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## Coordination Chemistry in Europe since Alfred Werner

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**Abstract.** The development of coordination chemistry in Europe since Alfred Werner's epoch-making 1893 publication is reviewed. Mention will be made of the work done by the German School (P. Pfeiffer, F. Hein, W. Hieber, W. Reppe, W. Klemm, E.O. Fischer), the French School (M. Délépine, R. Charronat, A. Joly, J.-P. Mathieu), the Scandinavian School (K.A. Jensen, J. Bjerrum, I. Leden, L.G. Sillen), the English School (F.G. Mann, J. Chatt, R.S. Nyholm, G. Wilkinson), the Russian School (L.A. Chugaev, I.I. Chernyaev, A.A. Grinberg, K.J. Jatzimirski), the Italian School (A. Miolati, L. Cambi, L. Malatesta, P. Chini), and the Swiss School (G. Schwarzenbach).

### Beitrag zur Konstitution anorganischer Verbindungen.

Von

ALFRED WERNER.

Mit 17 Figuren im Text.

Unter Metallammoniumsalzen versteht man Verbindungen, welche aus Metallsalzen dadurch entstehen, daß sich in ihr Molekül Ammoniakmoleküle einschieben, oder besser: Metallammoniumsalze sind Verbindungen, welche nach derselben Reaktion aus Ammoniak und Metallsalzen entstehen, nach der sich Chlorammonium aus Salzsäure (welche letztere ja das Haloidsalz des Wasserstoffes ist) und Ammoniak bildet.

Fig. 1. The title page of Alfred Werner's epoch-making publication

### FACTORS DETERMINING THE STABILITY OF COMPLEXES

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The objects of this paper are, firstly, to discuss in a general way, and to illustrate, some of the main conclusions from a paper which should appear this year (by Craig, Maccoll, Nyholm, Orgel and Sutton\*) and which was briefly reported in 1950 (I.C.I. Symposium on Co-ordination Chemistry) and, secondly, to show the connection between the point of view implicit therein and that adopted in another paper on complexes by one of us (Orgel, *J. Chem. Soc.* (1952) 4756) which was based on the Penney-Schlapp treatment of crystal fields.

Fig. 2. L.E. Orgel's contribution at the 1953 Copenhagen Symposium on Coordination Chemistry

This year marks the hundredth anniversary of the submission of Alfred Werner's epoch-making paper (Fig. 1) [1][2]. Furthermore, forty years have lapsed since the 'Symposium on Coordination Chemistry' was held in Copenhagen in August 1953 [3]. This was the first 'open' International Conference on Coordination Compounds. Some of the papers presented there proved to be of fundamental importance for the development of coordination chemistry, and thus this short historical account will be centered around that event.

Undoubtedly, the most seminal lecture presented at that Symposium was given by L.E. Sutton on some work by L.E. Orgel on 'crystal field theory' (Fig. 2) [4].

The fundamental aspects of this theory had been published several years earlier, but the mathematical language used by H. Bethe, W.G. Penney and R. Schlapp, as well as J.H. van Vleck, hindered the assimilation of these concepts by coordination chemists. It was the great insight and skill of L.E. Orgel, as well as his didactic talent, that encouraged experimentalists to use these ideas which contributed so significantly to the revival of inorganic chemistry [5].

This approach had a catalytic effect on theoretical, spectroscopic, and magnetic studies, particularly through the publications of H. Hartmann, C.K. Jørgensen, C.J. Ballhausen, J.S. Griffith, and C.E. Schäffer [6].

Furthermore, the  $\pi$ -bonding ideas, already current in 1953, for the cyano and carbonyl complexes, and later extended to the chemistry of what we now call 'soft donors' mainly by J. Chatt [7] (Fig. 3) and R.S. Nyholm [8], also got their first international baptism at this meeting.

As it befits a symposium held in Copenhagen, the study of complexes in solution was prominently featured. Clearly the revolutionary developments in that area had already occurred by 1953, but, once again, that symposium provided an open forum for a field which, up to that time, had been mainly a Scandinavian preserve.

