicobalt octacarbonyl with nitrogen bases, triphenylphosphine is used, for which like carbon monoxide double bonding to the metal is possible, then, depending on the solvent and reaction temperature the product may be the triphenylphosphine-substituted cobalt carbonyl or a disproportionation to Co^{+I} and Co^{-I} can take place. The formation of the five-coordinate cobalt tricarbonyl cation in this latter reaction represents the first experimental indication of the existence of cationic metal carbonyl complexes. In later work, even after his official retirement, Prof. Hieber made considerable contributions to the chemistry of these cationic systems, particularly for iron, ruthenium and osmium, as also for rhodium and iridium.

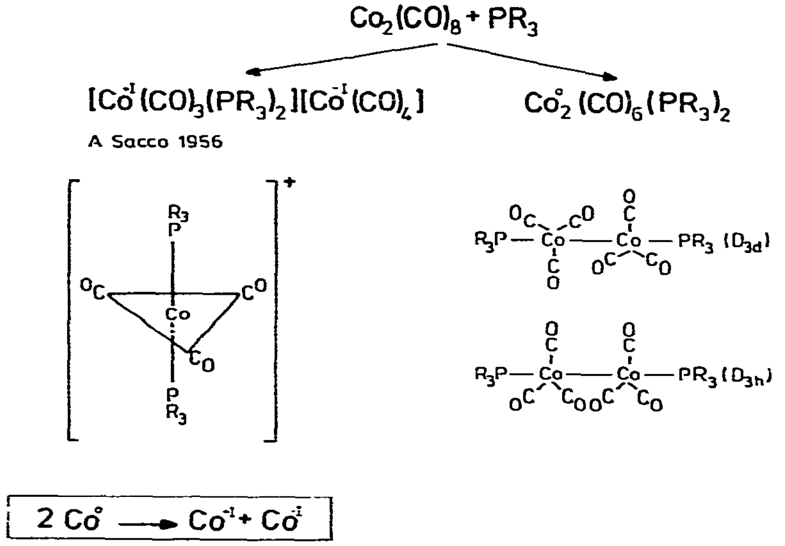


Fig. 11. Disproportionation and substitution of $Co_2(CO)_8$ (1958).

	decrease of π-acceptor character →				
Lewis base	$P(OC_6H_5)_3$	$P(C_6H_5)_3$	CNR	bipy, phen	pyr
$Cr(CO)_6$	subst.	subst.	subst.	subst.	subst.
$Mn_2(CO)_{10}$	subst.	subst.	disprop.	subst. and disprop.	disprop. (120°)
$Fe(CO)_5$	subst.	subst.	subst.	disprop. (80°C)	disprop. (80°C)
$Co_2(CO)_8$	subst.	subst. and disprop.	disprop.	disprop. (20°C)	disprop. (20°C)
$Ni(CO)_4$	subst.	subst.	subst.	disprop. (20°C)	disprop. (20°C)

Fig. 12. Reactions of 3*d*-metal carbonyls with Lewis bases (1961).

As to the question of whether the reactions of mono- and poly-nuclear metal carbonyls will give carbon monoxide substitution or disproportionation the acceptor and donor characteristics of the particular ligand are of deciding importance. The table shown in Fig. 12 was drawn up by Prof. Hieber in 1961. It is based on the research of several decades and represents an excellent summary of the reactions of metal carbonyls with Lewis bases.

In the series of ligands from triphenylphosphite through triphenylphosphine, isonitrile, the *N*-heterocyclics bipyridyl and phenanthroline to pyridine the tendency to cause disproportionation becomes steadily greater as the π-acceptor character of the ligand decreases, especially in the cases of the dinuclear carbonyls of manganese and cobalt. This tendency seems also to be influenced by the increasing electronegativity of the 3*d*-metals in the series from chromium to nickel.

The reduction of normal and substituted metal carbonyls with alkali metals has proved to be a most useful method for the preparation of carbonylmetallates containing only CO ligands or of carbonylmetallates with a mixture

$$\underline{1961:}\quad \overset{0}{Re}_2(CO)_{10} \xrightarrow[(CH_3)_2O]{Na/Hg} 2\,Na[\overset{-I}{Re}(CO)_5]$$

$$\underline{1961:}\quad \overset{0}{Co}_2(CO)_6(PR_3)_2 \xrightarrow[THF]{Na/Hg} 2\,Na[\overset{-I}{Co}(CO)_3PR_3]$$

$$\underline{1965:}\quad \overset{I}{Co}(CO)_2(P(OR)_3)_2Cl \xrightarrow[THF]{Na/Hg} Na[\overset{-I}{Co}(CO)_2(P(OR)_3)_2]$$

$$\underline{1960:}\quad Fe(CO)_2(NO)_2 \xrightarrow[THF]{Na/Hg} [Fe(CO)_3NO]^-$$

isoelectr. with $[Co(CO)_4]^-$

Fig. 13. Carbonylmetallates prepared by reduction with sodium amalgam.

