

MODERN INORGANIC SYNTHESIS

J. C. BAILAR, JR.

University of Illinois, Urbana, Illinois, U.S.A.

Inorganic chemistry covers such a wide variety of compounds and of bond types that it is a formidable undertaking to attempt to discuss methods of inorganic synthesis in a single lecture. Inorganic compounds range in bond type from the purely ionic to the purely covalent, and even a single "central atom" can vary widely in electronegativity and in oxidation state. Some compounds can be made in aqueous solution, whereas others are destroyed by traces of water; some exist only at low temperatures, and others can be formed only at very high temperatures. It is not possible here to outline methods of preparation for all of the types of inorganic compounds, and we must content ourselves with a survey of a few developments that have taken place in recent years.

A century ago, it was widely believed that each element, in its compounds, could show but a single oxidation state; this hypothesis was reluctantly abandoned as examples which could not be fitted into the pattern multiplied. With the advent of the electronic theory of valency, it was generally recognized that the transition metals and elements with one or more unshared pairs of electrons would be expected to show a range of oxidation states. There was a reluctance on the part of most chemists, however, to accept the fact that a transition metal which does not have too many electrons in the outer shells might show as many oxidation states as it has electrons in the $(n-1)d$ plus the ns shells. Recent researches on coordination compounds of the transition metals have done a good deal to dispel this reluctance, for it has been found that in union with coordinating agents which tend to π bond, and with which there is a large measure of "back bonding", a metal will show only low oxidation states, whereas with ligands which are highly electronegative, it tends to achieve high oxidation states. Coordinating agents which contain resonating systems in which electrons can "hide", allow both low and high oxidation states. Thus, by proper selection of the ligand, compounds may be prepared in which the metal (formally, at least) shows a wide variety of consecutive oxidation states, and a corresponding variety of magnetic and spectral properties. Whether one is justified in assigning the electrons to the metal, or to any one part of the complex, is doubtful, but by custom, it is considered that carbon monoxide and dipyriddy carry no charge, even in their complexes, and that a complexed fluoride or hydroxide ion still carries a charge of -1 .

Many years ago, Scholder¹ demonstrated that transition metals frequently achieve unusually high oxidation states when coordinated to hydroxo or oxo groups. Even before his time, this principle had been used in the preparation of chromates, manganates, and the less well-known ferrates. Klemm and his students have extended this work, and have also used fluoride in

place of oxide². Many of the metals which show a coordination number of four toward the oxo group show a coordination number of six towards the fluoro group, and a wide variety of complexes MF_6^{z-} has been formed. In the oxo series, the oxidation state of a metal may be determined by the tendency to form ions of the type MO_4^{z-} , and in the fluoro series, by the stability of the octahedral structure MF_6^{z-} . Experimentally, Klemm has mixed alkali metal salts and transition metal salts in various stoichiometric ratios, and has treated the mixtures with fluorine at elevated temperatures. In many cases, the resulting materials are compounds of the composition M'_xMF_6 . (M' is an alkali metal—the stabilities of the resultant compounds increase as M' is changed from Li to Na to K). The structures of these complexes have been established by X-ray analysis and by magnetic measurements. Some typical compounds which are formed in this way are shown in *Table 1*.

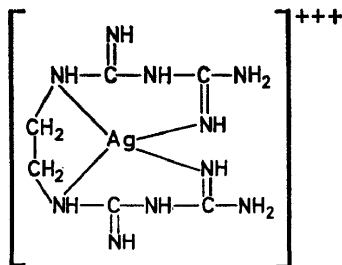
Table 1. Some fluoro complexes

| | | |
|-------------------|----------------------------------|---------------------------------|
| KReF ₆ | K ₂ TiF ₆ | K ₃ MnF ₆ |
| KRuF ₆ | K ₂ VF ₆ | K ₃ CoF ₆ |
| KOsF ₆ | K ₂ CrF ₆ | K ₃ NiF ₆ |
| KIrF ₆ | Cs ₂ CoF ₆ | K ₃ CuF ₆ |
| | K ₂ NiF ₆ | |

Metals which preferentially show a coordination number of four rather than six may also exhibit oxidation states higher than they usually show, as is exemplified by the formation of the compound $KAgF_4$.