Although the pioneering studies of the stabilities of metal complexes in solution had been carried out by R. Abegg, G. Bodländer, and N. Bjerrum during the first quarter of this century, it was Jannik Bjerrum who combined the intimate knowledge of his father's work and the use of the

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glass electrode, to produce the results first reported in his thesis, published in 1941 [9].

While on this topic, mention must be made of another fundamental thesis, that of *Ido Leden*, published in 1943 [10] (Fig. 4), which introduced the experimental methodology for the study of equilibrium constants based on the use of metal electrodes.

The Scandinavian School of solution chemistry soon after achieved world fame also through the contributions of *Sture Fronaens* [11], *Lars-Gunnar Sillen* [12], and *Sten Ahrlund* [13].

While on the topic of solution equilibria, it is appropriate to mention the work of *G. Schwarzenbach*, then at the University of Zurich. His fundamental studies of complex formation with aminopolycarboxylic acids and polyamines, published between 1945 and 1955, in addition to leading to major advances in analytical chemistry, allowed him to give a quantitative formulation of 'the chelate effect' [14].

Another fundamental observation, relating to the stability of complexes in solution, *i.e.*, the *Irving-Williams* series, was also presented for the first time at the Copenhagen Conference [15].

Finally, one cannot leave the field of solution chemistry without mentioning *M. Eigen's* major contribution in the field of kinetics. Double significance has to be attached to his work: firstly for the development of the experimental techniques, the measurement of the rates of  $H_2O$  exchange for a wide variety of metal ions, as well as their classification, and, secondly, for outlining the now familiar three step-mechanism [16].

Yet another classical picture in coordination chemistry was shown for the first time at the Copenhagen Conference, *i.e.*, *J. Chatt's* platinum-ethylene orbital interaction diagramme (Fig. 5) [17].

The postulation of a rational bonding scheme for metal-olefin interactions, involving the donation of metal  $\pi$ -electrons, first outlined by *M.J.S. Dewar* in 1951 [18] (Fig. 6), opened the way for further advances in the field of  $\pi$ -complexes and marked a revival in the field of metal-olefin complexes.

In this context, it is appropriate to recollect that Pt-olefin complexes were well known in *Alfred Werner's* time [19] as work on *Zeise's* salt had been carried out in the early 1820ies and first published in 1827. Later Pt-olefin coordination chemistry had been extensively studied by *A.D. Gelman* in Leningrad (as it was then) during the forties and early fifties [20].

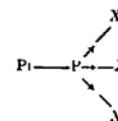
## THE CO-ORDINATE LINK IN CHEMISTRY

By Dr. J. CHATT

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EVIDENCE that the co-ordinate link may sometimes be represented more accurately by a double bond has been advanced by Phillips, Hunter and Sutton<sup>1</sup> to explain the observed low dipole moments and short interatomic distances in such substances as the phosphine oxides, and by Pauling<sup>2</sup> to explain the observed short interatomic distances in the metal carbonyls, nitrosyls and complex cyanides. That these effects are capable of other explanation has been shown by Wells<sup>3</sup>; yet on chemical grounds alone it appears that co-ordination occurs by two types of bond: (1) the classical co-ordinate link; and (2) a bond typified by the co-ordination of the olefines, for the formation of which it appears that *d* electrons from the metal as well as two electrons from the ligand are necessary.

In the platinumous complexes we have a  $\sigma$ -bond Pt-P, the classical co-ordinate link, formed by the combination of a filled  $3s3p^3$ -orbital of the phosphorus atom and a vacant  $5d$  orbital of the platinum atom, together with a  $\pi$ -bond formed by the overlap of a filled  $5d$ -orbital of the platinum atom and a vacant  $3d$ -orbital of the phosphorus atom. Thus the electrons for the  $\sigma$ -bond are supplied by the phosphorus atom and for the  $\pi$ -bond by the platinum atom; and as the electronegativity of X



increases, the drift of electrons forming the  $\pi$ -bond will partially neutralize the inductive effect of the atoms X. The availability of the lone-pair for  $\sigma$ -bond formation will thus not be impaired to the same extent as in the absence of a  $\pi$ -bond, so that in practice we find that the stability of the complex is not greatly affected by the electronegativity of X. In the boron series, where no *d*-electrons are available, we observe only the decreasing strength of the  $\sigma$ -bond as X increases in electronegativity from the stable tri-n-propyl phosphine complex through the weakly bound phosphorus trichloride complex, culminating in the complete disruption of the bond in such non-existent compounds as  $BF_3$ ,  $PF_3$ .

