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100 years of metal carbonyls: a serendipitous chemical discovery of major scientific and industrial impact *

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> "The metal carbonyls were at that time far from being firmly categorized as a class of compounds, and were considered by many as curiosities (...) I can even remember the occasional allusions to the strange nature of the work which was directed upon a field where success was hardly to be expected."
>
> **Walter Hieber** (1895–1976);
> remarks on the early days of metal carbonyl research (Ref. 1b)

Introduction

In most areas of chemical research, organometallic compounds are important auxiliary species even if they do not play a key role. A basic and thorough understanding of organometallic chemistry is necessary when chemists use organometallics to aid organic syntheses, including those of natural products of complex architecture, when catalytic processes not just stoichiometric bond-making is being discussed, when effects of metal or metal oxide surfaces on carbon-containing compounds are being studied, or finally when the action of metals, light or heavy on biological systems is under investigation. The explosive topic of the threatening to life by some heavy metals should remind us that we can only approach the mystery of Pandora's box if we open it and examine its contents with caution. Hundred years of metal carbonyl history [1] serve well to remind us once again of the ever present widespread implications of chemistry. The historical review

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* This contribution is a translated and slightly expanded version of the article entitled "100 Jahre Metallcarbonyle: Eine Zufallsentdeckung macht Geschichte" (4th Essay on Organometallic Chemistry) that appeared in "Chemie in unserer Zeit" (Weinheim/Germany), Vol. 22 (1988), p. 113–122. The author is greatly indebted to his colleagues Helmut Behrens (München), Pierre Braunstein (Strasbourg), and Wolfgang Beck (München), as well as to the BASF Aktiengesellschaft (Ludwigshafen/Rhein), Ruhrchemie AG (Oberhausen), and the Max-Planck-Institut für Kohlenforschung (Mülheim/Ruhr) for valuable biographical information and especially for some of the pictures. (3rd Essay on Organometallic Chemistry: W.A. Herrmann, KONTAKTE (Darmstadt), (1988) (1), p. 3).

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below seeks to outline the development of transition metal carbonyl chemistry from its very beginning when Ludwig Mond and his co-workers discovered the prototype, tetracarbonylnickel. For many decades, metal carbonyl research was confined to European laboratories.

Winnington / England: Gas-battery and nickel carbonyl

In 1872 the chemist Ludwig Mond (1839–1909), who came from the Hessian town Kassel [2], founded the ammonia-soda factory of Winnington in the English county Cheshire. His partner in this joint venture was John T. Brunner, son of a Swiss teacher whom he had first met in Widnes. After Mond (Fig. 1) had finished his studies at the polytechnic in his hometown Kassel, he went on to the universities of Marburg and Heidelberg, where he received his scientific moulding especially through the famous chemists Hermann Kolbe (1818–1884) and Robert Bunsen (1811–1899). Subsequently he worked in the chemical industry in various places in Germany and Holland. His first visit to England was in 1862. There he intended to utilize his own, patented, process for the recovery of sulphur from soda residues, and with this very economical process he succeeded in John Hutchinson's factory in

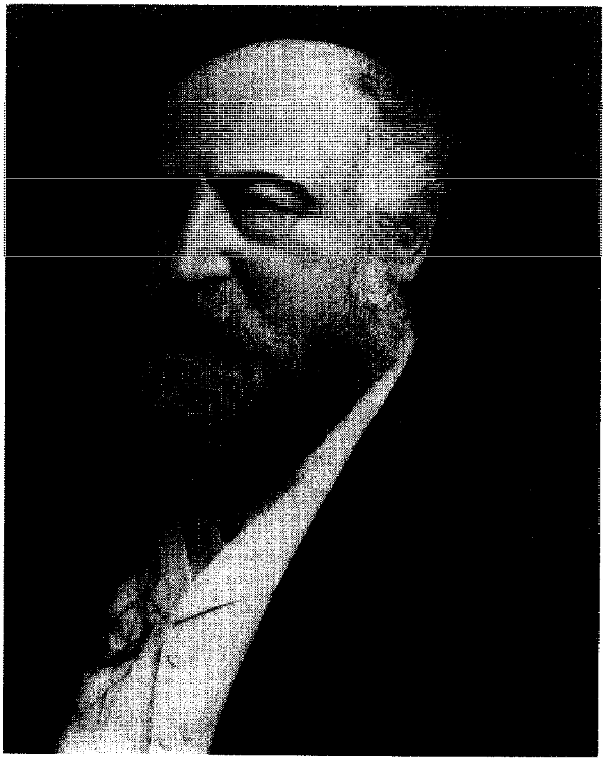

Fig. 1. Ludwig Mond (1839-1909) with whom the German chemists Carl Langer and Friedrich Quincke discovered the first binary metal carbonyl $Ni(CO)_4$ one hundred years ago. Mond became a very rich man. For example, he bought the Palazzo Zuccari in Rome, which he filled with works of art. Also Mond sponsored research work all over Europe; for example, he donated about 5 million marks from his personal fortune to various research institutions, notably in Heidelberg, München, and London.

Widnes. Two years later, in 1864, he moved to Utrecht in order to build and direct a Leblanc-Soda and Bleaching-Powder Factory. After another two years, in 1866, he finally settled in England and became an English citizen. Drawing on information from Ernest Solvay (1838–1922), whom he had met during a trip to Bruxelles, Mond decided to introduce the ammonia-soda process to England. His factory developed very well, becoming the biggest producer of soda in Europe, and employed no less than 4000 workers in the year 1910. The businessman and scientist Mond maintained a vigorous inventive output, as demonstrated by his list of 49 English patents. For example, he and his assistant Carl Langer improved the so-called gas-battery that had been invented by Grove in 1839 and involved the generation of electricity from air and the hydrogen of generator gas. These investigations had to be interrupted not only because of the relatively low efficiency of such batteries, but also because in the meantime other gas engines had made such great progress that development of the gas-battery seemed no longer to be attractive.

Moreover, in 1868 the Brunner–Mond Company faced the problem of recovery of chlorine lost during the ammonia-soda process. The origin of the subsequent discovery of nickel carbonyl found in the proposal: "...Chlorammonium durch Erhitzen zu dissoziieren und in diesem Zustande auf Metalle oder Oxide einwirken zu lassen. Die Salzsäure sollte sich mit dem Metall oder Oxid verbinden und das Ammoniak (sollte) freiwerden (...). Nickeloxid in der Form von porösen Pillen angewendet ... gab im Laboratorium sehr befriedigende Resultate. Als jedoch die Versuche in großem Maßstabe in Winnington fortgesetzt wurden, waren die Resultate infolge des Zerfallens der Nickel-Pillen unbefriedigend (...). Dieser Mißerfolg mit den Nickel-Pillen führte uns zu dem vorher erwähnten Verfahren, Kohlenoxid und Kohlenwasserstoffe aus Gasmengen zu entfernen und durch dieses zum Nickelcarbonyl." [3] * Carl Langer who had studied in the school of Victor Meyer (1848–1897), and who became a co-worker of Ludwig Mond in 1884, describes the discovery as follows [3]: "Diese Versuche waren schon längere Zeit im Gange, als wir durch einen Zufall das Nickelcarbonyl entdeckten. Wir behandelten ... in einem Verbrennungsrohr Nickel mit Kohlenoxid und leiteten die entweichenden Gase, um sie unschädlich zu machen, in einen Bunsen-Brenner. Mein Assistent (F. Quincke; addition made by the author) ... ersuchte mich, den Apparat abzustellen, da er früher nach Hause gehen müsse. Einige Zeit nachdem ich die Erhitzungsflamme abgestellt hatte, bemerkte ich, daß die Flamme des Brenners, in welchen das entweichende Gas einströmte, eine eigentümliche grünlich-gelbe Färbung zeigte, die stärker wurde, als sich das Rohr abkühlte. Mein erster Gedanke war, daß Arsen im Kohlenoxid vorhanden sein müsse, da dasselbe mit gewöhnlicher Schwefelsäure dargestellt war; ich erhitzte daher das Glasrohr, durch welches das

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* "... to treat metals or (metal) oxides with heat-dissociated ammonium chloride. The hydrochloric acid thus formed should react with the metal or the (metal) oxide, and ammonia should be liberated (...). Nickel oxide used in the form of porous tablets (...) yielded satisfactory results in the laboratory. However, when the experiments were continued on a large scale in Winnington, the results were unsatisfactory owing to decomposition of the nickel tablets (...). This failure with the nickel tablets led us to the above-mentioned process for removing carbon monoxide and hydrocarbons from gas mixtures, and through this process to nickel carbonyl."