All the fluoro compounds which are listed in *Table 1* are highly coloured crystalline solids, which are sensitive to moisture, and which have strong oxidizing properties.

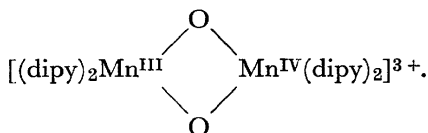
Other ligands which stabilize high oxidation states are the biguanides. For example, Rây *et al.*^{3, 4} prepared an extremely stable silver(III) complex of ethylenebisbiguanide, the formula of which Rây writes as:



This is obtained simply by mixing aqueous solutions of silver nitrate, ethylenebisbiguanide, and potassium peroxydisulphate. The magnetic properties of this salt are consistent with the assumption that it contains trivalent silver.

α, α -Dipyridyl is a coordinating ligand which stabilizes the existence of both

high and low oxidation states. Treatment of a mixture of silver ion and dipyriddy with peroxy sulphate in aqueous solution allows the formation of the stable, green $[\text{Ag}^{\text{II}}(\text{dipy})_2]\text{S}_2\text{O}_8$, from which the peroxy sulphate anion can be eliminated by metathesis with other salts. Similarly, a mixture of manganese sulphate and dipyriddy, upon treatment with peroxy sulphate, gives greenish-black crystals which contain both $\text{Mn}(\text{III})$ and $\text{Mn}(\text{IV})$ ⁵. These are supposedly:



On the other hand, coordination with dipyriddy frequently facilitates the reduction of metals to unusually low oxidation states, as is illustrated by the work of Herzog and others. Herzog has shown that when a suspension of dry chromium(II) bromide in a solution of tetrahydrofuran is shaken with metallic sodium, deeply coloured solutions are formed, from which black crystals of $[\text{Cr}(\text{dipy})_3]^0$ separate⁶⁻¹⁰. The covalent character of this material is attested by its volatility and by its solubility in non-polar solvents, such as benzene. It is insoluble in, and unreactive towards, water.

During the reduction of the chromium from the +3 state to the zero state, the metal passes through the +2 and +1 states. The latter seems to be formed with surprising ease, for the tetrahydrofuran suspension of $[\text{Cr}(\text{dipy})_3]\text{Br}_2$ has the blue colour of the $[\text{Cr}(\text{dipy})_3]^{\text{+1}}$ ion, formed by disproportionation, even before the addition of the reducing agent.

The interconversions between the different oxidation states in these chromium-dipyriddy complexes are readily reversible, and Herzog has shown that when solutions containing equivalent amounts of the red $[\text{Cr}(\text{dipy})_3]^0$ and yellow $[\text{Cr}(\text{dipy})_3]^{\text{+2}}$ are mixed, blue $[\text{Cr}(\text{dipy})_3]^{\text{+1}}$ is formed.

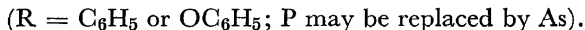
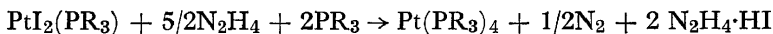
Similarly, Herzog has shown that $[\text{V}(\text{dipy})_3]^{\text{+2}}$ can be reduced, step by step, to $[\text{V}(\text{dipy})_3]^-$, in which the metal, formally at least, is in the -1 oxidation state^{11, 12}. The reduction of $[\text{V}(\text{dipy})_3]^{\text{+2}}$ to $[\text{V}(\text{dipy})_3]^0$ takes place with surprising ease, being effected by magnesium powder in 50 per cent methanol. The reduction of the non-ionic complex to the -1 stage requires a powerful reducing agent (lithium aluminium hydride, in suspension in tetrahydrofuran) but the reaction proceeds essentially quantitatively, $\text{Li}[\text{V}(\text{dipy})_3] \cdot 4\text{THF}$ separating from the solution as very dark coloured crystals. It is interesting that the V(I), 0, and (-1) complexes have the same colours as the isoelectronic chromium complexes—red, blue, and red, respectively. In the vanadium series, as with the chromium complexes, the steps of the reduction are readily reversible, and Herzog has shown that the $[\text{V}(\text{dipy})_3]^-$ ion can be oxidized stepwise by the addition of iodine, until $[\text{V}(\text{dipy})_3]^{\text{+2}}$ is formed. The addition of more iodine does not oxidize the vanadium further, but gives a polyiodide.