Fig. 3. J. Chatt's publication on  $\pi$ -bonding effects in complexes with phosphorus donors

# POTENTIOMETRISK UNDERSÖKNING AV NÅGRA KADMIUMSALTERS KOMPLEXITET

AKADEMISK AVHANDLING

SOM MED VEDERBÖRLIGT TILLSTÅND FÖR VINNANDE  
AV FILOSOFISK DOKTORSGRAD VID LUNDS UNIVERSITET  
KOMMER ATT TILL OFFENTLIG GRANSKNING FRAM-  
LÄGGAS Å KEMISKA INSTITUTIONENS FÖRELÄSNINGS-  
SAL FREDAGEN DEN 21 MAJ 1943 KL. 10 P. M.

AV

IDO LEDEN

FIL. LIC., III



L U N D

GLEERUPSKA UNIV.-BOKHANDELN

Fig. 4. The title page of I. Leden's thesis

However, it was only after 1953 that olefin complexes of practically all the transition elements were prepared and an extensive coordination chemistry of the acetylenes was developed.

At this point, it is appropriate to make a short digression from the presentation of organometallic chemistry and mention the discovery and study of the *trans*-effect and the work done by the Leningrad School of coordination chemistry. The founder of that school was *L.A. Chugaev* who introduced into Russia *Alfred Werner's* postulates. His ideas concerning 'the mutual

influence of atoms in molecules' led to the formulation of the *trans*-effect by his pupil *I.I. Chernyaev* [22].

The empirical rules of the *trans*-effect, elaborated by chemists of the Leningrad school, were rationalized by *A.A. Grinberg*, *B.W. Nekrassow* [23], and, later, by *J.K. Syrkin* [24]. Valuable physico-chemical data were also provided by *K.B. Jatzimirski* [25]. Furthermore, *Grinberg's* book summarized the state of knowledge in this area current in the late 40ies [23].

*Chat's* ideas on the *trans*-effect were also sketched out at the Copenhagen Con-

ference and were published two years later [26]. A similar explanation was independently provided by *L.E. Orgel* [27].

Going back to organometallic chemistry, where European chemists featured so prominently, one notes that the early developments in this field occurred mainly in two areas: the metal-carbonyl compounds and the compounds containing metals bonded to organic fragments.

At the time of the publication of *Alfred Werner's* fundamental paper, many metal-carbonyl compounds were known, the first group being *P. Schützenberger's* Pt-carbonyl halides, published in 1868 [28]. However, great activity in this area started with the work of *L. Mond* who described the preparation of Ni-carbonyl in 1890 [28], of Fe-carbonyl in 1891 [28] (also reported independently by *Berthelot*) and of the carbonyls of Co and Mo in 1910 [28].

However, soon after, the most significant discoveries in this area came from the (then) Technische Hochschule München. For three quarters of a century, a succession of very eminent coordination chemists pioneered not only the field of metal-carbonyl compounds (*W. Manchot* and *W.*

