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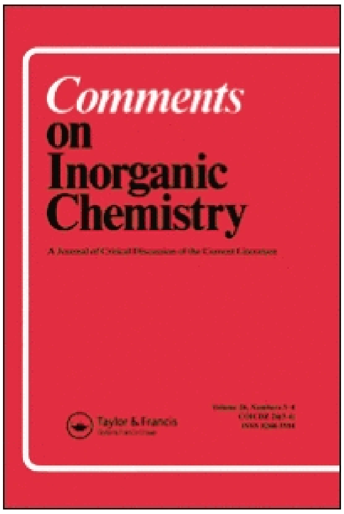

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Low and High Oxidation States in Organometallic Chemistry

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Low and High Oxidation States in Organometallic Chemistry

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A total of 14,000 organometallic compounds synthesized and characterized up to a few years ago are listed in the "Dictionary of Organometallic Chemistry," while the properties and chemistry of these compounds are described on 8,500 printed pages of "Comprehensive Organometallic Chemistry" edited in 1984. Why has there been ever-increasing worldwide activity in organometallic chemistry since the days when ferrocene showed up in the literature? More importantly, what appear to be the future main lines of research and to which goals should we dedicate our efforts? This Comment,[1] based on a historical background, endeavors to exemplify the present status of organometallic chemistry within the spectrum of the neighboring disciplines of chemistry. By virtue of several examples of the author's scientific interests, one particular area of research will be discussed that has largely been neglected in organometallic chemistry up to the present.

Key Words: *organometallic chemistry of rhenium, history, metal–carbon bonds, trends*

I. FROM "CACODYL" TO FERROCENE

When Mr. Cadet de Gassicourt, a military pharmacist in Paris, had his "fuming arsenical liquid" ("Alkarsin," "cacodyl," $(CH_3)_4As_2$)

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as the very first "organometallic" compound in hand,[2] Lavoisier was not yet at the Guillotine nor had he come through with his new theory of oxidation that would finally have a strong accelerating effect upon the development of the entire field of natural science.[3] Cadet's discovery, though merely resulting quite accidentally from work with "invisible inks," received visible influence to science through Bunsen who established the chemical structure many years later.[4] He also got his young student Frankland to make diethyl zinc, the first alkyl compound of a transition metal to be discovered.[5,6]

Since Frankland's work had not been directed towards the formation of metal–carbon bonds but rather to the generation of the "free radical" $\{C_2H_5\}$, the synthesis of further metal alkyl compounds could not receive broad attention at that time. It was only around the turn of our century that the discovery of organomagnesium compounds by Barbier and his student Grignard was recognized as useful in organic synthesis.[6] It is thus not surprising in retrospect that the two other basic types of organometals—olefin and carbonyl complexes—were also found by serendipity, and once again their roots can be followed back to the 19th century. The Danish pharmacist W. C. Zeise recognized the first olefin complex as early as 1829 when he heated solutions of platinum chlorides in ethanol adding potassium chloride for work-up[7]; he was attacked by the famous Justus von Liebig in a very harsh manner for the interpretation of his results, but nonetheless Zeise became confirmed through subsequent work of Birnbaum who synthesized similar platinum compounds directly from ethylene.[8] Finally, a compound of composition $Ni(CO)_4$ came to light in 1890 as a result of the German research group, consisting of Mond, Langer and Quincke, inquiring into some corrosion problems that had happened at nickel valves in a Solvay factory in England.[9] It was Walter Hieber who thirty years later took up this subject in a systematic way, consequently establishing metal carbonyls as a class of compounds on their own.[10]

While it is true that the recognition of stable bonds between transition metals and π-aromatic compounds such as cyclopentadienyl and benzene[11–14] opened up a renaissance era of chemistry, the influence on the hitherto rapid development of what is called "organometallic chemistry" by earlier pioneering work performed during the first decades of this century is also obvious.[15] On the other hand, prominent successes of organotransition metal compounds in industrial catalytic processes have clearly advanced the field and preferred it over other areas of chemical research. Organometallic chemistry since the early fifties presents a unique example of "technology push/market pull" effects. The Nobel Prize awarded to E. O. Fischer and G. Wilkinson in 1973 marked a first culmination point. At that time there was no major technical process, be it on the basis of carbon monoxide, acetylene, or ethylene, that was not taking advantage of the catalytic power of transition metals or organometallic species derived therefrom.[16–18] By no means complete, Fig. 1 nevertheless presents several milestones of organometallic chemistry, and shows how basic research (bottom part) has interacted with commercial applications in the chemical business (upper part of Fig. 1). The economic impact of transition metal catalysis is enormous; alone, linear polyethylene and isotactic polypropylene following Ziegler's 1953 discovery of the "Metallorganische Mischkatalysatoren" were valued at 8.7 billion dollars in 1980 on the U.S. market.[19]

II. WHAT MAKES ORGANOMETALLIC COMPOUNDS SO UNIQUE?

Bonds between transition metals and carbon or hydrogen ligands may vary over a broad range in thermodynamic terms. It is not so much bond energies, however, that make organotransition metal compounds so unique for technical applications but rather the kinetic lability of hydrocarbon groups once attached to metals. Let us consider a transition metal that is surrounded by the "typical ligands" carbon monoxide, alkyl, olefin, and hydrogen. Although a compound assembling these ligands all at the same time (Fig. 2) is not yet available, the basic reactivity features of salient importance to catalysis can be pointed out here. First, migration of an alkyl group to metal-attached carbon monoxide (no. 1) involves one of the major carbon–carbon bond forming reactions so we encounter them in hydroformylation or in the Monsanto acetic acid process. Another carbon–carbon bond making case (no. 2)