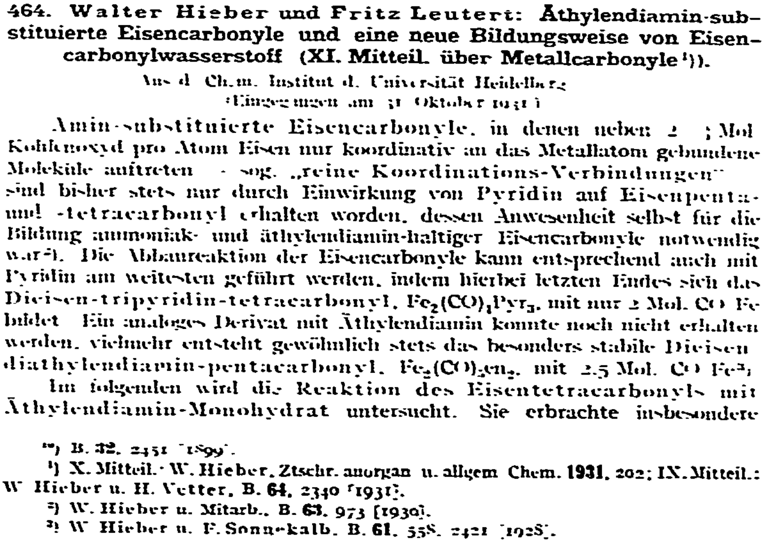
of ligands. Some examples are presented in Fig. 13. In 1960 this method was utilized for the first preparation of the nitrosyl tricarbonylferrate anion which is isoelectronic with the tetracarbonylcobaltate anion.

One of the most exciting high points of Prof. Hieber's research career has definitely been the discovery of the carbonyl hydrides of iron and cobalt; a result which opened up the chemistry of a whole new class of interesting and characteristic compounds. The first result, that of the formation of iron carbonyl hydride by decomposition of ethylenediamine adducts of iron carbonyl with acids, was published by Prof. Hieber as early as 1931 in "Berichte der Deutschen Chemischen Gesellschaft" (Fig. 14).

At this point I should like to quote what Prof. Hieber himself wrote about this early discovery in the 1970 volume of "Advances in Organometallic Chemistry". He wrote: "Already in the early experiments involving treatment of iron tetracarbonyl with ethylenediamine hydrate, we observed that upon acidification of the solutions an extraordinarily intense repugnant smell was released. I can still clearly remember the day when I, together with my co-workers Leutert and Vetter, at the Heidelberg Institute, was able to freeze out a volatile water-clear liquid from the decomposition of the ethylenediamine-containing iron carbonyls, identifying it as $H_2Fe(CO)_4$".

The famous paper entitled "Base reactions of iron pentacarbonyl and the formation of iron carbonyl hydride" appeared in "Zeitschrift für anorganische und allgemeine Chemie" in 1932 (Fig. 15).

The isolation of the free iron carbonyl hydride (Fig. 16), prepared by acidification of the alkaline solution, was at first particularly difficult because of its extreme instability and was only achieved after fractional distillation in high vacuum. In later work at the Technische Hochschule München, the carbonyl hydride of cobalt was made by the base reaction of dicobalt octacarbonyl which I have described earlier (Figs. 10 and 16).



464. Walter Hieber und Fritz Leutert: Äthylendiamin-substituierte Eisencarbonyle und eine neue Bildungsweise von Eisencarbonylwasserstoff (XI. Mitteil. über Metallcarbonyle[1]).

Aus d. Chem. Institut d. Universität Heidelberg.
(Eingegangen am 31. Oktober 1931.)

Amin-substituierte Eisencarbonyle, in denen neben 2 [illegible] Mol Kohlenoxyd pro Atom Eisen nur koordinativ an das Metallatom gebundene Moleküle auftreten — sog. „reine Koordinations-Verbindungen" — sind bisher stets nur durch Einwirkung von Pyridin auf Eisenpenta- und -tetracarbonyl erhalten worden, dessen Anwesenheit selbst für die Bildung ammoniak- und äthylendiamin-haltiger Eisencarbonyle notwendig war[2]). Die Abbaureaktion der Eisencarbonyle kann entsprechend auch mit Pyridin am weitesten geführt werden, indem hierbei letzten Endes sich das Dieisen-tripyridin-tetracarbonyl, $Fe_2(CO)_4Pyr_3$, mit nur 2 Mol. CO/Fe bildet. Ein analoges Derivat mit Äthylendiamin konnte noch nicht erhalten werden, vielmehr entsteht gewöhnlich stets das besonders stabile Dieisen-diäthylendiamin-pentacarbonyl, $Fe_2(CO)_5en_2$, mit 2.5 Mol. CO/Fe[3]).

Im folgenden wird die Reaktion des Eisentetracarbonyls mit Äthylendiamin-Monohydrat untersucht. Sie erbrachte insbesondere