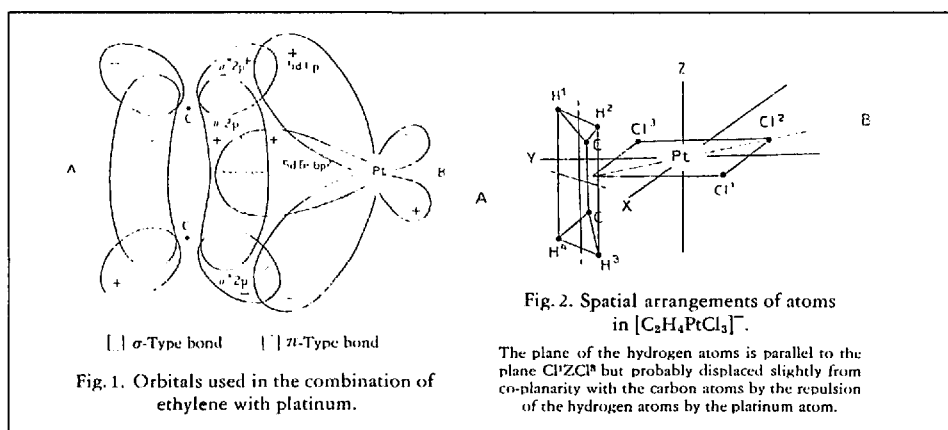


Fig. 5. The Pt-ethylene bonding scheme as presented at the Copenhagen Conference

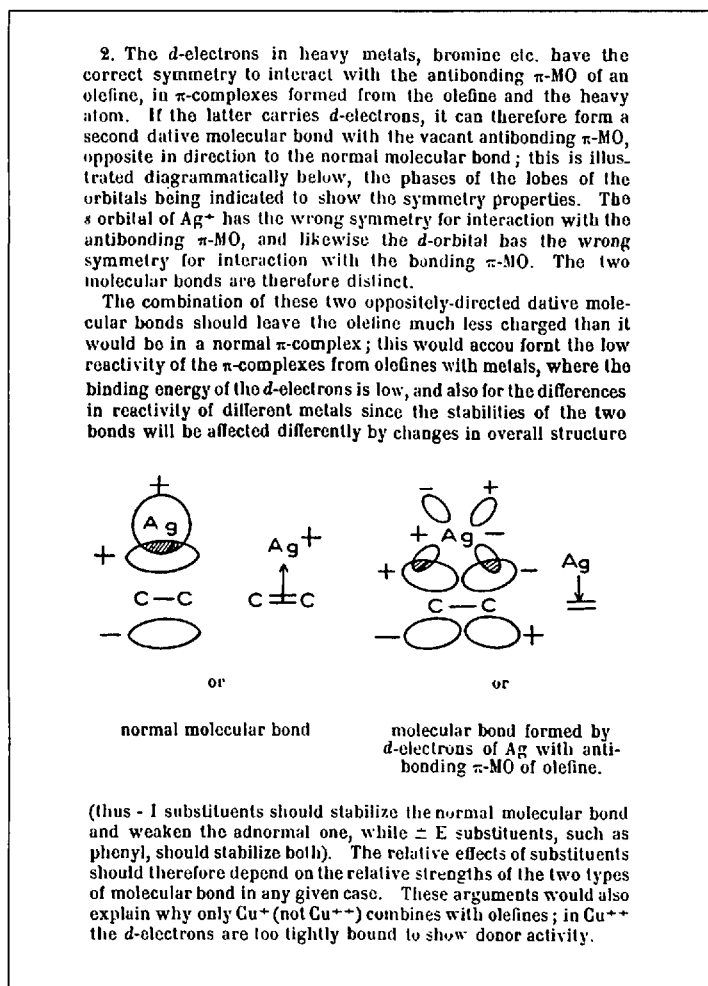


Fig. 6. M.J.S. Dewar's bonding scheme for silver olefin interactions

### Zur Frage eines Wolfram-Carbonyl-Carben-Komplexes

Von Prof. Dr. E. O. Fischer und Dipl.-Chem. A. Maasböl  
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Setzt man  $W(CO)_6$  unter Stickstoff in Äther mit  $LiC_6H_5$  um, so erhält man ohne Eliminierung von CO-Liganden durch nucleophile Addition ein orangegelbes, wasserlösliches, diamagnetisches Anion, das sich als Tetramethylammoniumsalz fällen läßt. Das orangefarbene, feinkristalline Produkt hat die Zusammensetzung  $[N(CH_3)_4][W(CO)_5COC_6H_5]$  Fp = 102,5 °C (Zers.). Das Anion ist mit Säuren protonierbar. Bei Versuchen, das beim Ansäuern entstehende, in Äther aufgenommene, freie „Hydrid“ zu isolieren, wurde nach Abziehen des Lösungsmittels nur  $W(CO)_6$  und Benzaldehyd beobachtet. Das in verdünnter Lösung stabile, protonierte Produkt läßt sich in guten Ausbeuten mit Diazomethan methylieren. Nach Chromatographie und Sublimation im Hochvakuum bei 45–50 °C isoliert man orangefarbene, diamagnetische, in organischen Medien gut lösliche Kristalle vom Fp = 59 °C. Analyse und Molekulargewichtsbestimmung belegen die Zusammensetzung  $W(CO)_5(COC_6H_5)(CH_3)$ .

In analoger Weise erhält man durch Addition von  $LiCH_3$  an  $W(CO)_6$  in Äther und durch Fällung als  $[N(CH_3)_4]$ -Salz aus wäßriger Lösung gelbes, diamagnetisches  $[N(CH_3)_4][W(CO)_5COCH_3]$  Fp = 143 °C. Sein Anion reagiert bei der Protonierung und anschließenden Methylierung mit  $CH_2N_2$  zu gelbem, diamagnetischem, flüchtigem  $W(CO)_5(COCH_3)(CH_3)$  vom Fp = 52 °C.

Fig. 7. E.O. Fischer's first publication on carbene complexes