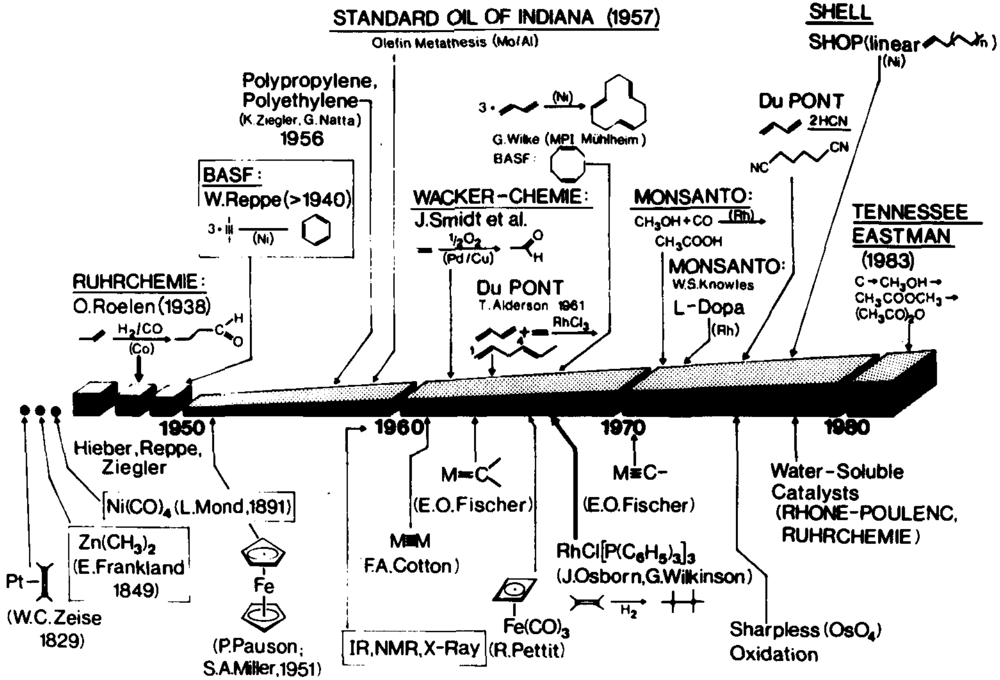


FIGURE 1 Some important landmark discoveries in organometallic chemistry.

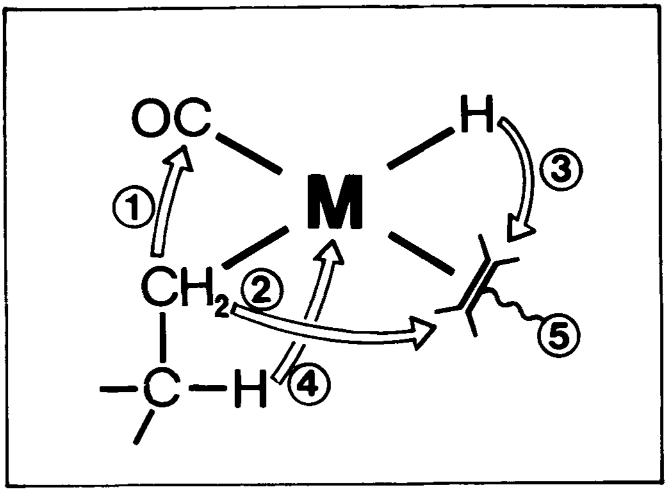


FIGURE 2 The five most important reaction modes of organometallic compounds (see text).

comprises coupling of alkyls and olefins in a metal's environment, with the most celebrated example being Ziegler–Natta low-pressure polymerization of ethylene and propylene.[20] Olefins may also combine with hydrido groups (no. 3) whose reaction ultimately produces alkanes from olefins. This process may proceed stereoselectively if prochiral olefins and optically active catalysts or cocatalysts are used (e.g., L-DOPA from substituted cinnamic acid; Monsanto).[21] Hydrogenation catalysts of this type (rhodium) may show up with enzyme-like chiral specificity. Hydrogen atoms in β-carbon positions of a metal-attached alkyl group feature a special rearrangement reaction in that they are transferred to the metal atom at very low activation energies (no. 4); termination steps of certain hydrocarbon chain growth reactions (e.g., Fischer–Tropsch hydrocarbon synthesis)[22] will generally follow this pathway. Finally, metal-induced cleavage of carbon–carbon bonds as strong as those in olefins are to be noted here (no. 5). The so-called olefin metathesis reaction, most likely operating via metallacyclobutanes, offers an opportunity for synthesizing high-value added chemicals or certain polymers by virtue of this technique (e.g., special olefins as insect pheromones, polyacetylene from cyclooctotetraene, rubber elastomers, etc.).[23]

The catalytic power of the metal–hydrogen and metal–carbon bond outlined in Fig. 2 arises from an "activation" of these groups which basically is due to "kinetic labilization." The wide-scope effects of metals upon such groups interacting with each other can be tuned by auxiliary ligands, with phosphanes encompassing the most important ones in industrial applications.

Metal-centered assembly reactions exemplified in Fig. 2 are balanced by electronic (e.g., metal charge, ligand basicity) and steric means (metal size, ligand bulk) in a very delicate way. The basic features of industrially important carbon–carbon and carbon–hydrogen bond forming reactions are nevertheless very similar, comprising metal–ligand pre-dissociation (e.g., Rh-PR_3), pre-coordination of substrate (e.g., C_2H_4, CO), oxidative addition (e.g., H_2, CH_3I), alkyl migration (no. 1 in Fig. 2), and reductive elimination of products (e.g., alkane, aldehyde). All these essential steps occur at relatively *low-valent transition metals*, with the change of oxidation states during a given process being ±2. Since unsaturated hydrocarbons (alkenes and alkynes, etc.), alkyl groups and carbon monoxide coordinate much better to low-valent rather than to high oxidation state transition metals, it becomes evident that literally all catalytic and most organic stoichiometric reactions involving these entities comprise low oxidation state transition metal chemistry.[24]

It is exactly this statement that focusses on most, if not all, of organometallic chemistry since the golden days of ferrocene. Textbooks, handbooks, and encyclopedias deal with a total of ca. 14,000 organometallic compounds, by far most of which present the metal in the lower oxidation state range near zero.[25–27] Sufficient thermal stability of these compounds facilitating their isolation and characterization, followed by chemical reactivity studies, further explains why they have become so large in number.