Gas in den Brenner geleitet wurde, um einen Arsen-Spiegel zu erhalten. Der Spiegel trat auch sofort auf, bestand aber nicht aus Arsen, sondern aus Nickel!" *

The synthesis of pure tetracarbonylnickel, a colourless, water-clear liquid that boils at 42° C, was published by Mond, Langer, and Quincke in 1890 under the title "Action of carbon monoxide on nickel" [4] (see p. 1–5). One year later papers on pentacarbonyliron, synthesized similarly, appeared in the literature. The businessman Mond immediately recognized the industrial potential of these volatile compounds: thus an English patent (no. 12626) for a new process for making metallic nickel was granted to him in 1890. According to this patent, nickel-containing ores are first roasted (calcined), then treated at temperatures as low as possible with generator gas or water gas, and finally the nickel thus produced is 'volatilized' as tetracarbonylnickel, $Ni(CO)_4$, by treatment with carbon monoxide. The mixture of the excess of carbon monoxide and tetracarbonylnickel thus produced is heated to 180° C, at which temperature extremely pure metallic nickel is deposited. The carbon monoxide is recycled. Only because Mond could not find appropriate licensees did he found the "Mond-Nickel Co., Ltd.". This company carried out the extraction of nickel by the process specified in the above-mentioned patent, and in 1910 produced 3000 tons of nickel at a purity level of 99.9%. A convincing proof of the very great engineering achievements of the team centred on Ludwig Mond can be found in the fact that original cases of poisoning (resulting from the high toxicity of tetracarbonylnickel) were overcome after a short period. Actually, the BASF Aktiengesellschaft in Germany nowadays produces almost 10,000 tons per year of pentacarbonyliron, $Fe(CO)_5$, which is used for matins iron and iron oxide pigments (e.g., for use in magnetic tapes).

Ludwig Mond encouraged subsequent research work on metal carbonyl compounds in this company, and Hirtz and Cowap succeeded in synthesizing cobalt, molybdenum, and ruthenium carbonyl derivatives. However, after Mond's death in 1909, these promising research activities dried away rather quickly.

Early experiments on the metal fixation of carbon monoxide

It is undoubtedly due to the industrial success of the Mond Nickel process that scientific interest in other volatile metal carbonyls persisted in spite of the rather pessimistic conclusion of the original publication: "Numerous experiments were made to obtain similar compounds of carbon monoxide with other metals. Notably those with cobalt, iron, copper, and platinum have only led to negative results although they were carried out at temperatures from 15° to 750° ". [4] The reader

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* "These experiments had been going on for quite some time when we discovered nickel carbonyl by serendipity. We treated ... nickel in a combustion tube with carbon monoxide and vented the gases through a Bunsenburner in order to render them harmless. My assistant (F. Quincke) (...) asked me to turn off the apparatus because he had to go home early. Some time after I had turned off the flame, I noticed that the flame of the burner into which the gas was introduced showed a strange greenish-yellow colour, which became stronger as the tube cooled down. My first idea was that arsenic must be present in the carbon monoxide because the latter was generated from ordinary sulphuric acid. I therefore heated the glass tube through which the gas has been passed before it reached the burner, in order to produce an arsenic mirror. A mirror did indeed develop immediately, but did not consist of arsenic but rather of nickel!"

Fig. 2. M. Paul Schützenberger (1829–1897) was professor of chemistry at the Ecole de Chimie at Mulhouse and director of this institution. He later became a professor in Strasbourg and (in 1870) in Paris.

should note that no single binary carbonyl of either copper or platinum has yet become available.

The reader is also reminded that the attachment of carbon monoxide to metals had already been undertaken around the middle of the 19th century, but with little success: The only carbonyl-containing metal compound which survived later investigation came from M.P. Schützenberger (Fig. 2), who synthesized dicarbonyl dichloroplatinum, $Pt(CO)_2Cl_2$, in 1886 in the Alsatian Strasbourg (Fig. 3) [5]. Several years before, Justus von Liebig (1803–1873) had put his hopes on the synthesis of new organic basic chemicals through a "potassium carbonyl", KCO. As shown much later, the original mixture of compounds that Liebig had obtained from potassium metal and carbon monoxide is ionic in nature, and contains, for example, the potassium salts of dihydroxyacetylene and of hexahydroxybenzene [6]. Only recently has the attachment of dihydroxyacetylene to a metal been achieved, indirectly, in the cation $[(dmpe)_2Ta(H)(HO\text{-}C{\equiv}C\text{-}OH)Cl]^+$ (dmpe = $(CH_3)_2PCH_2$-$CH_2P(CH_3)_2$); here, as in the original Liebig experiments, the C_2 building block is formed from two molecules of carbon monoxide [7]. The ionic isomers "NiC_4O_4"

1868	$Pt(CO)_2Cl_2$	M.P.Schützenberger
1890	$Ni(CO)_4$	L.Mond et al.
1891	$Fe(CO)_5$	L.Mond,F.Quinke, M.Berthelot
1905	$Fe_2(CO)_9$	J.Dewar,H.O.Jones
1907	$\{Fe(CO)_4\}_n$ $(n = 20)$*	
1910	$Co_2(CO)_8$ $Co_4(CO)_{12}$	L.Mond et al.
1910	$Mo(CO)_6$	L.Mond et al.
1927/28	$Cr(CO)_6$ $W(CO)_6$	A.Job et al.

Fig. 3. Metal carbonyls from 1868 until 1928. Schützenberger succeeded in synthesizing the first well-defined metal carbonyl complex several years before Mond, Langer and Quincke, but he was dealing with compounds containing other ligands as well as carbon monoxide. Until Hieber's work, which started in 1927, there had been only a very few reports on metal carbonyls in the literature. (* = $Fe_3(CO)_{12}$).

and "FeC_5O_5" of tetracarbonylnickel and pentacarbonyliron, respectively, should be mentioned here as curiosities [8].

Sabatier and Senderens: catalytic hydrogenation at nickel

Stimulated by the discovery of tetracarbonylnickel, several other laboratories focused their activities upon the attachment to metals of molecules similar to carbon monoxide. A landmark in the development of catalysis emerged from the laboratory of Paul Sabatier in Toulouse shortly before the turn of this century (1897) [9] *: "Nous avions espéré que des fixations analogues pouraient avoir lieu pour les mêmes métaux à partir d'autres molécules gazeuses incomplètes, telles que l'oxyde azoteux, l'oxyde azotique, le peroxyde d'azote, l'éthylène, l'acétylène. (...) C'est donc avec cette idée, que nous devions reconnaître inexacte, que nous avons essayé l'action de l'éthylène, sur les mêmes métaux, et tout d'abord sur le nickel réduit. — Si on dirige l'éthylène sur la colonne de nickel, il n'y a à froid aucune réaction. Il n'y en a pas davantage à 100°, 200°, 250°, mais a partir de 300°. Le phénomène d'incandescence et de destruction du gaz, se produit, donnant non seulement du charbon et de l'hydrogène, mais une forte proportion d'éthane, qui avait dû être engendré par hydrogénation de l'éthylène grâce à une propriété spéciale du nickel, se révélant ainsi un catalyseur d'hydrogénation: ce qui fut confirmé de suite par une expérience directe."

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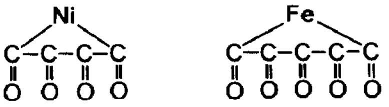
* "We had hoped that similar fixations could be achieved with the same metals for other unsaturated gaseous molecules such as dinitrogen oxide, nitrogen oxide, nitrogen dioxide, ethylene, acetylene, (...) Acting on this idea, which we came later on to recognize as incorrect, we investigated the action of ethylene upon those metals, and especially on reduced nickel. — When ethylene is passed through a column containing nickel, no reaction occurs at ordinary temperature. At 100, 200, and 250 ° C there is still no reaction, but above 300 ° C the column starts to glow and the gas begins to decompose; not only carbon and hydrogen are produced, but also rather large amounts of ethane. The latter compound must have come from hydrogenation of ethylene resulting from some special property of nickel, which metal appeared to be a hydrogenation catalyst. This explanation was subsequently confirmed by direct experiment.



Ni(CO)$_4$ Fe(CO)$_5$

Fig. 4. Original formulae of tetracarbonylnickel and pentacarbonyliron as commonly found in chemistry textbooks around 1925.

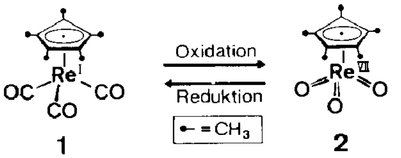
Only as recently as 1973 (!) did the Mülheim group centred on G. Wilke succeed in making the first binary ethylenenickel complex of formula $\text{Ni}(\eta^2\text{-C}_2\text{H}_4)_3$, which is thermally rather labile but was nevertheless obtained as crystals [10].