The anionic vanadium (-I) dipyriddy complex is particularly interesting, but it is not unique, for Herzog and his colleagues have isolated corresponding (-I) compounds of manganese and titanium.

Zerovalent dipyridyl complexes have been formed for metals of wide variety. Lithium forms both $\text{Li}(\text{dipy}) \cdot \text{dioxan}$ and $\text{Li}_2(\text{dipy})_2\text{THF}$, but in no other case are two atoms of metal known to be attached to a single dipyridyl molecule. Light metals such as beryllium and magnesium show a coordination number of four, attaching themselves to two dipyridyl molecules. Most of the heavier metals show a coordination number of six, and uranium, of eight¹⁰. All of the complexes must be handled in the complete absence of air, so experimental work with them is tedious and slow. In the solid state, some of them, at least, are pyrophoric.

Waind and Martin¹³ have used a different approach in studying the dipyridyl complexes. They reduced $[\text{Co}(\text{dipy})_3]^{+++}$ polarographically and showed that both $[\text{Co}(\text{dipy})_3]^{++}$ and $[\text{Co}(\text{dipy})_3]^+$ were formed. Having demonstrated the stability of these species, they isolated each of them, as the perchlorate salts. The divalent ion is obtained by mixing a solution of cobalt(II) with dipyridyl. It is readily converted to the trivalent ion by mild oxidizing agents such as iodine, or air. The monovalent ion is obtained by reduction of either of the others by sodium amalgam.

Among the complexing agents that seem to always stabilize low valence states, the classic examples are carbon monoxide and the olefins, which will be discussed in a slightly different connection a little later. But these are no longer exceptional cases. A large number of isonitrile complexes containing metals in very low oxidation state have been obtained, and it has been known for some years that phosphorus trihalides will displace carbon monoxide from nickel carbonyl to form $\text{Ni}(\text{PX}_3)_4$. Malatesta and Cariello¹⁴ have reported the similar reaction:



These zerovalent platinum compounds are soluble in benzene and chloroform, but only slightly so in alcohols. Surprisingly, they are stable in the air. If one does not use an excess of ligand in the preparation, $\text{Pt}(\text{PR}_3)_3$ is formed instead of $\text{Pt}(\text{PR}_3)_4$. This is also stable in the air.

Closely related to the compounds containing metals of low oxidation state are those containing complexed hydridic hydrogen. Our knowledge of these is due chiefly to Chatt and his colleagues. If stable hydrido complexes are to be obtained, it is essential that the nature of the metal in the complex be modified by the presence of suitable chelating groups. In most cases, it is also essential that a reducing agent be present to generate the hydrogen. For example, the action of hydrazine on $(\text{P}\phi_3)_2 \text{PtCl}_2$ gives a good yield of $(\text{P}\phi_3)_2 \text{PtHCl}$, which is a white, crystalline compound, quite stable toward air and moisture. It is known in both *cis* and *trans* forms^{15,16}. Shaw and Chatt have synthesized a series of ruthenium and iridium hydrido complexes, using only ethanol as the reducing agent¹⁷. Thus, $\text{Ir}(\text{PEt}_2\phi)_3\text{Cl}_3$, when treated with potassium hydroxide in ethanolic solution, gives first $\text{Ir}(\text{PR}_3)_3\text{HCl}_2$, and then $\text{Ir}(\text{PR}_3)_3\text{H}_2\text{Cl}$. In a solution of potassium hydroxide in hot $\text{CH}_3\text{OCH}_2\text{CH}_2\text{-OH}$, the dihydrido complex may be reduced to the trihydride, $\text{Ir}(\text{PR}_3)_3\text{H}_3$.