III. FROM LOW TO HIGH OXIDATION STATES

Much less work has been done by organometallic chemists on systems in *high oxidation states* so typical of inorganic transition metal chemistry.[28] In this context, the two Nobel Prize winners of 1973 may be referred to. While they both started their work with ferrocene and related compounds of other metals, Fischer continued on low oxidation states with the discovery of metal–carbene and metal–carbyne compounds (Fig. 1).[29] Wilkinson departed for the highest possible oxidation states and arrived at the tungsten and rhenium hexamethyls.[30] Not too many chemists have followed Wilkinson's path,[31] mainly because high oxidation state organometals have some intrinsic problems, such as low kinetic stability, making them harder or even unpleasant[32] to deal with.

While it is true that bonds between transition metals and halogen or oxygen ligands are stronger than those involving alkyl groups within a given class of compounds, transition metal alkyls are *grosso modo* thermodynamically as stable as their main group congeners. Although little data are available about the M–C bond strength, mean bond dissociation energy *D* data tell us the close thermodynamic resemblance within the *entire range* of element-to-carbon bonds (160–360 $kJ \cdot mol^{-1}$). Furthermore, the rather similar mean bond dissociation energies of *zero*-valent hexacarbonyltungsten, $W(CO)_6$ (ca. 180 $kJ \cdot mol^{-1}$), and *hexa*-valent hexamethyltungsten, $W(CH_3)_6$ (ca. 160 $kJ \cdot mol^{-1}$), wipes out the prejudice of "inherent instability" attached to high oxidation state organometals (Fig. 3).[33]

The kinetic origin of transition metal alkyls' "instability" (e.g., concerted pathways such as β-elimination) will not be further discussed.[25,34]

IV. π-AROMATICS AT RHENIUM(I) AND RHENIUM(VII): "STABLE" OR "UNSTABLE"?

The data mentioned in the previous paragraph must not be misinterpreted. It remains a given fact that the prototypical π-acceptor ligands such as carbon monoxide, etc., only survive at low-valent transition metals, and MO theory does explain in simple terms why $W(CO)_6$ is stable whereas the cation $[W(CO)_6]^{3+}$ escapes isolation. For the same reasons π-aromatic ligands, such as the ubiquitous cyclopentadienyl system, are associated with metals in lower oxidation states. One would thus have expected that an oxidic rhenium(VII) moiety would "chew up the organic ligand."[35]

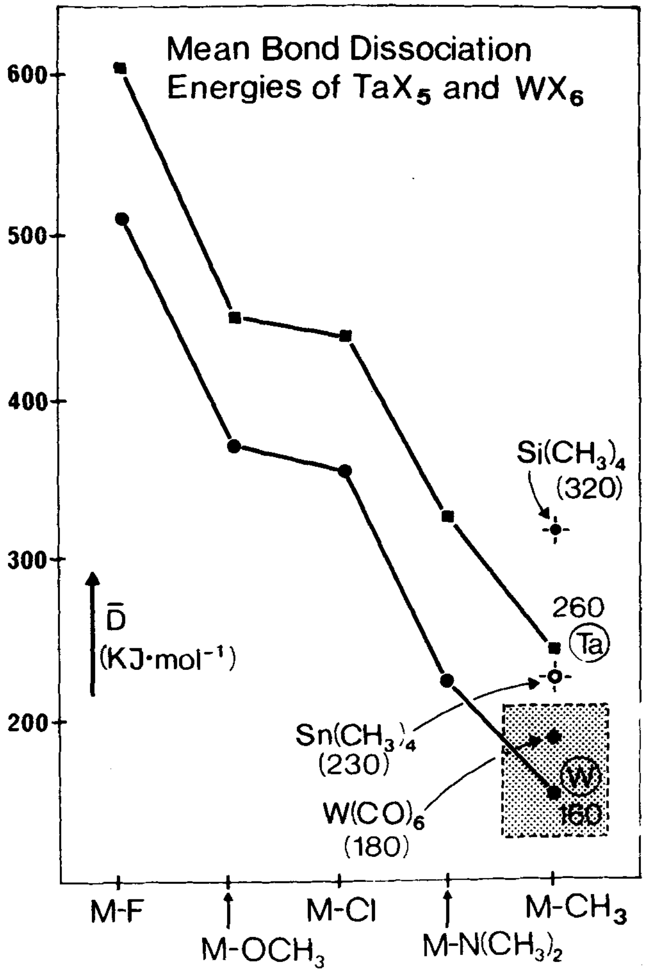
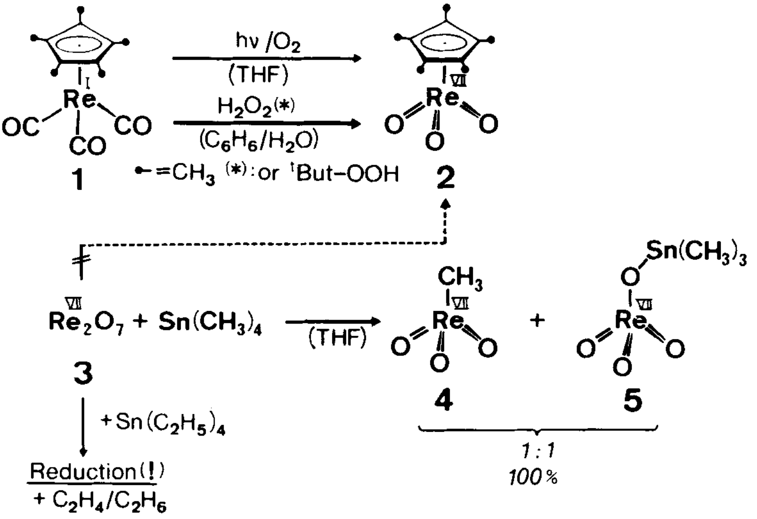


FIGURE 3 Mean bond dissociation energies of pentavalent tantalum and hexavalent tungsten compounds (data taken from Refs. 33a and 16b).