## Katalytische Umsetzungen von Olefinen an Platinmetall-Verbindungen

### Das Consortium-Verfahren zur Herstellung von Acetaldehyd

Von Dr. J. SMIDT

zusammen mit Dr. W. HAFNER, Dr. R. JIRA, Dr. J. SEDLMEIER, Dr. R. SIEBER,  
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Consortium für elektrochemische Industrie GmbH., München

Es wird über einen neuen Weg der katalytischen Oxydation von Olefinen mit Platinmetall-Verbindungen berichtet. Mit Sauerstoff und Oxydationsüberträgern gelingt eine kontinuierliche, selektive Umsetzung zu Carbonyl-Verbindungen, die offensichtlich über Edelmetall-Olefin-Komplexe abläuft. Die Oxydation ist auch bei anderen ungesättigten Verbindungen möglich und eröffnet neue präparative Möglichkeiten. Die Methode ist Grundlage aussichtsreicher technischer Verfahren für die Herstellung von Carbonyl-Verbindungen aus niederen Olefinen, insbesondere von Acetaldehyd aus Äthylen.

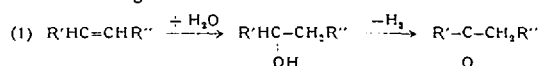
#### Einleitung

Über die Oxydation von Olefinen mit Sauerstoff zu Aldehyden und Ketonen wird seit mehreren Jahrzehnten berichtet. Das Problem hatte anfangs nur vereinzelte Forscher interessiert. Später und besonders in letzter Zeit wurde es wegen seiner zunehmenden wirtschaftlichen Bedeutung von einem weiteren Kreis, vornehmlich von Industrielaboratorien bearbeitet, da Olefine heute wohlfeile Rohstoffe sind.

Die chemische Technik verwendet für die Produktion der niederen Aldehyde und Ketone aus Olefinen mit gleicher Anzahl Kohlenstoffatome Verfahren mit zwei getrennten Reaktionsschritten:

1. Hydratisieren des Olefins zum Alkohol,

2. Dehydrieren oder Oxydieren des Alkohols zur Carbonyl-Verbindung.



Man hat sich vielfach bemüht, diese beiden Schritte in einem Verfahren zu vereinen; dazu geben technische und wirtschaftliche Gesichtspunkte genügend Anreiz. Es ist aber bis heute nicht gelungen, hierbei die gleich guten Ausbeuten wie bei den 2-Stufen-Verfahren zu erhalten.