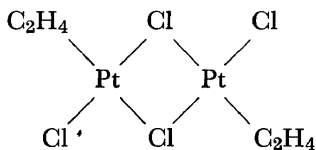
Under some conditions, the alcohol is both oxidized and reduced, and a carbonyl hydrido complex is formed. Thus, an ethanolic solution of potassium hydroxide and $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\phi)_6]\text{Cl}$ yields $[\text{Ru}(\text{PR}_3)_3(\text{CO})_2\text{H}]$ and methane.

In connection with the hydrido complexes, the work of Vaska and DiLuzio¹⁸ is particularly significant. They have shown that $[\text{Ir}(\text{P}\phi_3)_2\text{COCl}]$, dissolved in benzene, absorbs hydrogen gas to give $[\text{Ir}(\text{P}\phi_3)_2\text{COH}_2\text{Cl}]$, the iridium being oxidized from the + I to the + III state, and at the same time, being changed in coordination number from four to six. The dihydrido complex is stable in the air, but is light sensitive when exposed to air. Upon treatment of the dihydrido complex with hydrochloric acid, the two hydrido groups are replaced by chloride, the first one fairly readily, but the second only with difficulty. In this connection, it is worthy of note that Vaska¹⁹ has found that $\text{Ir}(\text{PR}_3)_2\text{COCl}$ will also add oxygen to give the peroxo complex $\text{Ir}(\text{PR}_3)_2\text{COClO}_2$, from which the oxygen is released upon heating. All of these compounds are readily prepared, and are quite stable.

Just as adjustment of the properties of a heavy metal by suitable coordination facilitates the formation of hydrido complexes, it also makes possible the formation of some remarkable organometallic compounds. Thus, Closson, Kozikowski, and Coffield²⁰ have synthesized the remarkable compound $\text{CH}_3\text{Mn}(\text{CO})_5$ by the action of methyl iodide on sodium manganese carbonyl, dissolved in tetrahydrofuran. They also observed that tetrahydrofuran solutions of sodium manganese carbonyl and acetyl chloride react to give $\text{CH}_3\text{COMn}(\text{CO})_5$, which in turn, can be converted to methyl manganese carbonyl by heating. The latter reaction is reversible, for under a pressure of 35 atm of carbon monoxide, methyl manganese carbonyl is converted to the acetyl compound. This "insertion reaction" furnishes a basis for many important catalytic processes. Cobalt octacarbonyl has been used in such reactions more extensively than has the manganese compound, for it is easier to obtain, and more stable. Methyl cobalt carbonyl, $\text{CH}_3\text{Co}(\text{CO})_4$ is prepared by the action of methanol on $\text{HCo}(\text{CO})_4$. Upon treatment with carbon monoxide, under pressure, it is converted to the acetyl derivative, which can, in turn, be hydrogenated to give any of a variety of products, *e.g.*, ethane, ethanol, and acetaldehyde. The parent compound $\text{HCo}(\text{CO})_4$, upon carbonylation and hydrogenation, gives methanol, formaldehyde or $\text{CH}_3\text{Co}(\text{CO})_4$, depending upon the temperature and pressure. These reactions are the basis of the Fischer-Tropsch synthesis.

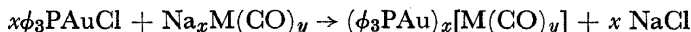
There are many other examples of metal-organic compounds, but time does not permit a discussion of them here. One can only mention the cyclopentadiene complexes, the benzene-chromium complex and its analogues, and the remarkable compounds formed in the Ziegler-Natta catalytic polymerizations.