However, it doesn't! When the half-sandwich rhenium(I) carbonyl complex **1** is treated with hydrogen peroxide (or *tert.*-butyl hydroperoxide) in a boiling two-phase water/benzene system for several hours, its "oxidized relevant" **2** shows up in yields above 70% according to Scheme 1.[36,37] This latter compound, exhibiting three oxo groups in place of the original carbonyl groups is also



SCHEME 1

formed by air oxidation of **1** under photolysis conditions.[38] The oxo compound **2** of trigonal pyramidal structure[37,39] (Fig. 4) forms bright-yellow crystals that do not show any sign of decomposition below 250°C. The compound can be sublimed *in vacuo* at ca. 110°C without deterioration. It is obvious then that in spite of the highest possible oxidation state of rhenium to be attributed to this compound through PE spectroscopic data,[38] highly oxidized metals are in fact compatible with π-aromatic ligands.

Compound **2** suffers partial displacement of the π-bonded pentamethylcyclopentadienyl group in the (mechanistically unexplored) reaction with triphenylphosphane *in the presence of air oxygen*; the structurally interesting oligonuclear derivatives **7** and **8** are the final products. They both contain perrhenate (ReO_4) ligands and anions, respectively (Scheme 2).[37] It is not yet clear as to whether ring ligand displacement starts off at the (isolable) rhenium(V) species **6**. It is suspicious, however, that the last-named compound undergoes quantitative oxidation to the (electronically interesting)[40] trinuclear product **8** (BF_4^- instead of ReO_4^-)[41] while air oxidation of **6** cleanly recovers the parent rhenium(VII) compound **2**.[37]

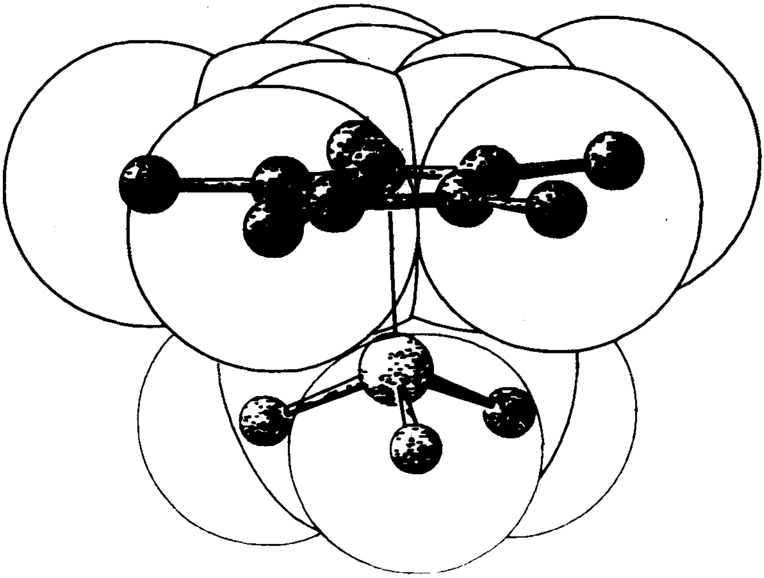
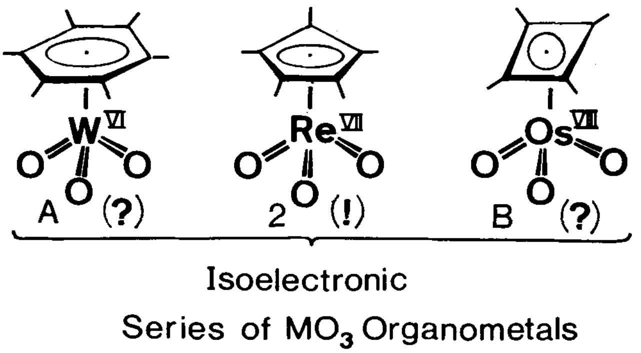
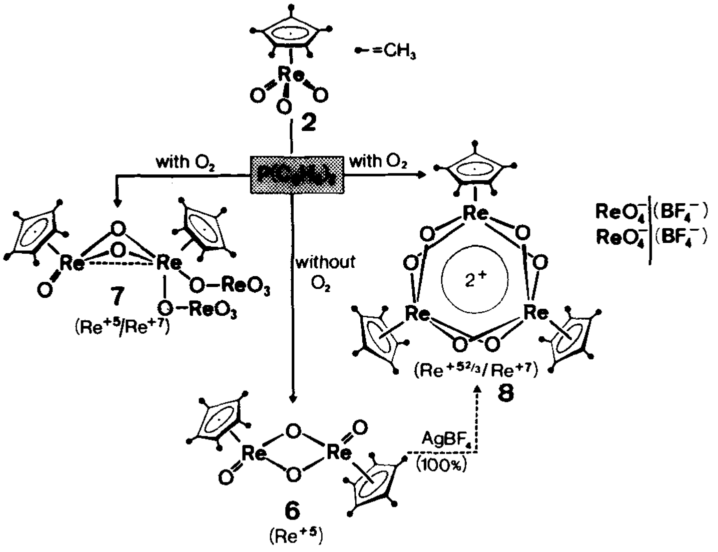


FIGURE 4 Pictorial representation of trioxo(η^5-pentamethylcyclopentadienyl)rhenium(VII) (**2**) including a space-filling model drawing. The structure is adapted from the X-ray diffraction data of the related derivative (η^5-$C_5Me_4Et)ReO_3$(**2a**) (Ref. 39).