Wir haben unsere Arbeiten auf dem Gebiet der Olefin-Oxydation, insbesondere der Oxydation von Äthylen, Ende 1956 aufgenommen. Nach entmutigenden Vorversuchen zeichnete sich bald die Möglichkeit ab, Olefine mit

Fig. 8. The first publication describing the Wacker process

Hieber [28]), but also to that of the metal-nitrosyl compounds (*Manchot* and *F. Seel* [29]), the cyano and acetylide complexes, particularly of metals in low oxidation states (*R. Nast* [30]) and last, but certainly not least, the metal  $\pi$ -complexes (*E.O. Fischer*, of whom more will be said later). Their contributions are such that it would not be possible to do justice to them in the available space. As mentioned earlier, the synthetic chemistry of the metal-carbonyl compounds was actively pursued by *Manchot*. However, our knowledge of this class of compounds and particularly of their reactivity comes mainly from the work of *Hieber* [28].

The discoveries in the field of metal-carbonyl chemistry in Germany had not passed unnoticed in industrial circles in that country and led to the development of important synthetic applications in the field of homogeneous catalysis. Prime among these discoveries are *O. Roelen's* hydroformylation reaction [31] and the *W. Reppe's* syntheses based on acetylene chemistry [32].

One of the most notable absents at the Copenhagen Conference was *E.O. Fischer*. Much could be said about the leading role he played in the field of metal-cyclopentadienyl complexes and related areas of coordination chemistry. As this work has

received ample recognition with the award of the Nobel Prize in 1973 [33], it is appropriate to single out here another series of studies that came out of his laboratory, *i.e.*, the coordination chemistry of the carbenes [34] (*Fig. 7*) and carbynes.

At this point, it is not inappropriate to reflect on the vagaries of fate concerning discoveries. Carbene complexes, albeit derived from isonitrile compounds, had been obtained by *Chugaev* in 1925 [35] and arene complexes by *F. Hein* in 1919 [36], but the chemists of that period lacked both the means for the full characterization of these compounds, and the basis for the theoretical interpretation of their bonding modes had yet to be developed. Is this still possible in coordination chemistry today?

In the context of developments in organometallic chemistry, it is worth recalling that it really became industrially relevant through the work of *K. Ziegler* and *G. Natta* in the field of olefin polymerization [37], recognized with the award of a Nobel Prize in 1963, and that of *G. Wilke* on a wide range of complexes and reactions of new types [38]. The achievements of *Ziegler* and *Wilke*, as well as many younger colleagues, have made the 'Max Planck Institute für Kohlenforschung' in Mülheim a 'temple' of organometallic and coordination chemistry.

Another example of an important industrial process based on organometallic coordination chemistry is the 'Wacker Process' [39] (*Fig. 8*).

Academic studies of organo-transition-metal compounds had also been taking place in England, *e.g.*, discovery of some stable gold- and platinum-alkyl derivatives by *W.J. Pope* [40].

However, further developments in this area had to wait for the realization that the formation of stable transition-metal compounds containing metal-carbon  $\sigma$ -bonds requires that the ordinary rules of coordination chemistry should be adhered to. Thus, following these principles *Chatt* prepared the first Pt<sup>II</sup>-alkyl compounds in the early fifties (these studies were extended later and first published in 1959) [41] and *G. Wilkinson* proceeded with remarkable speed in the field of the metal-cyclopentadienyl complexes [42]. The transatlantic race between *Fischer* and *Wilkinson* that followed became an all European effort with *Wilkinson's* move to London.

Talking about this early work, I wonder how many readers have actually seen *Keeley* and *Pauson's* 1951 Nature article [43] (*Fig. 9*)?

The realisation that the stability of ferrocene was connected with the '18-elec-

tron rule' opened the floodgates of synthetic organometallic chemistry: this rule and a simple *Hückel* MO model were used to guide the preparation of hundreds of compounds. A striking example of this approach was the theoretical prediction by *H.C. Longuet-Higgins* and *L.E. Orgel* of the stability of the cyclobutadiene complexes [44]. The preparation of the first compound was reported by *R. Criegee* and *G. Schroder* in 1959 [45].