The first metal-olefin complexes were prepared almost a century and a half ago, but they were very poorly understood until recent years, when modern valence theory threw new light upon them. Three types of these complexes have long been known: (i) Salt-like complexes, exemplified by Zeise's salt, $\text{K}[\text{PtC}_2\text{H}_4\text{Cl}_3]$. These are soluble in water, and are slowly hydrolysed by it to give a variety of products including acetaldehyde. (ii) Dinuclear complexes, such as:



These are soluble in non-polar solvents, but insoluble in water. (iii) Non-ionic, mononuclear complexes, such as $[\text{PtCl}_2\text{QC}_2\text{H}_4]$, where Q represents a molecule of quinoline or similar nitrogen base. As might be expected, these, too, are soluble in non-polar solvents. In recent years, several new types have been synthesized. For example, it has been shown that a diolefin can link itself to either one atom of metal, forming a sort of chelate ring, as exemplified by $\text{PdCl}_2\text{C}_4\text{H}_6$, or to two metal atoms to give a compound such as $\text{K}_2[\text{Cl}_3\text{PtC}_4\text{H}_6\text{PtCl}_3]$. Nearly all of these are crystalline compounds which show little tendency to rearrange to polyolefins.

Another example of the profound effect which coordination produces on the properties of metals is furnished by the syntheses of compounds containing metal-metal bonds. Until recent years, such substances were thought to be rare, but it is now known that under proper conditions, a great variety of them can be prepared. Nyholm, Coffey, and Lewis²¹ have suggested that the metal atoms must be in a low oxidation state, that each should have an odd number of spin-paired electrons (d^5 , d^7 , d^9 or d^{10s-1}), and that they should be attached to ligands which are not too highly electronegative. In the well-known dimeric carbonyls $\text{Co}_2(\text{CO})_8$ and $\text{Mn}_2(\text{CO})_{10}$, these conditions are fulfilled. They are also fulfilled in the interesting gold compounds $\phi_3\text{PAu}[\text{Mn}(\text{CO})_5]$, $(\phi_3\text{PAu})_2[\text{Fe}(\text{CO})_4]$ and $\phi_3\text{PAu}[\text{Co}(\text{CO})_4]$, all of which are readily synthesized, in non-polar media, by the reaction



Most of these gold compounds are stable towards light, air, and water, but are destroyed by acids and oxidizing agents. The tin compound, $\phi_3\text{Sn}[\text{Mn}(\text{CO})_5]$ which is structurally related to $\phi_3\text{PAu}[\text{Mn}(\text{CO})_5]$, is remarkably stable; treatment with chlorine does not rupture the metal-metal bond, but gives $\text{Cl}_3\text{Sn}[\text{Mn}(\text{CO})_5]$ and chlorobenzene²².

The recently discovered complex $[\text{Pt}(\text{SnCl}_3)_5]^{-3}$ has been shown²³ to contain platinum-tin bonds, and, by analogy, it is believed that $(\phi_3\text{P})_2\text{Pt}(\text{SnCl}_3)\text{Cl}$ and $(\phi_3\text{P})_2\text{Pd}(\text{SnCl}_3)\text{Cl}$ do also. All of these complexes have the remarkable property of catalysing the hydrogenation of two, but only two, of the three double bonds in linolenic esters and in cyclooctatriene²⁴. In each case, they are virtually without effect on the third double bond. With linoleic esters, the phosphine complexes catalyse the hydrogenation of one of the double bonds, but not the second. These complexes are readily obtained as crystalline solids by the addition of tin(II) chloride to solutions of $(\phi_3\text{P})_2\text{PtCl}_2$ or $(\phi_3\text{P})_2\text{PdCl}_2$ in a mixture of benzene and methanol. However, the metal-metal bonds in them are evidently not very strong, for the complexes are obtained only if a large excess of tin(II) chloride is present in the solution. It is suggested that the complex forms a sort of chelate ring, by attachment of two double bonds to the two metals. One of the double bonds (probably the one attached to the platinum) is activated by this union and

can be hydrogenated, whereupon the ring is broken. This process can be repeated, but when only one double bond remains, ring formation is no longer possible, and the catalytic function is lost.