Being convinced that high-aromatic ligands may indeed survive at even the highest possible oxidation states of transition metals, we may speculate a bit about other congeners still to be discovered. If the isoelectronic principle holds, then benzene (or at least hexamethylbenzene) should interact with the WO_3 fragment to give

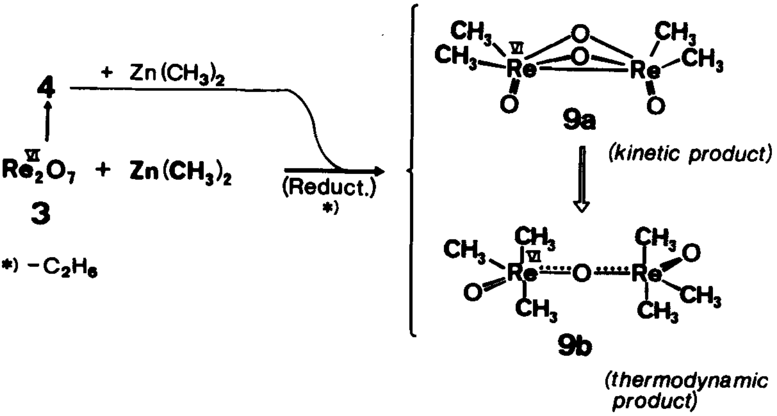




SCHEME 2

(stable?) **A**. On the other hand, one should not be surprised to see a cyclobutadiene ligand in the osmium compound **B** someday. At least in these two compounds, additional prerequisites for thermal stability are fulfilled: they belong to the third row transition metals that generally form more stable, less oxidizing high-valent compounds than their "lighter brothers." Second, the coordination numbers are high enough to avoid kinetic lability, which would result in aggregation to dimers or oligomers. (For this latter reason, the vanadium(V) compound of formula (η^5-C_5H_5)VO_2 announced by Russian workers[42] turned out to be trimeric.[43])

If we were to discover catalytic properties of the organorhenium(VII) oxide **2**, the observed partial ring ligand displacement (see formula) would not look like a good perspective for such applications. We were thus forced to develop a better reproducible synthesis of the simpler methyl derivative $(CH_3)ReO_3$ (**4**), which is an air-stable sublimable compound that had previously been noted by Beattie and Jones.[44] To make a long story short, we have succeeded in synthesizing **4** *quantitatively* by treating dirheniumheptoxide with tetramethyltin according to Scheme 1.[45,46] The second product, colorless as well, but unlike **4** not sublimable in



SCHEME 3

a vacuum, turned out to be the perrhenyl ester **5** that had been obtained by *Schmidbaur et al.* along a different route.[47] We shall later address the fact that $Re_2O_7/Sn(CH_3)_4/Al_2O_3$ comprises the most effective catalyst/cocatalyst system in the heterogeneous metathesis of functionalized olefins (nitriles, carboxylic esters).[48]

Reduction to rhenium(VI) occurs upon treatment of either Re_2O_7 (**3**) or CH_3ReO_3 (**4**) with dimethylzinc; the diamagnetic, dinuclear compounds of compositions $(CH_3)_4Re_2O_4$ (**9a**; kinetic product) and $(CH_3)_6Re_2O_3$ (**9b**; thermodynamic product) are formed (Scheme 3).[46]

Since the two organorhenium(VII) oxides **2** and **4** differ by a total of nine (!) carbon (plus twelve hydrogen) atoms, the methyl compound **4** should have a much broader reactivity pattern than the π-aromatic congener **2** for simple steric grounds. A comparison, based on space-filled models presented in Fig. 5, amplifies this statement. While in the *pentamethylcyclopentadienyl* complex **2** the metal atom is almost completely buried under the rather bulky ring ligand, thus excluding reaction pathways from this particular side of the molecule, the *methyl* compound **4** is accessible for reagents at the metal (Fig. 6). Most of compound's **2** chemistry should therefore occur at the oxygen atoms, unless (sterically very unpretentious) molecules can directly attack the metal atom between the three oxo groups.

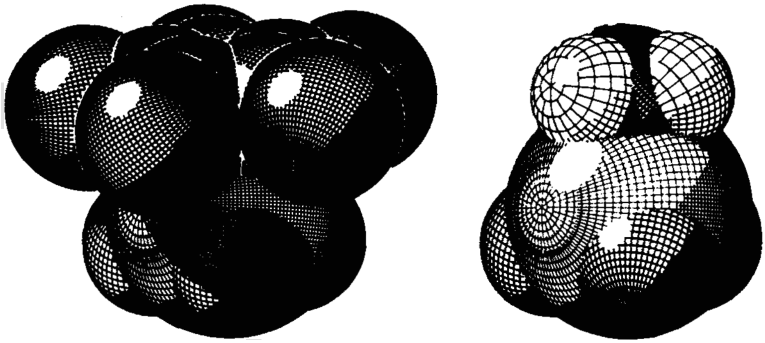


FIGURE 5 Space-filling models of compounds **2** (left) and **4** (right). The space-filling model of **2** corresponds to an X-ray structural analysis (Ref. 39) and uses reasonable van der Waals radii of rhenium(240), carbon(160), oxygen(140), and hydrogen atoms (120 pm). The same intermolecular Re-O-distances (170 pm) are assumed for compound **4** which has not yet yielded single crystals suitable for X-ray diffraction. A rhenium–methyl single bond distance of 210 pm seems reasonable from the structural data obtained for $(CH_3)_4Re_2O_4$ (Ref. 46).