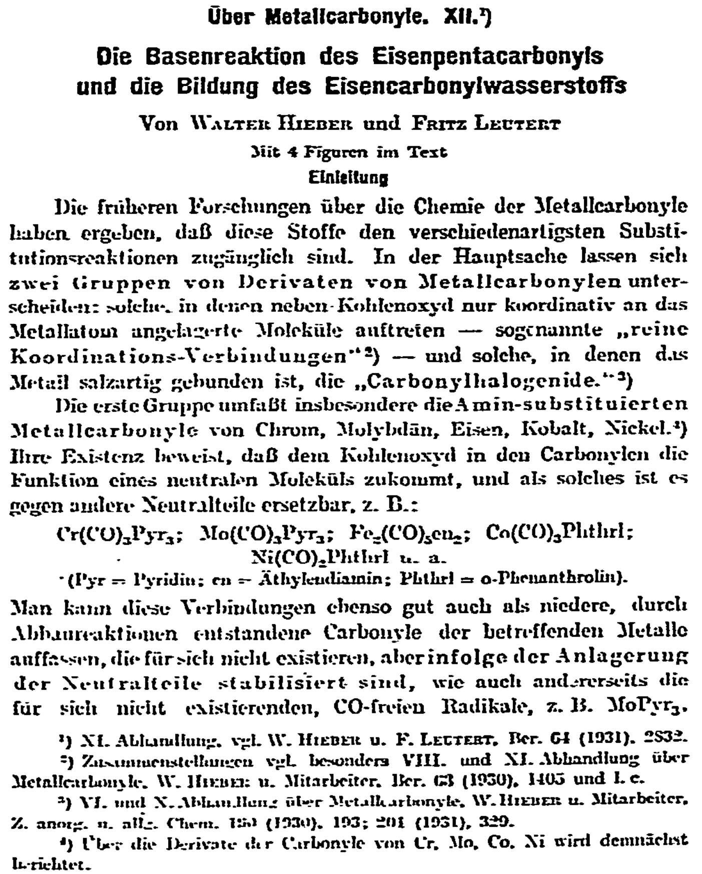
**) B. 32, 2351 [1899].

[1] X. Mitteil.: W. Hieber, Ztschr. anorgan. u. allgem. Chem. **1931**, 202; IX. Mitteil.: W. Hieber u. H. Vetter, B. **64**, 2340 [1931].

[2] W. Hieber u. Mitarb., B. **63**, 973 [1930].

[3] W. Hieber u. F. Sonnekalb, B. **61**, 558, 2421 [1928].

Fig. 14. Reprinted from Ber. Deutsch. Chem. Ges., 64 (1931) 2832.



Über Metallcarbonyle. XII.[1]

Die Basenreaktion des Eisenpentacarbonyls und die Bildung des Eisencarbonylwasserstoffs

Von Walter Hieber und Fritz Leutert

Mit 4 Figuren im Text

Einleitung

Die früheren Forschungen über die Chemie der Metallcarbonyle haben ergeben, daß diese Stoffe den verschiedenartigsten Substitutionsreaktionen zugänglich sind. In der Hauptsache lassen sich zwei Gruppen von Derivaten von Metallcarbonylen unterscheiden: solche, in denen neben Kohlenoxyd nur koordinativ an das Metallatom angelagerte Moleküle auftreten — sogenannte „reine Koordinations-Verbindungen"[2] — und solche, in denen das Metall salzartig gebunden ist, die „Carbonylhalogenide."[3]

Die erste Gruppe umfaßt insbesondere die Amin-substituierten Metallcarbonyle von Chrom, Molybdän, Eisen, Kobalt, Nickel.[4] Ihre Existenz beweist, daß dem Kohlenoxyd in den Carbonylen die Funktion eines neutralen Moleküls zukommt, und als solches ist es gegen andere Neutralteile ersetzbar, z. B.:

$Cr(CO)_3Pyr_3$; $Mo(CO)_3Pyr_3$; $Fe_2(CO)_5en_2$; $Co(CO)_3Phthrl$;
$Ni(CO)_2Phthrl$ u. a.

*(Pyr = Pyridin; en = Äthylendiamin; Phthrl = o-Phenanthrolin).

Man kann diese Verbindungen ebenso gut auch als niedere, durch Abbaureaktionen entstandene Carbonyle der betreffenden Metalle auffassen, die für sich nicht existieren, aber infolge der Anlagerung der Neutralteile stabilisiert sind, wie auch andererseits die für sich nicht existierenden, CO-freien Radikale, z. B. $MoPyr_3$.

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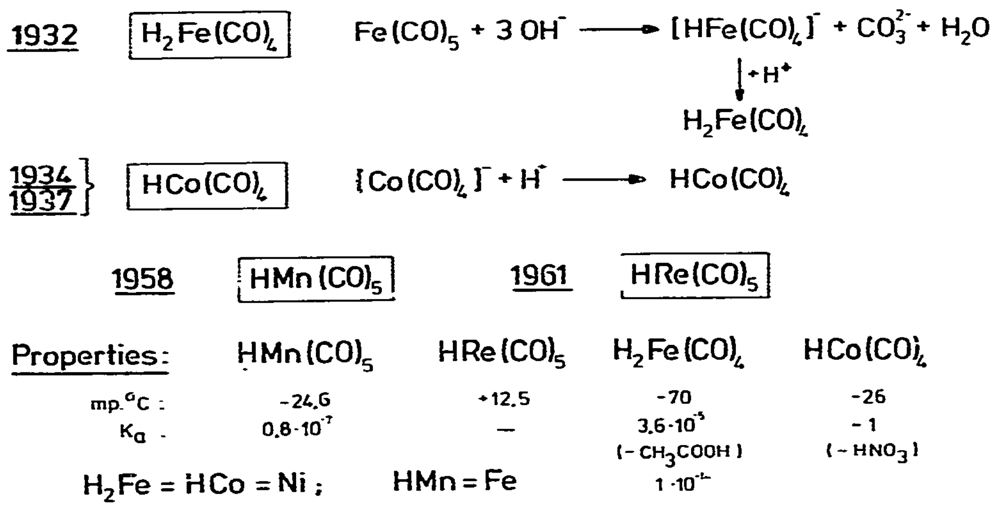
[1] XI. Abhandlung, vgl. W. Hieber u. F. Leutert, Ber. 64 (1931), 2832.