The commercially important tin–nickel plating bath may also contain a complex containing a metal–metal bond, but there is, as yet, no experimental evidence of this. A solution containing Sn^{2+} and Ni^{2+} gives, upon electrolysis, a plate containing a disproportionate amount of tin, for the reduction potential of tin is much lower than that of nickel. If, however, the bath contains an excess of fluoride ion, the composition of the plate is relatively independent of the ratio of the concentrations of the metal ions in the bath, and approximates 1:1²⁵. There is much evidence to support the belief that the metals are contained in a 1:1 complex, but little evidence on the nature of the complex.

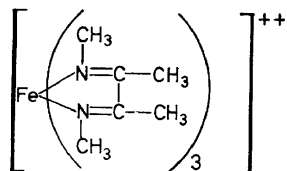
A final example of the effect of ligands on the properties of metals may be found in the nature of thiocyanate complexes. Metals of the first transition series usually attach themselves to the thiocyanate group through the nitrogen atom, while heavier metals attach themselves to the sulphur atom. Chemists have long speculated whether there might not be a metal, which, under suitable conditions, could attach itself in either way. It remained for Basolo *et al.*^{26, 27} to demonstrate that, when in union with suitable ligands, palladium behaves in this way. They reasoned that strong π -electron acceptors should make the *d*-electrons of the metal less available for donation to the thiocyanate group, and thus decrease or remove the source of the additional stability of the metal–sulphur bond. They were able to isolate both kinds of linkage isomers of $\text{Pd}(\text{AsR}_3)_2\text{X}_2$ and $\text{Pd}(\text{dipy})\text{X}_2$. They also showed that both steric and electronic factors are important, for spectral evidence indicates that $[\text{Pd NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2 \text{SCN}]^+$ contains a metal–sulphur bond, whereas $[\text{Pd}(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2\text{NCS}]^+$ contains a metal–nitrogen bond. The ligands would be expected to produce approximately the same electronic effects, so it is believed that in this case, the difference is steric. The angular M–SCN group would have a much larger steric requirement than the linear M–NCS group.

In the field of coordination chemistry, there is a great need for improved methods of preparing compounds of known configuration. In this respect, our knowledge of the chemistry of platinum is far more advanced than that of the other metals, chiefly due to the work of the Russian inorganic chemists. Some fine synthetic work has been done by Essen *et al.*^{28–32} on the preparation of platinum(IV) compounds of known configuration. They have isolated five of the 15 racemic forms of $\text{Pt}(\text{py})\text{NH}_3(\text{NO}_2)\text{IClBr}$. They first formed square planar platinum(II) complexes of known configuration, and then oxidized these to the platinum(IV) compounds, simultaneously increasing the coordination number of the platinum to six. In forming the desired planar isomers, the investigators depended upon the *trans* effect. The principle is not new, but the handling of the reactions to give reasonable yields of the selected isomers was of the highest order of excellence.

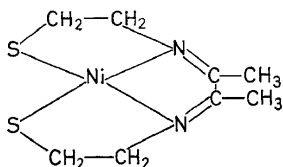
In synthesizing complexes of the other transition metals, there are as yet few guiding principles. It is well established that a chelating ligand must occupy *cis* positions, so replacement of such a ligand may give a *cis* complex, especially if the replacement takes place under very mild conditions, or in

the solid state. However, in the chemistry of the lighter transition metals, rearrangements are common and the configuration of the product of a replacement reaction is not certain.

The work of Busch³³ on the use of chemical "templates" also deserves mention. Busch has, for example, shown that although methylamine and diacetyl normally react to give polymeric materials, in the presence of iron(II) ions, they form the monomeric complex:

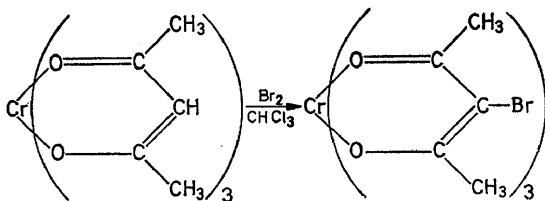


Similarly, $\text{NH}_2\text{CH}_2\text{CH}_2\text{SH}$ normally reacts with diacetyl to give mercaptals and thiazolines, but in the presence of nickel(II) ion, the product is:

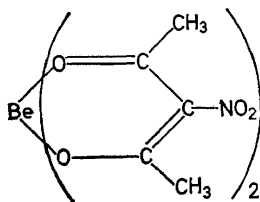


It is believed that in these and similar cases, the metal ion tends to hold the reactive groups in the proper position to react in the desired way.