V. π-ACCEPTOR VERSUS π-DONOR LIGANDS

Bursten *et al.* have raised the basic question of *d*-electron count versus stability of high- and low-valent piano-stool complexes.[49] To this end, they have subjected the structurally analogous compounds **C** and **D** of idealized C_s-symmetry to Fenske–Hall molecular orbital calculations. The following message becomes evident from Fig. 7: (i) The tungsten(II) nitrosyl complex **C** gets two of its metal-based 5d orbitals significantly stabilized as a result of interaction (4a′ and 3a″) with the very strong π-acceptor ligand

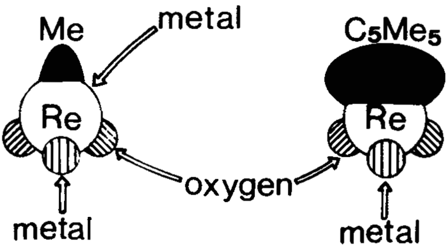


FIGURE 6 Possible sites of reactivity of the organometal oxides **4** (left) and **2** (right).

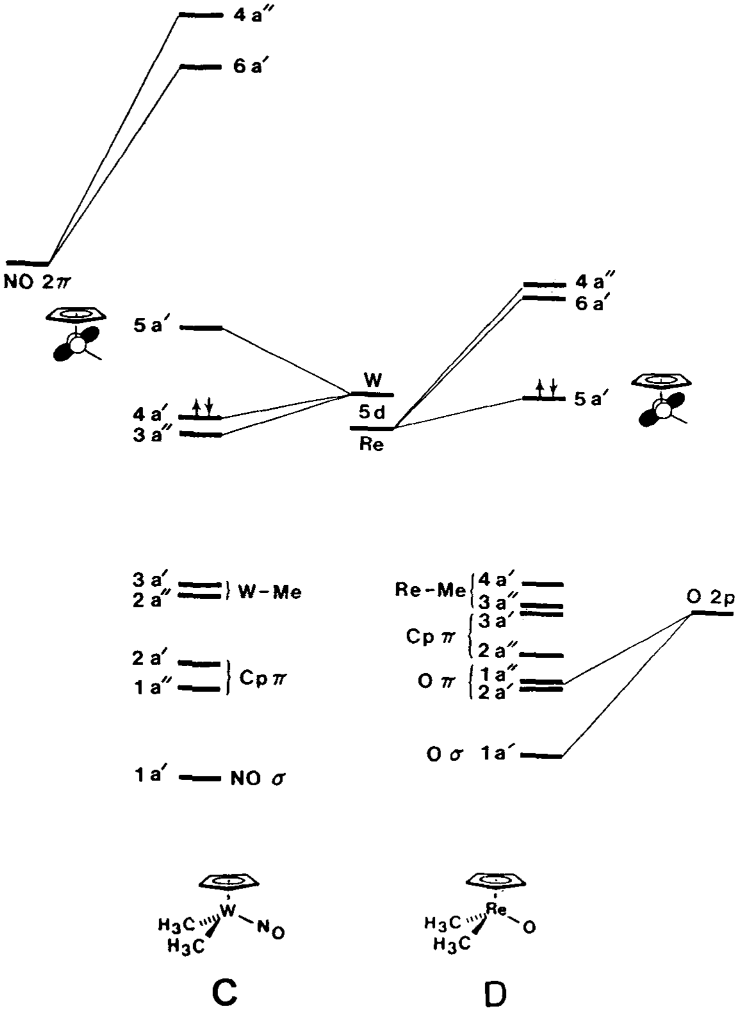


FIGURE 7 Simplified molecular orbital diagram of d^4-tungsten and d^2-rhenium compounds **C** and **D**, respectively (taken from Ref. 49). The neopentyl derivative $(\eta^5\text{-}C_5H_5)W(NO)(CH_2CMe_3)_2$ of type **C** is a known, stable compound: P. L. Legzdins, S. J. Rettig, L. Sanchez, B. E. Bursten and M. G. Gatter, J. Amer. Chem. Soc. **107**, 1411 (1985). The ring-substituted derivative $(\eta^5\text{-}C_5Me_5)Re(O)(CH_3)_2$ and a series of higher alkyl homologues have been synthesized and structurally characterized (Ref. 37).

nitric oxide. By way of contrast, the 5a′ orbital remains nonbonding because the methyl ligands function only as σ-donors in the present case. The splitting of the metal "t_{2g}" set amounts to 2.23 eV according to these calculations. (ii) The opposite picture emerges for the rhenium(V) oxo complex **D**. Since a single oxo atom is a very good π-donor ligand (as well as a good σ-donor), it interacts with the rhenium-centered 5d orbitals to destabilize two levels by 2.36 eV. The nonbonding 5a′-type orbital becomes the homo because of the d^2 configuration of the metal atom.

As a conclusion, the stability of the 16-electron complex **C** (d^4-W^{+2}) is attributed to the nonbonding 5a′ orbital generated by the strong π-acceptor ligand NO. On the other hand, the 18-electron rule must no longer be considered in the case of high-valent organometals as the *d*-orbital levels are generally destabilized by π-donors such as the oxo group and would rather remain unoccupied. The *entire* pseudo-t_{2g} set of orbitals is destabilized when the metal atom is surrounded by at least *two* oxo ligands. Compounds of this type should exibit a d^0 electron count. While this seems true for most examples, the d^2-Re^V alkyne complexes of composition

$$CH_3ReO_2(RC{\equiv}CR)^{50}$$

(see Section VII) look like exceptions to this rule.