In textbooks of the twenties and thirties one finds structural formulae that assigned carbon–carbon bonds to metal carbonyls (Fig. 4). However, other criteria for their classification remain impressive in retrospective. Thus the noble gas rule first formulated by N.V Sidgwick (1874–1952) has stood the test as a "Leitmotiv" for the synthetic metal carbonyl chemist up to the present. The formulation of a double bond between nickel and carbon in tetracarbonylnickel by I. Langmuir (1881–1957) was verified by subsequent spectroscopic and structural investigations, as well as by molecular orbital calculations, and so the old "resonance" valence-bond formulation **A** may still be used.

$$\overline{\text{Ni}}-\text{C}\equiv\text{O}\,|^{+} \leftrightarrow \text{Ni}=\text{C}=\underline{\text{O}}$$

(**A**)

In the fifties the Dewar–Chatt–Duncanson model of the so-called "π-acidic ligands", originally developed for metal complexes of olefins, was also applied to carbon monoxide. It is precisely this π-acid effect ("π-backbonding") which stabilizes low oxidation states of the metal in transition metal carbonyls and the derivatives thereof. By contrast, the (σ- and) π-base ligand oxygen stabilizes the high oxidation states of the metal. The typical examples **1** and **2**, taken from a series of so-called half-sandwich complexes, underline this statement, as do the methyl complexes **3** and **4** (Fig. 5).



1 **2**

$(\text{CH}_3)\text{Re}^{\text{I}}(\text{CO})_5$ $(\text{CH}_3)\text{Re}^{\text{VII}}\text{O}_3$

3 **4**

Fig. 5. Carbon monoxide stabilizes low oxidation states of transition metals (compounds **1** and **3**), while the oxo ligand favours high metal oxidation states (compounds **2** and **4**; see text).

Pioneering work at Würzburg, Jena, Heidelberg, Stuttgart, and München: Walter Hieber and the Metal Carbonyls

Research on metal carbonyls quickly came to an end shortly after Ludwig Mond's death. Strangely enough, the work of the French research group centred around A. Job has attracted little attention: In 1927/28 this group synthesized the nowadays important compounds hexacarbonyl-chromium and -tungsten, $Cr(CO)_6$ and $W(CO)_6$, respectively, thus revealing the great potential of this area of research [11]. Around that time the research work of the then 32 year old Professor Walter Otto Hieber (1895–1976) [12] was initiated. Hieber had received his doctorate under Rudolf Weinland (1865–1936) at Tübingen (1919) and achieved his "Habilitation" five years later, again under Weinland. His first "Habilitationsthese" reflects the then modern language of the Swiss Nobel Prize winner Alfred Werner (1866–1919), whom we regard as the father of coordination chemistry: "Es ist nicht angängig, die Nebenvalenz lediglich als Restvalenz oder zersplitterte Hauptvalenz zu betrachten." * It is evident that Hieber (Figs. 6–9) was raised in the spirit of the Wernerian coordination theory: his doctoral thesis on "Komplexe des dreiwertigen

Fig. 6. The German chemist Walter Otto Hieber, the "pioneer of metal carbonyls" (born Dec. 12, 1895 and died Nov. 29, 1976).

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* "It is not possible to consider the "Nebenvalenz" only as residual valency or as divided (split) "Hauptvalenz".

Fig. 7. Walter Hieber (left) and his student and successor Ernst Otto Fischer at the "Metallcarbonyl-Tagung" at Ettal/Bavaria in 1974. Hieber is the father of the chemistry of metal carbonyls, because he developed this field of chemical research through his systematic investigations into a generally recognized important branch in chemistry. He directed the Anorganisch-chemisches Laboratorium of the Technische Hochschule (Universität) München for thirty years, until he was given emeritus status in 1964.

Eisens mit Unterphosphoriger Säure" provides clear proof that Hieber had heard of tetracarbonylnickel for the first time when he was "Vorlesungsassistent" under Weinland at the Würzburg University: "... veranlaßte mich mein unvergeßlicher Lehrer R.F. Weinland zum Aufbau einer Demonstration des Nickelcarbonyls, damals noch aus aktivem Metall im Kohlenmonoxydstrom. Seitdem verließ mich nicht mehr der Gedanke, mich mit Metallcarbonylen experimentell zu befassen. Denn es fiel mir auf, daß vom rein chemischen Verhalten dieser Stoffe trotz der bedeutungsvollen Entwicklung des Mond-Langer-Prozesses zur Aufarbeitung der

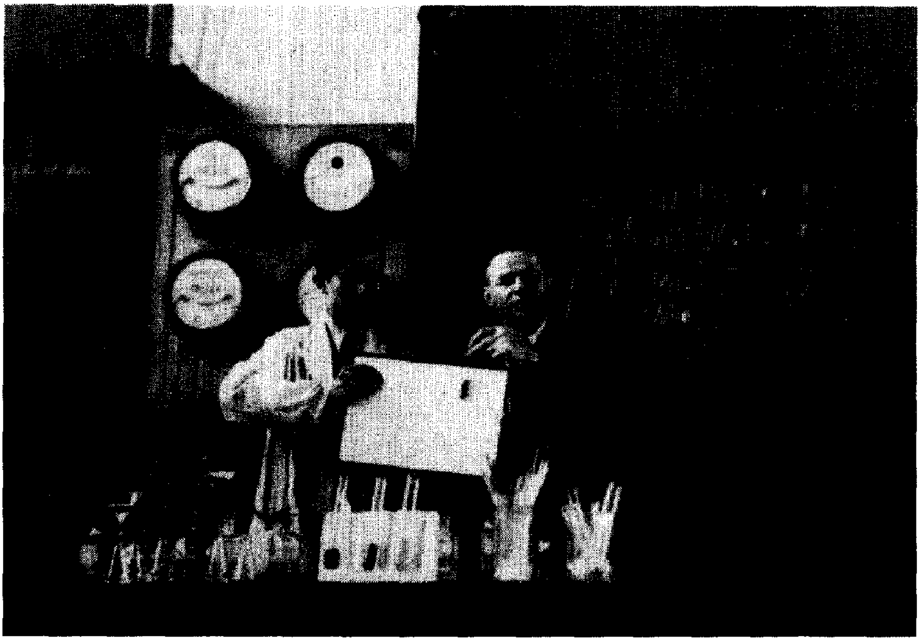

Fig. 8. Hieber with his chief assistant Helmut Behrens in the early fourties during a lecture on a laboratory course at the then Technische Hochschule München.

Fig. 9a. Hieber with colleagues and doctoral students in front of the old chemistry building in the "Hochschulstraße" of the Technische Hochschule München (taken around 1950). This building (Fig. 9b) was demolished after the chemistry faculty of the university moved to Garching in 1976.

kanadischen Magnetkiese bis dahin nur recht wenig bekannt war. (...)Im Herbst 1927 nahm ich im chemischen Institut der Universität Heidelberg Versuche mit Eisenpentacarbonyl auf, das mir Herr Direktor Dr. A. Mittasch von der benachbarten Badischen Anilin- & Sodafabrik in Ludwigshafen/Rhein zur Verfügung stellte. Aus eigener Erfahrung, speziell mit Nickelcarbonyl, warnte er mich ausdrücklich vor den Gefahren im Umgang mit diesen heimtückischen, hochgiftigen Substanzen und

Fig. 10. Alwin Mittasch (1869–1953), research director of the "Ammonlabor" of the Badische Anilin- & Sodafabrik at Ludwigshafen/Rhein from 1922 until 1933. He was the first industrial chemist to become interested in catalytic aspects of metal carbonyl chemistry (cf., K. Holdermann, Chem. Ber., 90 (1957) XLI).

verband damit noch die Erklärung, es seien auf diesem Gebiet nach allen bisherigen Bemühungen schwerlich wissenschaftlich wertvolle Ergebnisse zu erwarten!" [13] *

Again stimulated by a public lecture held by Alwin Mittasch (Fig. 10) at the general convention of the "Verein Deutscher Chemiker" in Dresden on May 31, 1928, where Mittasch also pointed out the possibility of industrial production of iron carbonyl [14], Hieber stated [13]: "Meine Absicht zum konsequenten Ausbau des aufgegriffenen Arbeitsgebietes wurde damit besiegelt." **

Hieber was the son of Johannes Hieber who during the "Weimar Republic" was minister of education and finally state president of Württemberg. From his education he and his five brothers and sisters gained a deeply religious and, at the same time, liberal attitude. As a result, Hieber never became fond of the Nazi regime, although he managed to arrange for his Munich institute to continue research work

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* "... my unforgettable teacher R.F. Weinland encouraged me to set up a demonstration of a synthesis of nickel carbonyl by passing carbon monoxide over activated metal in 1921. Since that time I have always been interested in experimental studies on metal carbonyls. In the early years little was known of the chemical behaviour of these compounds in spite of the important development of the Mond–Langer process for the processing of Canadian magnetic pyrites ore. (...) It was only in the autumn of 1927 at the Institute of Chemistry of the University of Heidelberg that I began research experiments with iron pentacarbonyl, which was kindly provided by Dr. A Mittasch of B.A.S.F. in neighbouring Ludwigshafen-am-Rhein. On the basis of his own experience with nickel carbonyl he warned me emphatically of the danger inherent in the use of these highly toxic substances, coupling his warning with the comment that in this field one could only expect a great deal of trouble and results of little scientific value!"