In connection with the reactions of coordinated ligands, the work of Collman, *et al.*³⁴⁻⁴² also deserves mention. They have demonstrated that the chelate rings formed by 1,3-diketones have quasi-aromatic character, and can be brominated, acetylated and nitrated. For example:



The fact that the chelate ring is not fully aromatic is indicated by the failure of the brominated complex to undergo the Grignard reaction. However, Klein and Bailar⁴³ have shown that the nitro groups in bis-(3-nitro-2,4-pentanediono)-beryllium:



can be reduced, and that the resulting amine has at least some of the characteristic properties of organic amines.

Many other topics deserve mention in a paper of this sort, but have been omitted for lack of time. These would include the nitrogen-phosphorus polymers, the coordination polymers, the hydrides of boron, the compounds of the rare gases, the use of new reagents such as lithium boron hydride and lithium aluminium hydride, and the many improvements that have been made in techniques which are useful in synthetic work.

Inorganic synthesis has suffered badly because of the tendency of inorganic chemists to work empirically rather than to utilize the basic principles. In the newer fields of synthesis, such as the boron hydrides and the molecular sieves, physical principles have been used, and rapid progress has been made. In many of the older fields, on the other hand, the empirical methods and ideas of a generation ago have still not been replaced, and progress has lagged. For confirmation of this, one need only examine the syntheses of some of the "Werner complexes". This is a field which is badly neglected, and the study of which can yield rich returns.

References

- ¹ R. Scholder. Many papers, especially during the years 1952-1956, but extending to the present time.
- ^{2a} W. Klemm. *J. Inorg. Nucl. Chem.* **8**, 532 (1958)
- ^{2b} W. Klemm, J. Krause, K. Wahl, E. Huss, R. Hoppe, E. Weiss, and W. Brandt. *Forschungsber. Wirtsch. Verkehrsministeriums Nordrhein-Westfalen No. 160* (1955).
- ^{2c} W. Klemm. *Arbeitseinschicht Forsch. Landes Nordrhein-Westfalen No. 75*, 7 (1957).
- ^{2d} W. Liebe, E. Weise, and W. Klemm. *Z. anorg. allgem. Chem.* **311**, 281 (1961).
- ³ P. Rây, and K. Chakravarty. *J. Indian Chem. Soc.* **21**, 47 (1944).
- ⁴ D. Sen, N. N. Ghosh, and P. Rây. *J. Indian Chem. Soc.* **27**, 619 (1950).
- ⁵ R. S. Nyholm and A. Turco. *Chem. Ind. (London)* **1960**, 74.
- ⁶ S. Herzog. *J. Inorg. Nucl. Chem.* **8**, 557 (1958).
- ⁷ S. Herzog and W. Schön. *Z. anorg. allgem. Chem.* **297**, 323 (1958).
- ⁸ S. Herzog, K. Ch. Renner, and W. Schön. *Z. Naturforsch.* **12b**, 809 (1957).
- ⁹ S. Herzog and K. Ch. Renner. *Chem. Ber.* **92**, 872 (1959).
- ¹⁰ S. Herzog and W. Taube. *Z. Chem.* **2**, 208 (1962).
- ¹¹ S. Herzog and W. Taube. *Naturwiss.* **43**, 349 (1956).
- ¹² S. Herzog. *Z. anorg. allgem. Chem.* **294**, 160 (1958).
- ¹³ G. Waind and B. Martin. *J. Inorg. Nucl. Chem.* **8**, 551 (1958).
- ¹⁴ L. Malatesta and C. Cariello. *J. Inorg. Nucl. Chem.* **8**, 561 (1958).
- ¹⁵ J. Chatt and B. L. Shaw. *J. Chem. Soc.* **1962**, 5082.
- ¹⁶ J. C. Bailar, Jr. and H. Itatani. *Inorg. Chem.*, **4**, 1618 (1965).
- ¹⁷ B. L. Shaw and J. Chatt. Proceedings VII International Conference on Coordination Chemistry, Stockholm and Uppsala, p. 293 (1962).
- ¹⁸ L. Vaska and J. W. DiLuzio. *J. Am. Chem. Soc.* **84**, 679 (1962).
- ¹⁹ L. Vaska. *Science* **140**, 809 (1963).
- ²⁰ R. D. Closson, J. Kozikowski, and T. H. Coffield. *J. Org. Chem.* **22**, 598 (1957).
- ²¹ R. S. Nyholm, E. Coffey and J. Lewis. Proceedings VII International Conference on Coordination Chemistry, Stockholm and Uppsala, p. 66 (1962).