[2] Zusammenstellungen vgl. besonders VIII. und XI. Abhandlung über Metallcarbonyle. W. Hieber u. Mitarbeiter, Ber. 63 (1930), 1405 und l. c.

[3] VI. und X. Abhandlung über Metallcarbonyle, W. Hieber u. Mitarbeiter, Z. anorg. u. allg. Chem. 190 (1930), 193; 201 (1931), 329.

[4] Über die Derivate der Carbonyle von Cr, Mo, Co, Ni wird demnächst berichtet.

Fig. 15. Reprinted from Z. Anorg. Allg. Chem., 204 (1932) 145.



1932 $\boxed{H_2Fe(CO)_4}$ $Fe(CO)_5 + 3\,OH^- \longrightarrow [HFe(CO)_4]^- + CO_3^{2-} + H_2O$

$[HFe(CO)_4]^- \xrightarrow{+H^+} H_2Fe(CO)_4$

1934 / 1937 $\boxed{HCo(CO)_4}$ $[Co(CO)_4]^- + H^+ \longrightarrow HCo(CO)_4$

1958 $\boxed{HMn(CO)_5}$ 1961 $\boxed{HRe(CO)_5}$

Properties:	$HMn(CO)_5$	$HRe(CO)_5$	$H_2Fe(CO)_4$	$HCo(CO)_4$
mp.°C :	-24.6	+12.5	-70	-26
K_a .	$0.8 \cdot 10^{-7}$	—	$3.6 \cdot 10^{-5}$ (~ CH_3COOH) $1 \cdot 10^{-14}$	~ 1 (~ HNO_3)

$H_2Fe = HCo = Ni$; $HMn = Fe$

Fig. 16. Hydrido metal carbonyls I.

Thus this work from more than 40 years ago represents the first preparations of compounds containing hydrogen covalently bonded to transition metals. This bonding was immediately and completely correctly interpreted by Hieber and it led to the most useful concept that the H_2Fe and HCo (or HMn) groups can be regarded as pseudo-nickel and pseudo-iron atoms respectively. When one thinks that to date more than 300 hydrido complexes of the transition metals are known of which more than 100 are carbonyl hydrides then one has to appreciate the enormous importance that this early work of Prof. Hieber has had on the development of this particular area of chemistry. This is emphasized still further when one thinks of the role which hydride complexes now play in homogenous catalysis systems.

This early work by Walter Hieber represents masterpieces in the experimental art. Not only were these extremely sensitive compounds prepared in a pure form but they were also exactly analyzed. Further, data on their physical properties, which are still valid today, were determined in full.

In the winter of 1937, when I began my Diploma-work at the Technische Hochschule München as a student of Prof. Hieber, I saw for the first time the beautiful pale yellow crystals of cobalt carbonyl hydride which, after extremely

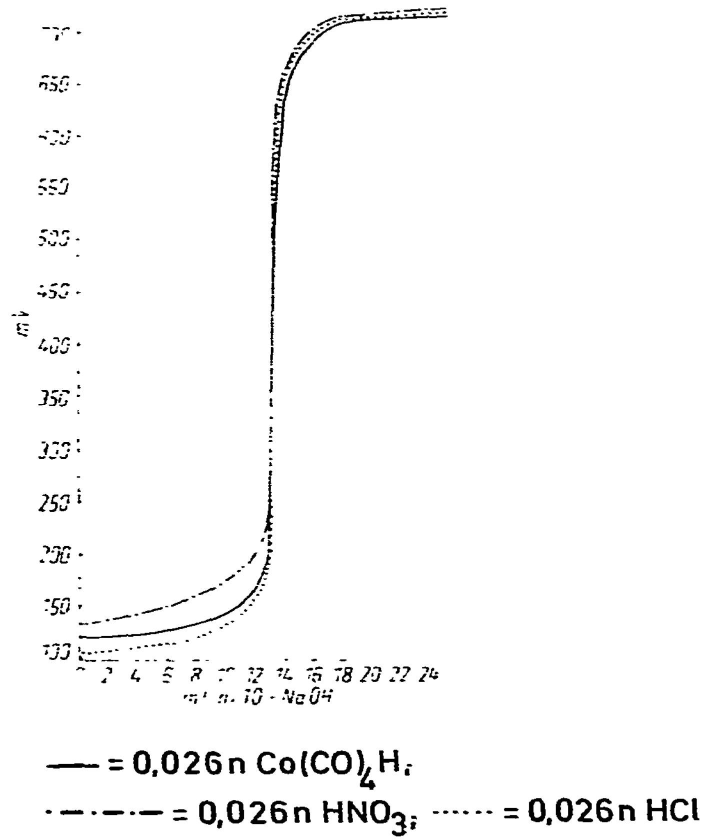


Fig. 17. Potentiometric titration curve of $HCo(CO)_4$ in methanol (0°C).

difficult experimentation, had been prepared by his co-worker Dr. Schulten. I can still clearly remember how great was the disappointment as it was found that over the weekend the cooling system had been inefficient and the wonderful product had decomposed to leave only dicobalt octacarbonyl.