** "It became my firm resolve to extend this field which I had just taken up."

even during World War II. The tenacious, highly disciplined, experimental chemist Walter Hieber turned out to be the most important and productive pioneer in metal carbonyl chemistry. Through his 249 original papers published over the course of forty years he helped this class of compounds to attrack worldwide attention, thus stimulating relevant activities in numerous laboratories in Germany and abroad. Furthermore, he and his co-workers made the most significant achievements in both the development of new synthetic methods and the understanding of the reaction patterns of metal carbonyls. A detailed historical analysis of these achievements would certainly be premature, and therefore not very convincing. It is clear, however, that Hieber was responsible for a considerable development of organometallic chemistry by virtue of the research on metal carbonyls stimulated by his work. Carbon monoxide is among the most important ligands at least in low-valent organometallic compounds; ethylene, acetylene, methyl and hydrido ligands are also important. Hieber and his co-workers systematically investigated the chemistry of these ligands by use of sophisticated experimental techniques that have become standard today. Complexes of nitrogen monoxide also result from their initiative, with particularly original contributions coming from Hieber's brilliant student Fritz Seel (1915–1987), who later became a professor at Saarbrücken University.

The "Hieber base reaction" of metal carbonyls

According to a hypothesis of H. Reihlen (1892–1950), metal carbonyls were regarded as metal salts of organic "pseudo acids" in which the carbon atoms formed a chain structure, with the metal charge "neutralized" through the oxygen atoms of the carbon monoxide ligands. In contrast, Hieber considered them as "element complexes" ("Elementkomplexe"). He therefore started his investigations with "Reaktionen und Derivate des Eisencarbonyls". He showed that carbon monoxide is easily replaced by chelating base ligands such as ethylenediamine, and it is not important in this context that the mainly ionic products were convincingly identified only much later; it is noteworthy that the very first "cluster" anions, such as $[Fe_2(CO)_8]^{2-}$, $[Fe_3(CO)_{11}]^{2-}$, and $[Fe_4(CO)_{13}]^{2-}$, were among such products. The principle of "Valenzdisproportionierung" governing the reactions of iron and cobalt carbonyls with bases formed the fundament from which shortly thereafter Hieber made a most spectacular achievement when he synthesized "Eisencarbonylwasserstoff", $H_2Fe(CO)_4$ (Figs. 11 and 12), while still at Heidelberg University [15]. This particular compound was the very first "Komplexhydrid" with the metal in a negative oxidation state: "Lebhaft erinnere ich mich noch an den Tag, als ich gemeinsam mit meinen Mitarbeitern F. Leutert und H. Vetter im Heidelberger Institut bei der Zersetzung des ethylendiamin-haltigen Eisencarbonyls mit Säuren eine flüchtige, wasserklare Flüssigkeit ausfrieren und als $H_2Fe(CO)_4$ identifizieren konnte." [13] *

The synthesis of this compound, stable in the pure state only below ca. −10 °C, represented a substantial step forward in handling extremely air and temperature sensitive coordination compounds, but other laboratories were slow to investigate

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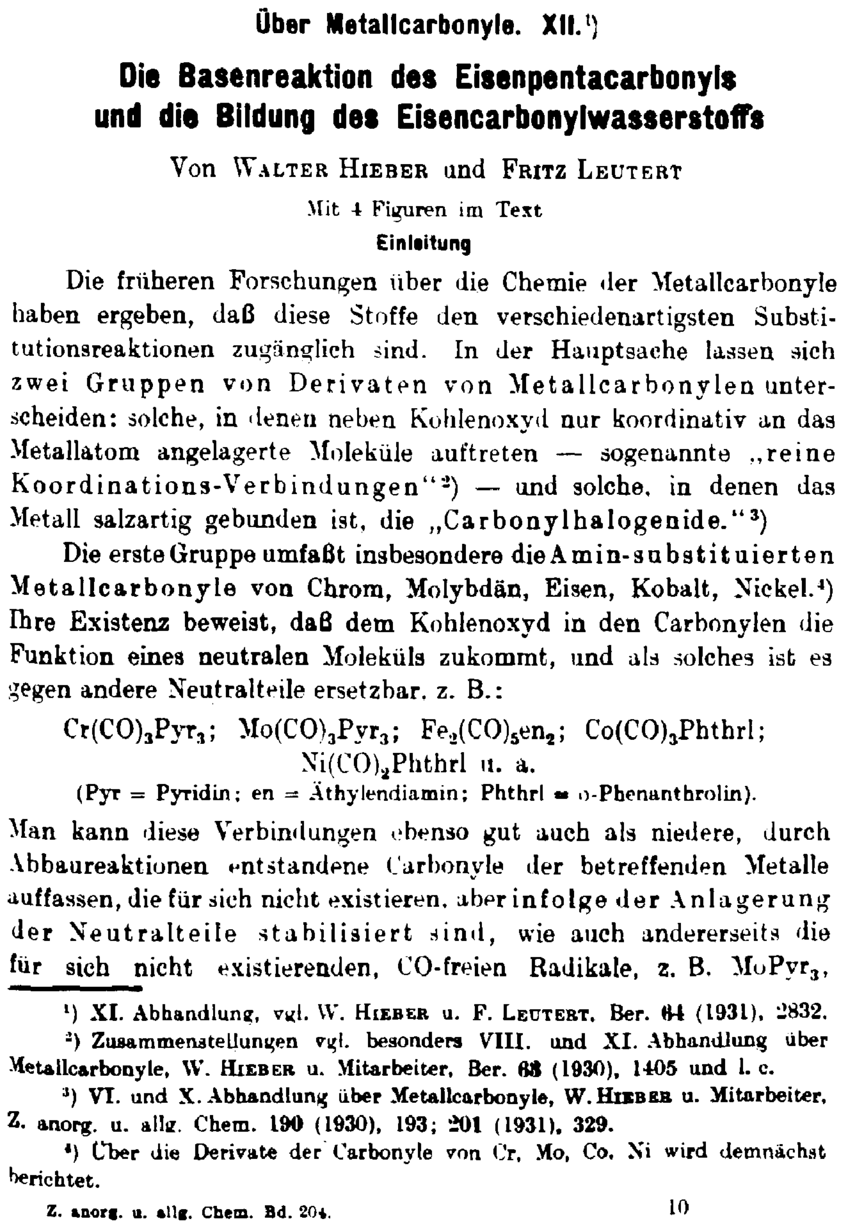
* "I still vividly remember the day when I, together with my coworkers F. Leutert and H. Vetter in the Heidelberg institute, was able to isolate a volatile, water-clear liquid from decomposition of ethylenediamine containing iron pentacarbonyl and to characterize this liquid as $H_2Fe(CO)_4$."



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.