J. C. BAILAR, Jr.

- ²² R. D. Gorsich. *J. Am. Chem. Soc.* **84**, 2486 (1962).
- ²³ R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg. *J. Am. Chem. Soc.* **87**, 658 (1965).
- ²⁴ J. C. Bailar, Jr. and H. Itatani. In the press; J. C. Bailar, Jr. and H. Tayin. Unpublished work.
- ²⁵ J. W. Cuthbertson, N. Parkinson, and H. P. Rooksby. *J. Electrochem. Soc.* **100**, 107 (1954).
- ²⁶ F. Basolo, W. H. Baddley, and J. L. Burmeister. *Inorg. Chem.* **3**, 1202 (1964).
- ²⁷ J. L. Burmeister, and F. Basolo. *Inorg. Chem.* **3**, 1587 (1964).
- ²⁸ A. D. Gel'man, and L. N. Essen. *Dokl. Akad. Nauk SSSR*, **75**, 693 (1950).
- ²⁹ L. N. Essen, and A. D. Gel'man. *Proc. Acad. Sci. USSR, Chem. Sec.* **108**, 309 (1956).
- ³⁰ L. N. Essen, and A. D. Gel'man. *Zh. Neorg. Khim.* **1**, 2475 (1956).
- ³¹ L. N. Essen, F. A. Zakharova, and A. D. Gel'man. *Zh. Neorg. Khim.* **3**, 2654 (1958).
- ³² L. N. Essen, and D. P. Alekseeva. *Zh. Neorg. Khim.* **6**, 857 (1961).
- ³³ D. H. Busch. *Advan. Chem. Ser.* **37**, 1 (1963).
- ³⁴ J. P. Collman, R. A. Moss, S. D. Goldby, and W. S. Trahanovsky. *Chem. Ind. (London)* **1960**, 1213.
- ³⁵ J. P. Collman, R. A. Moss, H. Maltz, and C. Heindel. *J. Am. Chem. Soc.* **83**, 531 (1961).
- ³⁶ J. P. Collman, and E. T. Kittleman. *J. Am. Chem. Soc.* **83**, 3529 (1961).
- ³⁷ J. P. Collman, R. L. Marshall, W. L. Young, and S. D. Goldby. *Inorg. Chem.* **1**, 704 (1962).
- ³⁸ J. P. Collman. *Advan. Chem. Ser.* **37**, 78 (1963).
- ³⁹ J. P. Collman, R. P. Blair, R. L. Marshall, and A. L. Slade. *Inorg. Chem.* **2**, 576 (1963).
- ⁴⁰ J. P. Collman, R. L. Marshall, W. L. Young, and C. T. Sears, Jr. *J. Org. Chem.* **28**, 1449 (1963).
- ⁴¹ J. P. Collman, *Inorg. Syn.* **7**, 134 (1963).
- ⁴² J. P. Collman, and W. L. Young. *Inorg. Syn.* **7**, 205 (1963).
- ⁴³ R. M. Klein, and J. C. Bailar, Jr. *Inorg. Chem.* **2**, 1187, 1190 (1963).