While the organometallic tide was submerging coordination chemistry, other important preparative studies had been taking place, *i.e.*, those of the complexing properties of phosphorus and related donors. This was not a new area: *Alfred Werner* had devoted a short section of his book to this topic (*Fig. 10*) [46]. As can be seen, much of the work had been done in

French chemical laboratories, but it had been also actively pursued in Swedish laboratories since the times of *C.W. Blomstrand* and was continued by *K.A. Jensen* in Copenhagen [47].

However, the best known Schools of phosphorus and arsenic coordination chemistry had their origin in the Cambridge Laboratory of *W.J. Pope*. This topic was then pursued there by *F.G. Mann* [48] and moved to Australia with *G.J. Burrows*. From there it came back to England with *R.S. Nyholm*. It also established itself at the *Butterwick Research Laboratories* through *F.G. Mann's* former pupil *J. Chatt*.

Although *R.S. Nyholm* was the first to show the versatility of chelating diarsines for the stabilization of both low and high oxidation states of transition-metal com-

plexes [49], he will be mostly remembered for his profound belief in inorganic chemistry and the masterly way in which he 'spread the new gospel', *e.g.*, in his Inaugural Lecture at University College in 1956 for which he chose the title 'The Renaissance of Inorganic Chemistry' (*Fig. 11*) [50].

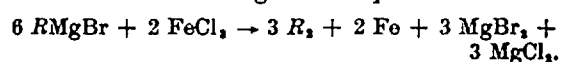
These developments were seminal for several other studies, *e.g.*, for the stabilization of very low oxidation states with triphenylphosphine by *L. Malatesta* [51], after his studies with isonitriles, and for the use of  $\text{PF}_3$  as a *pseudo*-CO donor by *Chatt* and by *Wilkinson* [52].

However, the most fruitful outcome of the coordination chemistry of phosphines was their use in homogeneous catalysis. A foremost example of this is *Wilkinson's* hydrogenation [53]. Subsequently, the use

### A New Type of Organo-Iron Compound

NUMEROUS investigators have studied the reaction of Grignard reagents with anhydrous ferric chloride, but have failed to isolate any organo-iron compounds or to produce any definite evidence for their formation in such reactions.

The statements by *Job and Reich*<sup>1</sup> and by *Champetier*<sup>2</sup>, that they have obtained stable ethereal solutions of compounds of the type  $\text{RFeI}$  by reaction of ferrous iodide with organo-zinc halides, are based solely on the formation of ferrous hydroxide on hydrolysis, and may be accounted for by the difference in solubility between ferrous and zinc hydroxides. Indeed, the evidence of *Champetier's* own experiments with Grignard reagents<sup>3</sup> suggests that such intermediates may be formed at low temperature, but are quite unstable above  $-40^\circ\text{C}$ . The normal reaction leads to reduction of the ferric salt and, with excess Grignard reagent, results in the formation of metallic iron according to the equation:



This reaction is of preparative value and has been shown to yield diphenyl from phenylmagnesium bromide in almost quantitative yield<sup>4</sup>.

As a possible route to 'fulvalene', we attempted to apply this reaction to *cyclopentadienylmagnesium bromide*. To a solution of this Grignard reagent (from 18 gm. ethyl bromide and 4 gm. magnesium in benzene with 11 gm. *cyclopentadiene*) was added an equivalent amount (9.05 gm.) of ferric chloride dissolved in anhydrous ether. After allowing the mixture to stand at room temperature overnight, it was refluxed (1 hr.) to ensure complete reaction, cooled and decomposed with ice-cold ammonium chloride solution in the usual manner. Evaporation of the dried organic layer yielded an orange solid (3.5 gm.). This was moderately soluble in ether, readily soluble in benzene and crystallized from methanol in large needles of melting point  $173\text{--}174^\circ\text{C}$ . (found: C, 64.6; H, 5.6; Fe, 30.1 per cent; molecular weight, by cryoscopic determination in benzene, 186.5.  $\text{C}_{10}\text{H}_{10}\text{Fe}$  requires: C, 64.6; H, 5.4; Fe, 30.0 per cent; molecular weight, 186.0). Iron was determined gravimetrically as  $\text{Fe}_2\text{O}_3$  after