Z. anorg. u. allg. Chem. Bd. 204. 10

Fig. 11. First page of the original publication on the base reaction of metal carbonyls (W. Hieber and F. Leutert, Z. Anorg. Allgem. Chem., 204 (1932) 145).

the chemistry of this class of apparently awkward compounds. Hieber and his co-workers soon isolated the isoelectronic cobalt carbonyl hydride of formula $HCo(CO)_4$, again a compound stable only at low temperatures. The Technische Hochschule München soon became the centre of a flourishing metal carbonyl chemistry. Walter Hieber was the director of the "Anorganisch-chemisches Laboratorium" there from 1935, succeeding Wilhelm Manchot (1849–1945). Education and research in this institution have been strongly influenced by various aspects of metal carbonyl chemistry up to the present, even after Ernst Otto Fischer took over

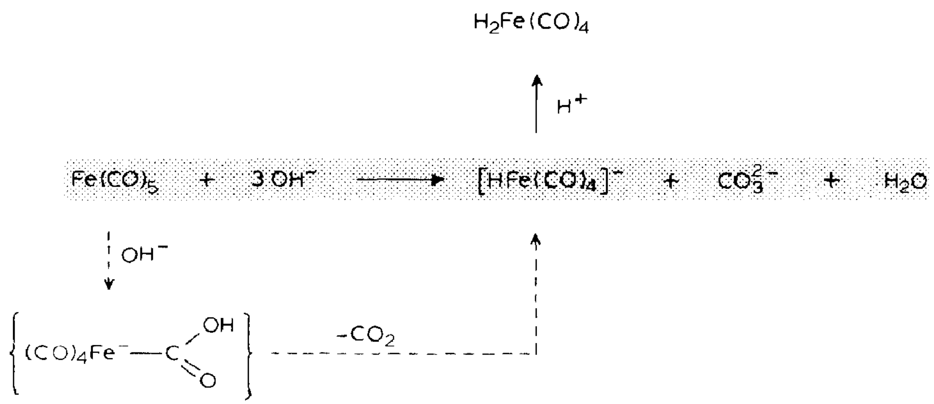

Fig. 12. The base reaction of pentacarbonyliron includes, as a key step, attack of a nucleophile (in this case OH^-) on a metal-coordinated carbonyl group. The intermediate metallacarboxylic acid spontaneously decomposes by decarboxylation to give a hydrido complex.

Walter Hieber's chair in 1964. A thorough characterization of the products of disproportionation of simple metal carbonyls was also carried out during the Munich era of Walter Hieber. Helmut Behrens, one of his students and later Professor of Inorganic Chemistry at the Universität Erlangen-Nürnberg, was the first person to use liquid ammonia in exploring the chemistry of metal carbonyls. Hieber and his co-workers also showed that the metal carbonyl hydrides act as Brønsted acids; thus $HCo(CO)_4$ is as strong an acid as nitric acid, while $H_2Fe(CO)_4$ can be compared with acetic acid in the first step of dissociation. In addition, many other examples of this class of compounds were synthesized, for example the volatile compounds $HMn(CO)_5$ (1958) and $HRe(CO)_5$ (1961) as well as $HV(CO)_5[P(C_6H_5)_3]$ (1962). Increasing replacement of carbon monoxide ligands by phosphanes increases the thermal stability of these derivatives, and at the same time lowers the degree of dissociation. While $HV(CO)_6$ is unstable and undergoes spontaneous decomposition

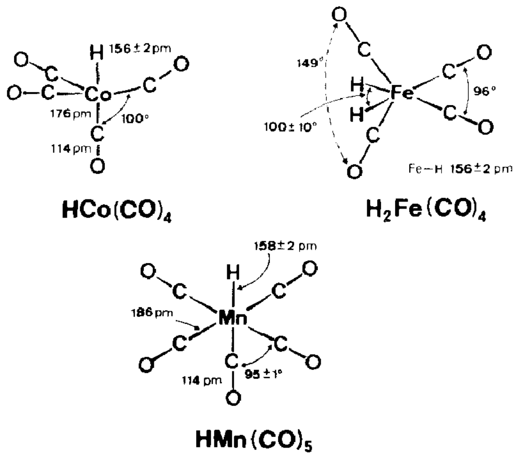

Fig. 13. Structures of important metal carbonyl hydrides, showing that the single hydrogen atom takes up its own coordination position on the metal atom.

according to eq. 1, the fully-substituted trifluorophosphane derivative $HV(PF_3)_6$,

$$HV(CO)_6 \rightarrow V(CO)_6 + \tfrac{1}{2}H_2 \tag{1}$$

made for the first time by the Hieber student Thomas Kruck (University of Cologne), is a crystalline compound and thermally stable up to 135 °C [16].

Hieber's intuition led him at an early stage of his work to suggest that the hydrogen atoms of metal carbonyl hydrides are directly attached to the metal atoms, but, this idea was resisted for decades, especially since an erroneous electron diffraction study of tetracarbonylhydridocobalt, $HCo(CO)_4$, was reported. The final confirmation of the hypothesis that the hydrogen atoms take up specific positions within the coordination polyhedra of such compounds (Fig. 13), came from single crystal neutron diffraction studies (e.g., of $HMn(CO)_5$ [17]), as well as from gas phase electron diffraction studies (e.g., of $HCo(CO)_4$ and $H_2Fe(CO)_4$ [18]). There are only a few exceptions in which the hydrogen atom is attached to the carbonyl oxygen atom in accord with the "isomerism" depicted in eq. 2 [19].

$$H{-}M{=}C{=}O \rightleftarrows M{\equiv}C{-}OH \tag{2}$$

Industrial intermezzo: Otto Roelen and Walter Reppe

Industrial activity began in the thirties alongside the investigations at the Technische Hochschule München. Their roots may be seen in the early coal-gas and synthesis gas chemistry. Franz Fischer and Hans Tropsch (Fig. 14 and 15) at the "Kaiser Wilhelm-Institut" in Mülheim/Ruhr had already discovered the "Synthol-Verfahren" for the production of liquid gasoline from synthesis gas by means of heterogeneous iron/cobalt catalysts in 1922. Otto Roelen, a former student of Franz Fischer, developed the so-called oxo synthesis ("hydroformylation") in 1938 when working as a chemist for the Ruhrchemie Company at Oberhausen (now Hoechst AG). Through this discovery, one of the most important landmarks in the development of industrial organometallic chemistry (eq. 3), aldehydes could be obtained from olefins, carbon monoxide, and hydrogen by catalytic means, with tetracarbonylhydridocobalt, $HCo(CO)_4$, serving as the immediate catalyst precursor. At present most industrial producers employ hydridocarbonyl derivatives of the more active and more selective rhodium compounds instead of the (much cheaper) cobalt homologues, and the most recent development involves use of water-soluble rhodium complexes in the Rhône Poulenc/Ruhrchemie process (Fig. 16) [20]. Phosphanes are still the most favoured ligands for this prototype of homogeneous organometallic catalysis. Hydroformylation is at present in the first rank of homogeneous catalytic processes in chemical industry, in terms of both output (ca. 8 billion tons of aldehydes world-wide) and value.

$$R{-}CH{=}CH_2 + CO + H_2 \rightarrow R{-}CH_2CH_2C({=}O)H \tag{3}$$

A further important development, which made a special contribution to the industrial acceptance of metal carbonyls, began at Badische Anilin- & Sodafabrik in Ludwigshafen/Rhein under the research director Walter Reppe (Fig. 17). The carbonylation reactions named after him are based on acetylene and its homologues, at that time the most important industrial starting materials for organic feedstock

Fig. 14. The first industrial metal-catalyzed reactions of carbon monoxide have their roots in the early work of Franz Fischer and Hans Tropsch (hydrocarbon synthesis) and that of Otto Roelen (hydroformylation). This picture was taken in 1932 on the occasion of a visit of Max Planck (second from right), the President of the Kaiser-Wilhelm-Gesellschaft zur Förderung der Wissenschaften, in the Institut für Kohlenforschung at Mülheim/Ruhr (now the Max-Planck-Institut für Kohlenforschung). The director of this institution, Franz Fischer (right), shows products of the Fischer-Tropsch synthesis to Max Planck; such products were manufactured in the institute. The picture also shows Walter Fleisst (left) and Otto Roelen (second from left), who at that time was in charge of the pilot plant. Otto Roelen (born in 1897) lives near Oberhausen (see also: O. Roelen: Erdöl und Kohle 31 (1978) 524). He discovered the hydroformylation process in 1938 when he was working with Ruhrchemie in Oberhausen ("oxosynthesis"; cf. Nachr. Chem. Techn. Labor. (Weinheim/Germany) 13 (1965) 49).

chemicals. It was soon not only possible to synthesize the important chemical

$$HC{\equiv}CH + CO + H_2O \rightarrow H_2C{=}CH{-}COOH \qquad (4)$$

acrylic acid (Fig. 18) according to eq. 4, but Reppe also reached the important goal of cyclotrimerization and cyclotetramerization of acetylene to yield benzene and cyclooctatetraene, respectively, by use of modified carbonylnickel catalysts. It is a convincing proof of Reppe's intellectual insight that even in his original publication in the year 1948 on the "Cyclisierende Polymerisation des Acetylens" * he depicted π-bonded acetylene ligands [21]!

New metal carbonyls, new syntheses

Novel high pressure techniques for the synthesis of new metal carbonyls were developed after Hieber took over the Munich laboratory at the Technische Hochschule. This work was very reliant on engineering since he had to provide his group

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* Ring-forming polymerization of acetylenes.