The carbonyl hydrides of manganese and rhenium which are more stable were prepared in 1958 and 1961 respectively (Fig. 16). Whilst the iron, manganese and rhenium compounds are only weakly or very weakly acidic in water the potentiometric titration curve of cobalt carbonyl hydride (Fig. 17) shows it to be only slightly weaker an acid than hydrochloric acid and a little stronger than nitric acid at the same very low concentrations. This titration curve is taken from a Hieber publication from 1953.

In the course of subsequent work not only were polynuclear carbonyl hydrides of iron prepared but also mononuclear phosphine and phosphite substituted complexes of manganese and cobalt were isolated. Some examples are given in Fig. 18. One of the most important characteristics of these cobalt compounds is that, as substitution of the carbon monoxide groups by phosphorus ligands increases, not only does the thermal stability in comparison with hydrido tetracarbonylcobalt increase but also the acidity decreases. The dicarbonyl compounds show no acidity at all in aqueous solution. In this context, I should like to mention the phosphine substituted carbonyl hydride of vanadium which was reported in 1962. The parent hydrido hexacarbonyl vanadium still remains to be isolated.

It was more than 40 years ago that Prof. Hieber began to concern himself with the question of the existence of organometal carbonyls with metal—carbon σ-bonds. "If the carbonyl hydrides are acidic in water, then", postulated Hieber, "one must be able to esterify them." This postulation forms the basis for 25 years of difficult research. This was how long it took to isolate the extremely unstable methyl tetracarbonyl cobalt from sodium tetracarbonylcobaltate and methyl iodide.

With the passage of time the interest throughout the world in the chemistry of metal carbonyls had steadily grown and an intensive international com-

1957 $\boxed{H_2Fe_4(CO)_{13}}$

1962 $\boxed{HV(CO)_5PPh_3}$
$Ka = 1{,}5 \cdot 10^{-7}$

1961 $\boxed{HCo(CO)_3P(OPh)_3}$ and $\boxed{HCo(CO)_3PPh_3}$

dec.> 0°C
$K_a = 1{,}13 \cdot 10^{-5}$

dec. > 20°C
$K_a = 1{,}09 \cdot 10^{-7}$

1965 $\boxed{HCo(CO)_2[P(OPh)_3]_2}$ and $\boxed{HCo(CO)_2(PPh_3)_2}$

mp. 88°C
dec. > 140°C

dec. > 120°C

Fig. 18. Hydrido metal carbonyls II.

petition developed with this expansion. Thus it is not surprising that the first preparation of an unsubstituted alkylmetal carbonyl, namely methylpentacarbonylmanganese, was reported by Coffield and co-workers in 1957 and a little later by the Hieber group. Nowadays it is not at all unusual for different laboratories to make the same important discovery at the same time and completely independently.

Figure 19 presents, for example, 4 different groups' contemporary work on the preparation and characterization of alkyl- and acyl-metal carbonyls of cobalt and rhenium and their perfluoro derivatives.

One can see from the melting points that the stabilities of the cobalt compounds substantially increase as the CO ligands are substituted by phosphines or when alkyl and acyl groups are replaced by their respective perfluoro analogues. It is also noteworthy that methylpentacarbonylrhenium is highly stable and indeed was isolated two years before the hydride complex $HRe(CO)_5$. It is quite definite that the development of this field would have followed a very different course had not the preparation of methyltetracarbonylcobalt been so difficult.

Prof. Hieber's group's researches between 1930 and 1955 on the various methods of preparation of known and unknown metal carbonyls have played a most important role in the development of metal carbonyl chemistry.

One striking example of preparative technique which owes a great deal to Prof. Hieber's pioneering work has been the method of reductive carbonylation. This most appropriate term was coined in 1961 by Podall but the method had then long been in use in Hieber's laboratory. With the exception of iron pentacarbonyl and nickel tetracarbonyl, which can be made by direct interaction of the metal with carbon monoxide, all the other metal carbonyls have to be made under reducing conditions in the liquid or solid state. Not only has re-

compound	mp. (°C)	ref.
$CH_3Co(CO)_4$	-44	W. Hieber et al. 1958
$CF_3Co(CO)_4$	13	W.R. McClellan 1961, W. Hieber et al. 1961
$C_3F_5Co(CO)_4$	38	F.G.A. Stone et al. 1965
$CF_3Co(CO)_3PPh_3$	168	W. Hieber et al. 1961
$CH_3Co(CO)_2[P(OPh)_3]_2$	50	R.F. Heck 1963
$CH_3COCo(CO)_4$	- 33	R.F. Heck et al. 1960
$CF_3COCo(CO)_4$	4	W. Hieber et al. 1961
$CH_3COCo(CO)_3PPh_3$	123	R.F. Heck et al. 1960/62
$CF_3COCo(CO)_3PPh_3$	172	W. Hieber et al. 1961
$CH_3Re(CO)_5$	120	W. Hieber et al. 1959
$C_5H_5Re(CO)_5$	46	W. Hieber et al. 1960
$C_2F_5Re(CO)_5$	39	F.G.A. Stone 1960
$CH_3CORe(CO)_5$	80	W. Hieber et al. 1960
$C_2F_5CORe(CO)_5$	81	F.G.A. Stone 1960

Fig. 19. Alkyl- and acyl-metal carbonyls.