VI. REDUCTIVE DEOXYGENATION AND OLEFIN METATHESIS

The simple organometal oxide **2** has yielded a large number of lower-valent derivatives that mostly exhibit *pentavalent* rhenium. This implies that at least one oxo group is being removed from the metal atom under such conditions.[37] We have already mentioned reduction of **2** by the *Lewis base* triphenylphosphane that gives the rhenium(V) dimer **6** under rigorous exclusion of air (Scheme 2). This particular compound has an interesting chain-type structure in the hydrated form which results from alkaline hydrolysis of the dichloro precursor (η^5-C_5Me_5)$ReOCl_2$ (Fig. 8).[51] The compound has proven to be a versatile intermediate for the synthesis of further derivatives, since it generally acts as a source of other-

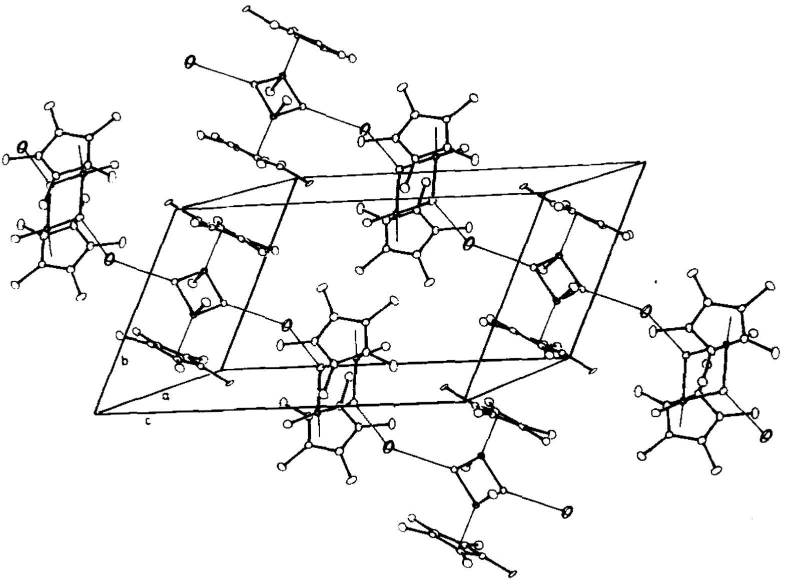
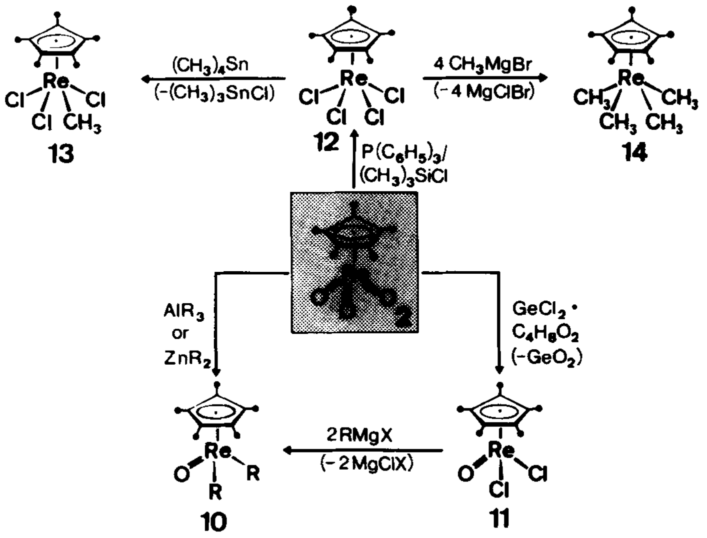


FIGURE 8 Unit cell representation of the structure of the hydrated dimer **6** (without hydrogen atoms). The compound crystallized from toluene at −25°C in the triclinic space group P1 (Int. Tab. No. 2). The individual dinuclear molecules display *trans* configuration of the terminal oxo and the π-bonded pentamethylcyclopentadienyl ligands, respectively. The distances between the water and rhenium oxygen atoms amount to 294.2 pm and 295.9 pm (Ref. 51).

wise not accessible $\{(\eta^5\text{-}C_5Me_5)ReO_2\}$ fragments. Cycloaddition reactions with ketenes and other heterocumulenes thus proceed cleanly and under mild conditions.[37]

Oxygen groups are also lost under the influence of *Lewis acids*. The most important d^2 rhenium(V) key compounds resulting from such reactions are summarized in Scheme 4.

The dialkyl series **10** can be obtained either *one* step from the parent compound **2** or, with more flexibility regarding the alkyl groups, in *two* steps via the dichloro compound **11** which in turn is easily accessible by means of (solvated) germanium(II) chloride.[37] The tetrachloro compound **12** undergoes selective monomethylation with tetramethyltin to form **13**,[52] while Grignard reagents (e.g., methylmagnesium bromide) rather unselectively give



SCHEME 4

the novel tetramethyl compound **14** as the first known homoleptic rhenium(V) hydrocarbon complex.[53]

Higher metal oxidation states (e.g., W^{+4}) are essential for olefin metathesis, a mechanistically interesting and commercially important process.[23] Since $Re_2O_7/Sn(CH_3)_4/Al_2O_3$ represents an effective (heterogeneous) olefin metathesis catalyst system,[48] it appeared obvious that the methylrhenium oxide **4** would be the key to this system. In fact, **4** catalyzes both ring opening polymerization of cyclopentene and metathesis of open-chained olefins in the presence of a Lewis acid ($AlCl_3 + Sn(CH_3)_4$).[46] The role of a Lewis acid has not yet been defined in the present case, but removal of an oxo group from the rhenium(VII) oxide **4** appears likely in light of the known related reaction[37]

$$(\eta^5\text{-}C_5Me_5)ReO_3 + Al(CH_3)_3 \rightarrow (\eta^5\text{-}C_5Me_5)ReO(CH_3)_2 + \cdots$$