Fig. 15. Pioneers of carbon monoxide chemistry in the Kaiser-Wilhelm-Institut für Kohlenforschung in Mülheim/Ruhr (1922): Director Franz Fischer (eight from left), "Abteilungsvorsteher" Hans Tropsch (ninth from left), Ph.D. student Otto Roelen (second from right) [Necrology on F. Fischer: H. Pichler, Chem. Ber., 100 (1968) CXXVII].

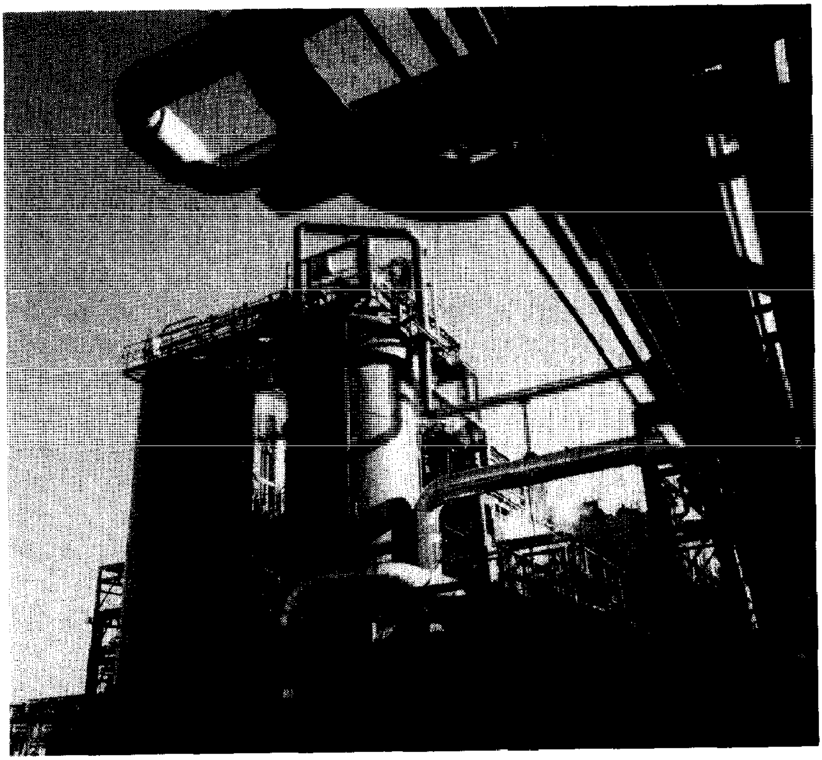


Fig. 16. Industrial oxo plant using the most modern process (water-soluble catalysts): Butyraldehyde synthesis from propene at Hoechst AG (Werk Ruhrchemie) at Oberhausen; the picture was taken in 1987.

Fig. 17. Metal-catalyzed technical reactions of acetylene were developed by Walter Reppe and his group from the early forties. Reppe (1892–1969) was a chemist at the Badische Anilin- & Sodafabrik at Ludwigshafen/Rhein, where he was in charge of the central R & D department from 1950. In 1952 he was elected a member of the Board of Directors. The so-called "Reppe Carbonylation Reaction" is named after him (see text).

with high-pressure autoclaves withstanding pressures up to 500 atm. At the beginning of this development, the notoriously high tendency for formation of metal carbonyls from the autoclave materials iron and nickel created great problems, which Hieber and his co-workers solved by lining the autoclaves with copper or silver. Depending on the reaction conditions and the scale of the reaction, rotating, shaking, or stirring autoclaves were employed. Metal carbonyls that could be made only in poor yields up to that time, such as hexacarbonyltungsten, suddenly became available in large amounts, e.g. from tungsten hexachloride in the presence of a "Beimetall" ("auxiliary metal") like copper that binds the halogen of the starting material. The hexacarbonyltungsten was made available in 1941 through a very effective solid state/gas phase procedure from tungsten hexachloride and carbon monoxide under high pressure in the presence of copper.

An outstanding example of the value of this procedure was provided by the synthesis of the long-sought-after rhenium carbonyl $Re_2(CO)_{10}$, which was first reported by Hieber and Fuchs during the Second World War. They made it in quantitative yield by reductive carbonylation of dirhenium heptoxide at elevated temperature in an autoclave in the absence of a solvent (Fig. 19) [22]. Carbon monoxide not only acts as a ligand in this particular reaction but also as the

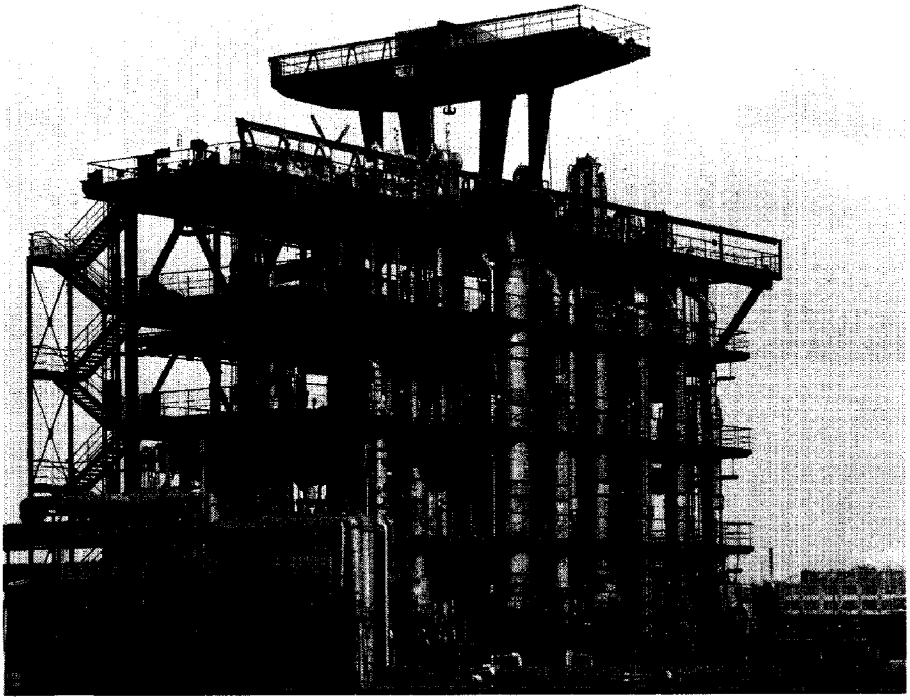
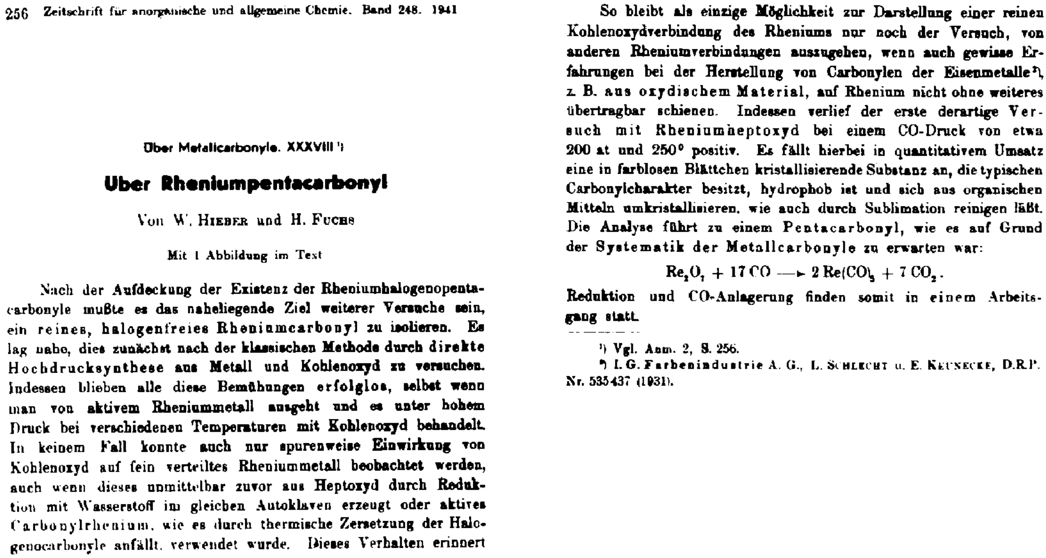


Fig. 18. A highlight of "Reppe-Chemie": acrylic acid plant of the Badische Anilin & Sodafabrik AG in 1962.