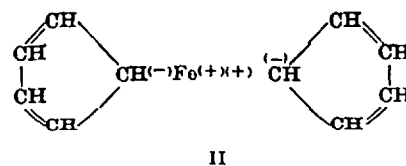
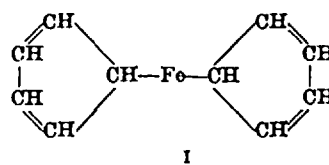
heating the compound with concentrated nitric acid under a reflux condenser.

The substance sublimes readily above  $100^\circ\text{C}$ . It is insoluble in, and apparently unattacked by, water, 10 per cent caustic soda and concentrated hydrochloric acid even at the boiling point. It dissolves in dilute nitric or concentrated sulphuric acid forming a deep red solution with strong blue fluorescence, but was partly recovered unchanged from the latter solution after standing at room temperature overnight.

The above analytical data leave no doubt that this compound is *dicyclopentadienyl iron* (I), formed according to the equation:



after initial reduction of the ferric salt by the Grignard reagent.



The remarkable stability of this substance is, of course, in sharp contrast to the failures of earlier workers to prepare similar compounds and must be attributed to the tendency of the *cyclopentadienyl* group to become 'aromatic' by acquisition of a negative charge, resulting in important contributions from the resonance form (II) and intermediate forms.

Our studies of this reaction and of other approaches to fulvalene are continuing.

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Aug. 7.

<sup>1</sup> *Job and Reich, C.R. Acad. Sci., Paris, 174, 1358 (1922).*

<sup>2</sup> *Champetier, Bull. Soc. chim. France, [4], 47, 1131 (1930).*

<sup>3</sup> *Gilman and Lichtenwalter, J. Amer. Chem. Soc., 61, 957 (1939).*

<sup>4</sup> *Brown, Nature, 165, 568 (1950).*

Fig. 9. Kealy and Pauson's 1951 Nature publication



Raman spectroscopy to coordination compounds.

Other Italian contributions which must be remembered are those of *L. Cambi* in the fields of metal-nitrosyl compounds [60] and sulfur coordination chemistry and of *P. Chini* whose name is particularly associated with transition-metal cluster chemistry [61]. The elegance of some of the polymetallic species produced in his laboratory borders on the artistic.

One important field remains to be mentioned: bioinorganic chemistry. Two European chemists stand out in particular in this area: its 'founder', *H. Erlenmeyer*, who published his first paper on this topic in 1951 [62] (*Fig. 12*) and *R.J.P. Williams* who is mainly responsible for giving it its 'new look' [63].

Last but not least, the progress of chemistry in general, and of coordination chemistry in particular, has been strongly linked to the development of physical techniques for the study of the constitution of known compounds. The spectroscopic work done by *J.-P. Mathieu* was mentioned earlier. However, the foremost European among such chemists was *W. Klemm*. His magnetochemical studies [64] provided a fundamental criterion for the classification of coordination compounds. He will also be remembered for the preparation of oxometallates and fluoro complexes with metals in very high oxidation states [65]. Furthermore, the availability of visible-UV spectrophotometers allowed the recording of innumerable spectra of coordination compounds, providing the experimental basis for the development of ligand field theory. Here the contributions made by *C.K. Jørgensen* [66] cannot go unacknowledged.

In conclusion, it is clear that during the last 40 coordination chemistry has been particularly exciting. Let us hope that the younger generation will be able to say the same of the next 40.

Obviously, an account of this type can only be incomplete and, therefore, the author should like to offer apologies for omitting numerous contributions which many readers may consider as being more fundamental than those mentioned above. Please attribute this to personal bias: a veteran of the coordination chemistry scene could not have remained uninfluenced by the events which came closest to his professional life!

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