1952:

$$Ni^{2+} + S_2O_4^{2-} + 4\,OH^- + 4\,CO \longrightarrow \overset{0}{Ni}(CO)_4 + 2\,SO_3^{2-} + 2\,H_2O$$

$$Co^{2+} + \tfrac{3}{2}S_2O_4^{2-} + 6\,OH^- + 4\,CO \longrightarrow [\overset{-I}{Co}(CO)_4]^- + 3\,SO_3^{2-} + 3\,H_2O$$

1955:

$$NiS + 5\,CO + 4\,OH^- \longrightarrow \overset{0}{Ni}(CO)_4 + CO_3^{2-} + S^{2-} + 2\,H_2O$$

$$2\,CoS + 11\,CO + 12\,OH^- \longrightarrow 2[\overset{-I}{Co}(CO)_4]^- + 3\,CO_3^{2-} + 2\,S^{2-} + 6\,H_2O$$

Fig. 20. Syntheses of metal carbonyls in the liquid phase.

ductive carbonylation been applied by Hieber's group and later by other laboratories to the preparation of pure carbonyls, but it also finds utility in the syntheses of metal carbonyl derivatives such as halogenometal carbonyls.

A suitable reducing agent together with CO can be used or CO itself can act as reducing agent. Figure 20 shows examples of liquid systems using normal CO pressures. In the first reactions, which, by the way, were described by E.O. Fischer in his doctoral thesis, dithionite is oxidized to sulfite. The lower examples show the oxidation of carbon monoxide molecules to carbonate.

One of the most important series of reductive carbonylation reactions to be carried out was that undertaken at the Technische Hochschule München starting in 1935 in which high pressures of carbon monoxide were used at temperatures of 150 to 250°C. To begin with, this work involved the development of high pressure apparatus. Apparatus had to be built which not only allowed for the extreme reaction conditions under carbon monoxide but also allowed the experiments to be carried out safely.

The reactions of anhydrous metal halides with carbon monoxide in the presence of copper or silver have been extremely successful, particularly in the case of iodides, which usually give quantitative yields of metal carbonyls (Fig. 21).

At this point I should like to mention an important result of a reductive carbonylation which was carried out in 1941. In the reaction of rhenium pentachloride with CO (Fig. 21), instead of the expected dirhenium decacarbonyl

1942

$$\left\{\begin{array}{l} FeJ_2 + 5\,CO + 2\,Cu \longrightarrow Fe(CO)_5 + 2\,CuJ \\ 2\,CoJ_2 + 8\,CO + 4\,Cu \longrightarrow Co_2(CO)_8 + 4\,CuJ \\ NiJ_2 + 4\,CO + 2\,Cu \longrightarrow Ni(CO)_4 + 2\,CuJ \end{array}\right.$$

1941:

$$WCl_6 + 6\,CO + 6\,Cu \longrightarrow W(CO)_6 + 6\,CuCl$$

1941:

$$ReCl_5 + 5\,CO + 4\,Cu \longrightarrow Re(CO)_5Cl + 4\,CuCl$$

1941:

$$Re_2O_7 + 17\,CO \xrightarrow[250°C]{250\ atm.} Re_2(CO)_{10} + 7\,CO_2$$

Fig. 21. Reductive carbonylation under CO pressure (200 atm, 200°C).

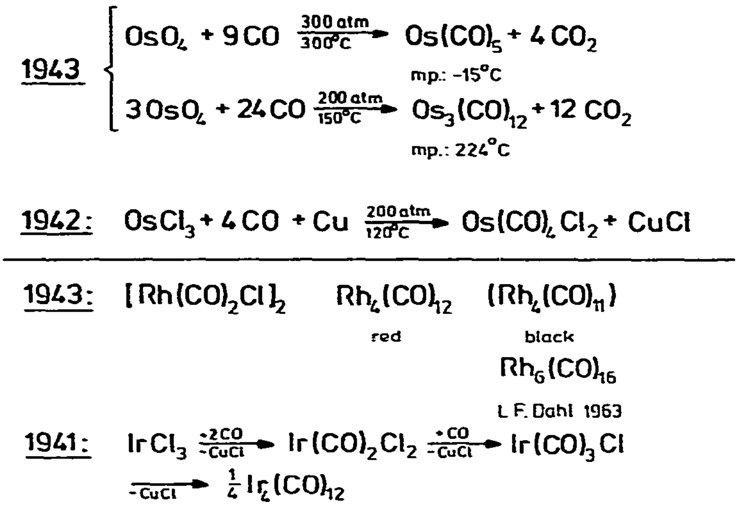


Fig. 22. Carbonyls and halogeno carbonyls of osmium, rhodium and iridium.

the extremely stable chloropentacarbonylrhenium was formed, the first rhenium carbonyl complex. There was naturally great excitement a little later when the first pure carbonyl of rhenium was prepared using high pressure systems. For this preparation dirhenium heptoxide was used as starting material.