256 Zeitschrift für anorganische und allgemeine Chemie. Band 248. 1941

Über Metallcarbonyle. XXXVIII[1]

Über Rheniumpentacarbonyl

Von W. Hieber und H. Fuchs

Mit 1 Abbildung im Text

Nach der Aufdeckung der Existenz der Rheniumhalogenopentacarbonyle mußte es das naheliegende Ziel weiterer Versuche sein, ein reines, halogenfreies Rheniumcarbonyl zu isolieren. Es lag nahe, dies zunächst nach der klassischen Methode durch direkte Hochdrucksynthese aus Metall und Kohlenoxyd zu versuchen. Indessen blieben alle diese Bemühungen erfolglos, selbst wenn man von aktivem Rheniummetall ausgeht und es unter hohem Druck bei verschiedenen Temperaturen mit Kohlenoxyd behandelt. In keinem Fall konnte auch nur spurenweise Einwirkung von Kohlenoxyd auf fein verteiltes Rheniummetall beobachtet werden, auch wenn dieses unmittelbar zuvor aus Heptoxyd durch Reduktion mit Wasserstoff im gleichen Autoklaven erzeugt oder aktives Carbonylrhenium, wie es durch thermische Zersetzung der Halogenocarbonyle anfällt, verwendet wurde. Dieses Verhalten erinnert

So bleibt als einzige Möglichkeit zur Darstellung einer reinen Kohlenoxydverbindung des Rheniums nur noch der Versuch, von anderen Rheniumverbindungen auszugehen, wenn auch gewisse Erfahrungen bei der Herstellung von Carbonylen der Eisenmetalle[2], z. B. aus oxydischem Material, auf Rhenium nicht ohne weiteres übertragbar schienen. Indessen verlief der erste derartige Versuch mit Rheniumheptoxyd bei einem CO-Druck von etwa 200 at und 250° positiv. Es fällt hierbei in quantitativem Umsatz eine in farblosen Blättchen kristallisierende Substanz an, die typischen Carbonylcharakter besitzt, hydrophob ist und sich aus organischen Mitteln umkristallisieren, wie auch durch Sublimation reinigen läßt. Die Analyse führt zu einem Pentacarbonyl, wie es auf Grund der Systematik der Metallcarbonyle zu erwarten war:

$$Re_2O_7 + 17\,CO \longrightarrow 2\,Re(CO)_5 + 7\,CO_2\,.$$

Reduktion und CO-Anlagerung finden somit in einem Arbeitsgang statt.

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[1] Vgl. Anm. 2, S. 256.

[2] I. G. Farbenindustrie A. G., L. Schlecht u. E. Keunecke, D.R.P. Nr. 535437 (1931).

Fig. 19. Original publication (Ref. 22) on the discovery and synthesis of decacarbonyldirhenium, $Re_2(CO)_{10}$. The manganese compound $Mn_2(CO)_{10}$ was later obtained by E.O. Brimm and co-workers of the Union Carbide and Carbon Corporation (J. Am. Chem. Soc., 76 (1954) 3831; structure: L.F. Dahl and R.E. Rundle, Acta Crystallogr. (Kopenhagen), 16 (1963) 419), $Tc_2(CO)_{10}$ was first reported by H.D. Kaesz et al. (J. Am. Chem. Soc., 83 (1961) 2953).

reducing agent. The reducing ability of carbon monoxide had been used before by Manchot and König (also Munich) when they observed reaction with osmium trichloride to form phosgene, $COCl_2$, and the then novel carbonylosmium chloride, $Os(CO)_3Cl_2$ [23]. Decacarbonyldirhenium, $Re_2(CO)_{10}$, is still synthesized by the old Hieber oxide process; the same procedure is also used for the production of the osmium carbonyls $Os(CO)_5$ and $Os_3(CO)_{12}$ from osmium tetroxide. Reductive carbonylation was later also used with organometal halides; the use of the high-pressure reaction is exemplified by the preparation of the half-sandwich complex $(\eta^5\text{-}C_5H_5)Nb(CO)_4$, and for the low pressure method by the preparation of the complexes $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ and $Au(CO)Cl$ [24]. In all these cases metal–halogen bonds are replaced by metal–carbonyl bonds. It is of interest that use of the direct synthesis discovered in Ludwig Mond's laboratory (e.g., metal plus carbon monoxide) is still restricted to nickel and iron, even 100 years after the initial discovery!

Reactions of metal carbonyls

The most important and synthetically useful reactions of metal carbonyls and their derivatives are outlined in Fig. 20. Although not always straightforward, carbon monoxide substitution (type 1) is generally induced by heat or light (or more recently by ultrasound activation). Since most metal carbonyls obey the noble gas rule (EAN rule), elimination of carbon monoxide entails formation of a (coordinatively unsaturated) 16-electron fragment, which in terms of a modern concept is "isolobal" with methylene, and so can dimerize with formation of a metal-to-metal double bond. In most cases, however, formation of binary metal carbonyl cluster compounds occurs when no other ligands are present. For example, Speyer and Wolf showed in the twenties that the gold-coloured enneacarbonyldiiron, $Fe_2(CO)_9$, is best synthesized by shining sunlight on a solution of pentacarbonyliron in glacial acetic acid [25], and this still provides an impressive laboratory course experiment.

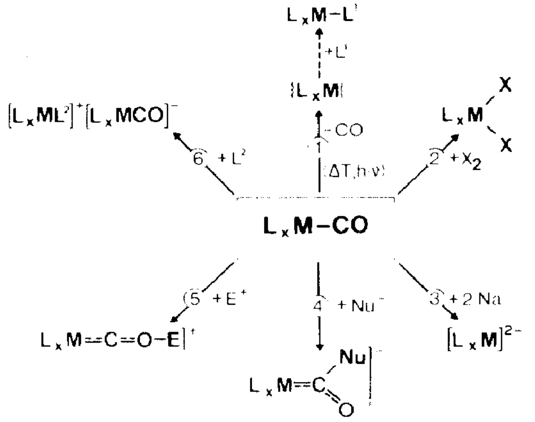

Fig. 20. Typical general reactions of metal carbonyls. (1) CO substitution; (2) oxidation, e.g. $Fe(CO)_5 \xrightarrow{Br_2} Fe(CO)_4Br_2$; (3) reduction, e.g. $Fe(CO)_5 \xrightarrow{+2Na} 2Na^+[Fe(CO)_4]^2$; (4) nucleophilic addition (Hieber base reaction); (5) electrophilic addition, e.g. $E = Mg^{2+}$; (6) disproportionation ($L^2 = NH_3$, etc.; e.g. $[Co(NH_3)_6][Co(CO)_4]_2$).

The substitution reactions are generally conducted in the presence of a ligand L^1, usually a phosphane, an isonitrile, an alkene, an alkyne, etc. and monosubstituted metal carbonyl derivatives are normally formed.

Metal carbonyls can also be oxidized to some extent, and reaction of the halogens with pentacarbonyliron to form the long-known complexes *cis*-$Fe(CO)_4X_2$ is a good example (type 2; Fig. 20). The metal carbonyl halides resulting from such oxidations (in many cases also obtainable by incomplete reductive carbonylation of metal halides) are in turn useful starting materials, especially for the formation of new metal-to-carbon bonds (e.g., alkylations by means of organo-lithium, -magnesium, -zinc, or -tin reagents).

Metal carbonyls also normally undergo reductive processes shown as reaction 3 in Fig. 20, alkali metals are especially effective for this purpose, and in recent years these metals have been used in the presence of crown ethers or cryptands in order to avoid subsequent formation of clusters. The commercially available reagent $Na_2[Fe(CO)_4]\cdot THF$, named after Collman, is a useful starting reagent for nucleophilic alkylation reactions in organic chemistry. The "carbonyl metallates" thus made available for literally all metal carbonyls, are not only useful in organic syntheses but also for further functionalization of this class of compounds, especially for the preparation of hydrido and alkyl complexes. The most recent examples of such carbonyl metallates are those synthesized by John E. Ellis, namely highly-reduced metal carbonyls, such as $[M(CO)_6]^{2-}$, of titanium and tantalum [26].

Reaction 4 in Fig. 22, involving nucleophilic addition to the electron-deficient carbon atom of a metal-attached carbonyl group, has become a powerful tool in synthetic organometallic chemistry since the prototype was discovered and described by Hieber ("Hieber base reaction"). Some variants are outlined in Fig. 21. Thus the formation of carbene complexes, first observed by E.O. Fischer and his group in 1964, from a metal carbonyl and lithium organic reagent is a typical base reaction; first forming an unstable zwitter-ion, trimethylamine oxide attacks a metal-attached CO group to yield 16e fragments via elimination of trimethylamine and carbon dioxide; the organometallic intermediates thus formed can dimerize to metal–metal double bonded species, and this is, in fact, one of the standard synthetic routes to such compounds. The action of azides on metal carbonyls represents an organometallic analogue of the so-called Curtius degradation of carboxylic azides. After initial nucleophilic attack of the azide ion upon the

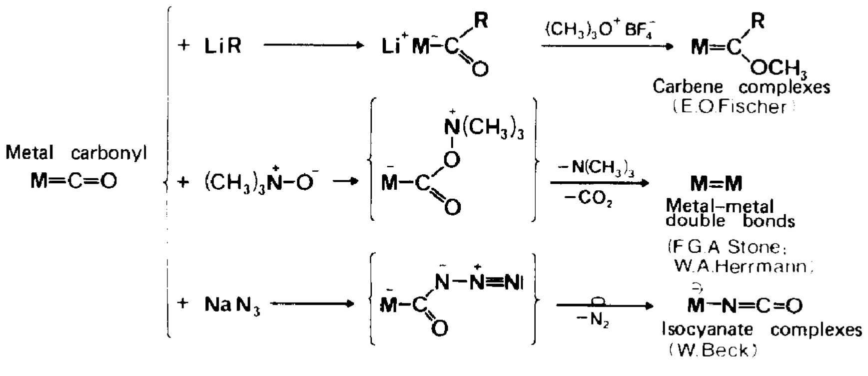

Fig. 21. Reactions of metal carbonyls with nucleophilic reagents (type 4 in Fig. 20).

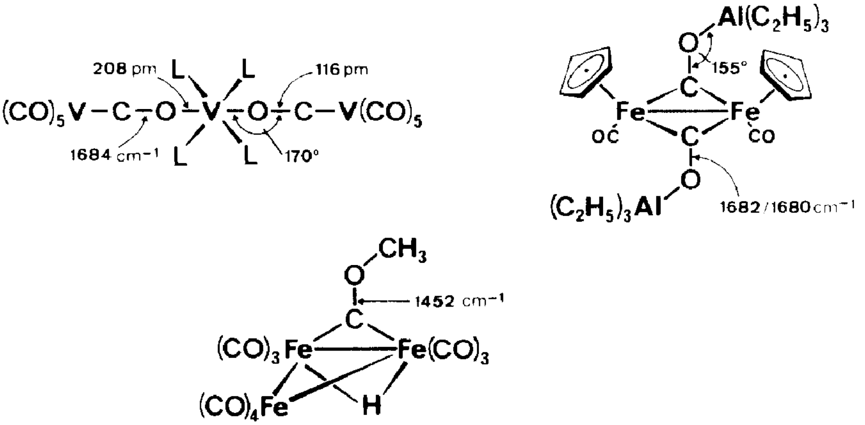

Fig. 22. If a metal-coordinated carbon monoxide is sufficiently nucleophilic, it can also form complexes via the oxygen atom. Shown are some typical early examples.

carbonyl group, clean rearrangement with concomitant elimination of dinitrogen occurs, and isocyanato complexes are usually formed in good yields (Fig. 21).

The long-standing problem of nucleophilic complexation, in other words the nucleophilicity of the oxygen end of metal-attached carbonyl groups, was resolved only in the seventies, mainly by D.F. Shriver [19]. It was found that Lewis acids such as aluminum trichloride can attach to the end of a metal carbonyl, in a reaction of type 5 (Fig. 20). Only bridging carbonyl groups are sufficiently nucleophilic, at least as far as electroneutral metal carbonyl derivatives are concerned. Addition of electrophiles is, of course, easier with (the anionic) carbonyl metallates. A particularly nice example of oxygen complexation was observed by Hieber's student Erwin Weiss (University of Hamburg): heating of hexacarbonylvanadium in the Lewis base solvent tetrahydrofuran (THF) yielded the trinuclear derivative $V_3(THF)_4(CO)_{12}$ in a "valence disproportionation" of type 6. The surprising and, at the same time, very straightforward, structure of this compound is shown in Fig. 22.

The circle is closed by considering the disproportionation reaction of metal carbonyls (type 6), discovered by Walter Hieber exactly 60 years ago. Base ligands L^2 are required in order to transfer the formally zerovalent metal into both a higher and a lower oxidation state, and "hard-base" ligands clearly prefer a higher metal oxidation state.

Structural studies of metal carbonyls began in 1939 but did not become an important feature until the development of modern X-Ray diffraction techniques around 1960 [28]. Thus the structure of $Fe(CO)_5$ (Fig. 23) was first studied as early as in 1939 by electron diffraction in the gas phase (R.V.G. Ewens and M.W. Lister, Trans. Farad. Soc., 35 (1939) 681), and was later refined by M.I. Davis and H.P. Hanson (J. Phys. Chem., 69 (1965) 3405): $d(\text{Fe–C})_{ax}$ 179.7(15) pm, $d(\text{Fe–C})_{eq}$ 184.2(15). In solution Berry pseudo-rotation site exchange presumably takes place. The first metal–metal bonded metal carbonyl was also structurally investigated in 1939 (H.M. Powell and R.V.G. Ewens, J. Chem. Phys., (1939) 286): $d(\text{Fe–Fe})$ 246 pm. The first unsupported metal-to-metal bond, however, was established much later in the case of $Mn_2(CO)_{10}$: L.F. Dahl and R.E. Rundle, Acta Crystallogr. (Kopenhagen), 16 (1963) 419 (D_{4d} symmetry, $d(\text{Mn–Mn})$ 292.3 pm). $Re_2(CO)_{10}$

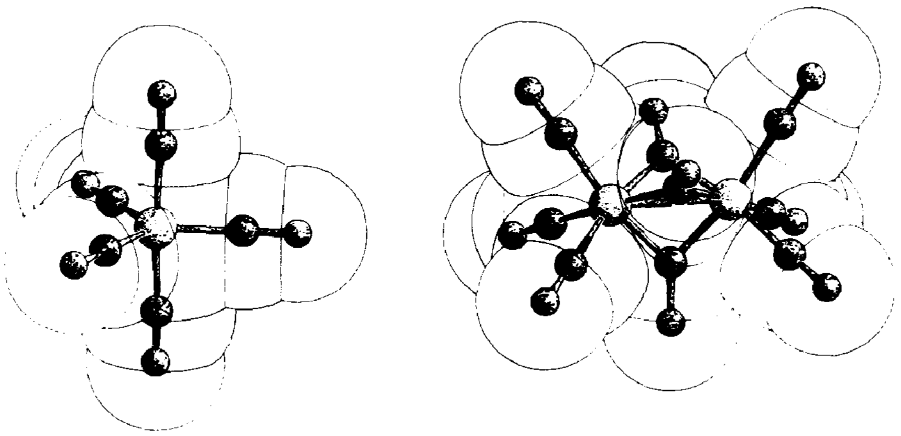

Fig. 23. Structures of the metal carbonyls $Fe(CO)_5$ and $Fe_2(CO)_9$.

has an analogous structure (L.F. Dahl, E. Ishishi, and R.E. Rundle, J. Chem. Phys., 26 (1957) 1750; *d*(Re–Re) 301 pm).

The next 100 years of metal carbonyls?

This question is a rhetorical one and thus does not warrant an answer. After the analysis in the above essay the question should instead stimulate the delineation of future lines of development. There is certainly no doubt that industrial catalysis and research into catalysis will remain the strongest field of metal carbonyls since many basic questions remain unanswered after 100 years. For example, we are yet a long way from truly "tailored" homogeneous and heterogeneous catalysts for industrial reactions of carbon monoxide in spite of decades of experience with the basic types of such processes. Many mechanisms of metal and metal carbonyl catalysis remain to be discovered. Our knowledge of the elemental steps of chemisorption of the carbon monoxide molecule at metal surfaces is relatively new and incomplete. Modern textbooks cannot yet give an account of the interaction of carbon monoxide with metal oxides. The questions of the advantages of molecular clusters among carbonyl compounds and of the importance of metal atom arrays in the catalytic chemistry of carbon monoxide remain unresolved as does the interlinkage of the two types of catalysis.

In homogeneous catalysis water-soluble metal carbonyl catalysts hold out the prospect of success similar to that achieved in recent years by the Rhône Poulenc/Ruhrchemie process for hydroformylation of propylene [20] in the presence of the hydrido carbonyl complex $H(CO)Rh[P(C_6H_4\text{-}m\text{-}SO_3^-Na^+)_3]_3$.

"Homologation" of metal carbonyls is an attractive goal, and not only from the point of view of synthesis. Seleno- and telluro-carbonyl complexes (involving CSe and CTe ligands) [29] could participate in metal-centered syntheses of selenium- and tellurium-containing heterocycles.

Carbon monoxide when bound to transition metals is both mobile and reactive at the same time. This feature must be exploited if 100 years of metal carbonyls are not to mark the end of a fascinating, innovative, illustrative, and valuable success of modern chemistry.

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