The same reaction principle was used in 1943 to prepare osmium pentacarbonyl and triosmium dodecacarbonyl (Fig. 22); which product is formed is dependent on the CO pressure and the temperature. In 1962 Dahl and his co-workers showed by X-ray studies, that in the trinuclear carbonyl, the three osmium atoms form a triangle having no CO bridges. With osmium trichloride as starting material the product is dichlorotetracarbonylosmium. Analogous

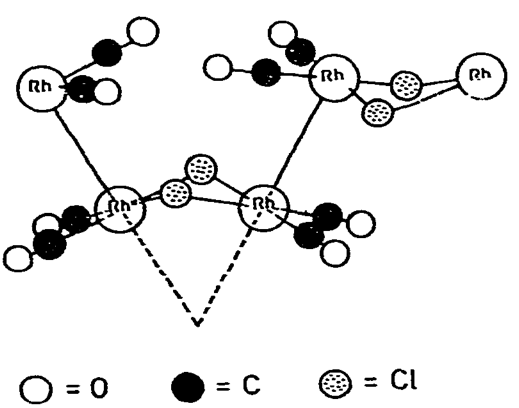


Fig. 23. Structure of $Rh(CO)_2Cl$ (L.F. Dahl, C. Martell and D.L. Wampler, 1961).

to the iron compound of the same formula this complex readily loses carbon monoxide on heating to give compounds having low CO content.

Rhodium carbonyls were prepared by Prof. Hieber by high pressure synthesis in 1943 (Fig. 22). Their structures were determined by Dahl and his group between 1961 and 1967. That of the cloro complex, given in Fig. 23, shows that it consists of two planar $Rh(CO)_2Cl$ groups bridged by chlorine. The angle between the planar groups is considerably less than 180° and the dimeric molecules are bonded by metal—metal bonds.

The compound which Hieber reported as $Rh_4(CO)_{11}$ has in fact been shown to be hexanuclear containing an octahedron of rhodium atoms and 16 CO groups. This error is very readily understood when one considers that the insolubility of this complex precluded molecular weight determination and that the analyses of both compounds are almost identical.

In the synthesis of the tetranuclear iridium carbonyl from iridium trichloride and carbon monoxide it has been shown convincingly that carbonyl halides exist as intermediates (Fig. 22). Thus one can often obtain yellow crystals of the tetranuclear carbonyl together with the brown carbonyl halide.

In contrast to the rhodium complex the tetranuclear iridium carbonyl was shown by Dahl and his co-workers in 1967 to contain no CO bridges. In 1961 Kaesz and co-workers, and independently Hieber's group, prepared ditechnetium decacarbonyl by high pressure synthesis. It has the same structure as the analogous manganese and rhenium carbonyls.

High pressure experiments with metal halides in the presence of halogen acceptor metals have led to the discovery of a further new class of compounds. Prof. Hieber has described these as "mixed metal carbonyls" (Fig. 24). If the reaction of cobalt(II) bromide with carbon monoxide at 200 atmospheres pressure and 200°C is carried out in the presence of zinc in place of copper, instead of the expected dicobalt octacarbonyl one obtains a zinc derivative which is characterized by linear Co—Zn—Co bonding. Mercury and cadmium form similar compounds. The reaction of $Co_2(CO)_8$ with cadmium shown in equation 2 of Fig. 24 is especially interesting since, as far as I am aware, it represents the first example in carbonyl chemistry of an "insertion reaction".

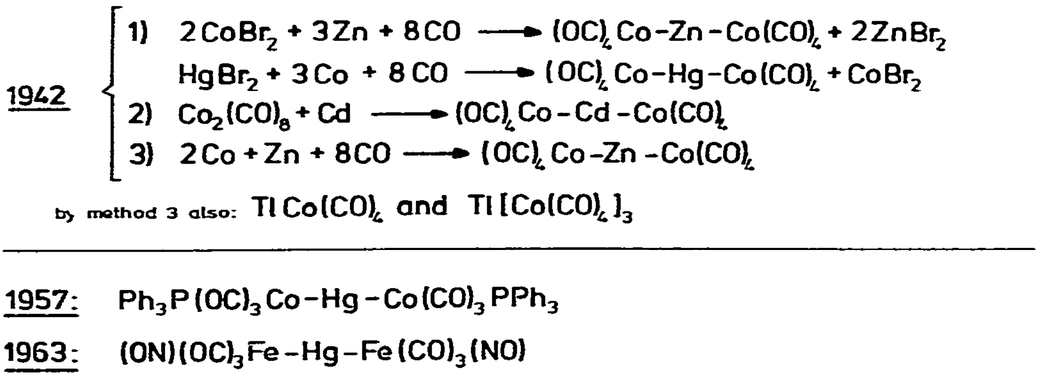


Fig. 24. Mixed metal carbonyls with post-transition metals (200 atm CO, 200°C).

The cadmium is inserted into the metal—metal bond of the dinuclear complex. All these complexes can be prepared by total synthesis shown in equation 3 of Fig. 24. The beautiful crystals of the thallium derivatives are especially worthy of mention. Edgell and his co-workers have recently shown by X-ray work that the thallium(I) derivative has a sodium chloride structure with discrete Tl^+ and $[Co(CO)_4]^-$ ions. Prof. Hieber's group has carried out a whole range of interesting reactions with these "mixed metal carbonyls", including CO substitution. The existence of the iron nitrosyl compound, which is isoelectronic with the cobalt species, has also been shown (Fig. 24).

I have already referred to some of Hieber's work on metal carbonyl halides. I think, however, that I should mention that as early as 1928 Hieber described the reaction of iron pentacarbonyl with iodine; this represents the first example of the reaction type which we now know as an "oxidative elimination". Figure 25 shows several carbonyl halides of iron with one, two and three CO groups as well as similar compounds of cobalt and rhenium. The number of experimental results which Prof. Hieber obtained over the years for the metal carbonyl halides of other transition metals is too great to allow a detailed description to be given here.

I hope, Professor Hieber, that you will excuse me for the fact that I have dealt with several of your research interests only briefly and that there are several topics which I have not mentioned at all. This is especially true of your important work on metal isonitriles and on the metal carbonyl nitrosyl research which began in 1930 and through the years has been added to continuously. You have also been greatly interested in those complexes which act as intermediates in metal carbonyl formation. I have already referred to the metal carbonyl halides. Others especially worth mentioning are the cyanocarbonylmetallates and the several types of polynuclear chalcogenometal carbonyls.

The dimeric sulphur-ligand carbonyl shown in Figure 26 was first described by you in 1937. In 1960 you assigned the structure on the basis of IR and dipole moment results. This structure has been shown to be completely correct by X-ray work carried out by Dahl's group in 1963.

With this piece of work I should like now to conclude this most incom-

$\boxed{Fe(CO)_4J_2}$ 1928: $Fe(CO)_5 + J_2 \longrightarrow Fe(CO)_4J_2 + CO$

1956–1962: $Fe(CO)_4J_2$; $Fe(CO)_3(TePh_2)J_2$; $Fe(CO)_2(PPh_3)_2J_2$; $Fe(CO)(CNR)_3J_2$

1965: $Co(CO)_3(PPh_3)X$ and $Co(CO)_2(PPh_3)_2X$ (X = Cl, Br, J)

1941: $Re(CO)_3\,pyr_2Cl$

$Re(CO)_3\,phen\,Cl$

1956: $[Re(CO)_4(PPh_3)_2]Cl$

Fig. 25. Halogenometal carbonyls.

plete report on your scientific work. Your excellent scientific accomplishments have been honoured many times in Germany and in other countries. The Universities of Heidelberg and Würzburg have awarded you honorary doctorates. The Bayerische Akademie der Wissenschaften and the Deutsche Akademie der Naturforscher in Halle have both made you a fellow of their organizations. The Gesellschaft Deutscher Chemiker awarded you the Alfred Stock Memorial Prize in 1951 and in 1959 you were made an honorary member of the British Chemical Society. In 1964 the same honour was bestowed upon you by the Swiss Chemical Society.

In the course of our 25 years of working together at the Technische Hochschule München between 1937 and 1962 we have experienced both good and bad times together. The atmosphere in the Munich Institute was happy and harmonious, but there was also sorrow. The bomb destruction which your institute suffered towards the end of the second world war brought a halt to your research for several years. After the war, however, the same tireless energy which you gave to scientific problems was applied to rebuilding your beloved institute.

I hope that in this talk I have succeeded in showing that the fascinating and exciting development of metal carbonyl chemistry provides an impressive example of the fact that real progress in science often results from discoveries, such as that of nickel carbonyl, which at first are difficult or even impossible to understand. This development of metal carbonyl chemistry has fundamentally influenced the whole of chemical thought. It has opened up the organometallic chemistry of the transition metals; it has played a most significant role in the development of bonding theories; it has presented new problems and new answers in structural chemistry; it has had important influence on catalytic and industrial process development and even has a relevance to biochemical research.

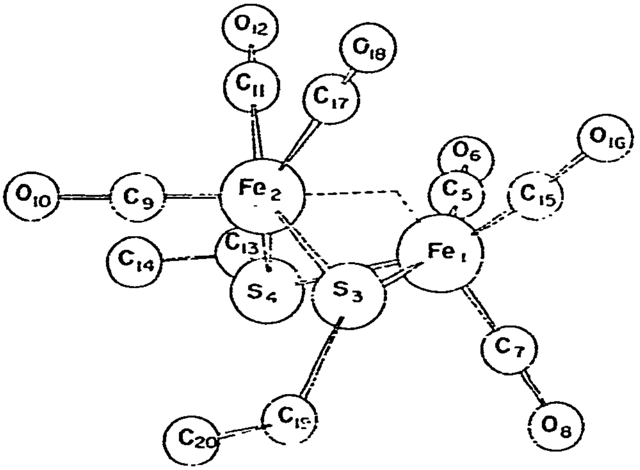


Fig. 26. The molecular configuration of $[C_2H_5SFe(CO)_3]_2$ (L.F. Dahl and C.H. Wei, 1962).

Your life work, Prof. Hieber, not only initiated these dramatic advances, but throughout 4 decades has served as a stimulating influence and example for continued development. In addition, it shows the fundamental importance of basic research which at first is always a venture into the unknown. You have put your whole life and personality into the service of science and it is in acknowledgement of this service that chemists from all over the world are gathered here in Ettal to express their gratitude.

Thank you Professor Hieber!