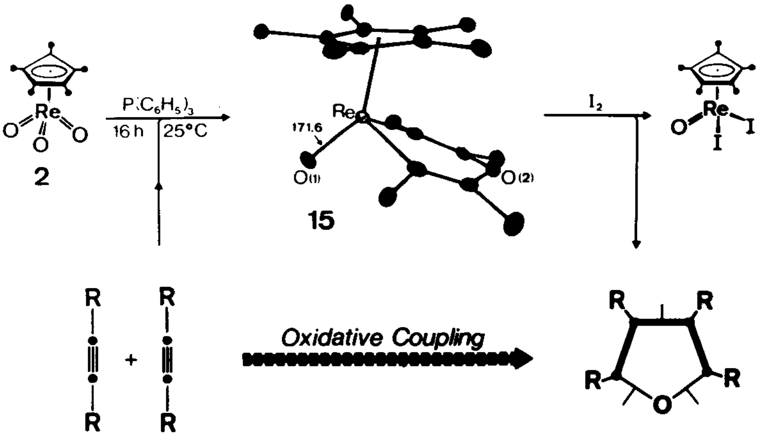
Compound **9b** which has the higher CH_3/Re ratio of 3/1 does affect olefin metathesis even in the *absence* of tetramethyltin but still requires $AlCl_3$.

VII. OXIDATIVE COUPLING OF ALKYNES

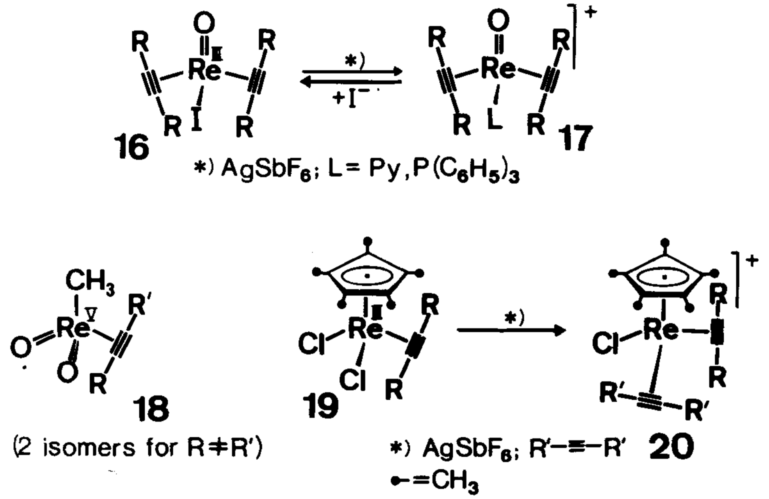
Oxidative coupling of two alkyne molecules would provide easy access to furanes, important compounds in industry. This simple-looking assembly reaction has been achieved in the *stoichiometric* reaction sequence of Scheme 5 by virtue of the organorhenium(VII) oxide **2**. The novel rhenium(V)-pyranes **15** are isolable intermediates that subsequently undergo double metal–carbon bond cleavage upon treatment with iodine.[54]

Once again, a *catalytic* means of coupling two alkynes together with an oxo group should be feasible at the right organometal oxide species. With imido (NR) groups at rhenium a synthesis of pyrroles could be in sight. An alkyne/alkyne/sulphur coupling reaction *catalyzed* by cyclopentadienyl cobalt complexes has just been announced by Bönnemann.[55]

The synthesis of heterocycles mentioned in the preceding paragraph warrant a better understanding of the largely unexplored interactions between alkynes and organorhenium fragments at intermediate oxidation states. While alkyne complexes generally exhibit the metal in low oxidation states, several rhenium compounds have recently become known to which this statement does not



SCHEME 5

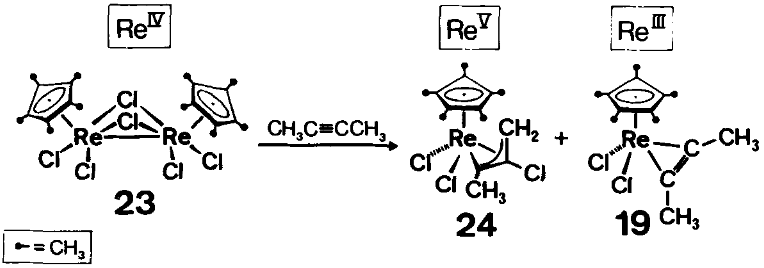


SCHEME 6

apply. Thus, trivalent rhenium is found in complexes of type **16**/**17**[56] and **19**/**20**.[56] (See Scheme 6.)

Clean substitution of alkynes for oxo groups occurs at methyltrioxorhenium(VII) (**4**) in the presence of (polymer-bound, insoluble) triphenylphosphane; a range of air-stable, diamagnetic compounds of general composition **18** (Re^{+5}) has thus become accessible.[50] The rhenium(III) alkyne compounds **19** (R = alkyl, aryl) can be made by reduction of the parent Re^{+5} compound tetrachloro(η^5-pentamethylcyclopentadienyl)rhenium (**12**) of Scheme 4.[57,58] In terms of further chemical transformations, chlorine replacement by oxo or alkyl groups at the stage of compounds **19** to give (η^5-C$_5$Me$_5$)ReO(η^2-RC≡CR) (**21**) and (η^5-C$_5$Me$_5$)ReR$_2$(η^2-RC≡CR) (**22**), respectively, proved particularly useful.

Another access to Re^{+3} alkyne complexes is redox disproportionation of the rhenium(IV) dimer **23** (Scheme 7). While the major products are the expected compounds **19** (Re^{+3}) and **12** (Re^{+5}), additional metal-to-carbon chlorine transfer and loss of a hydrogen atom (?), although mechanistically not yet understood, yields the rhenium(V) vinyl/carbene derivative of unexpected composition and structure **24**.[58,59]

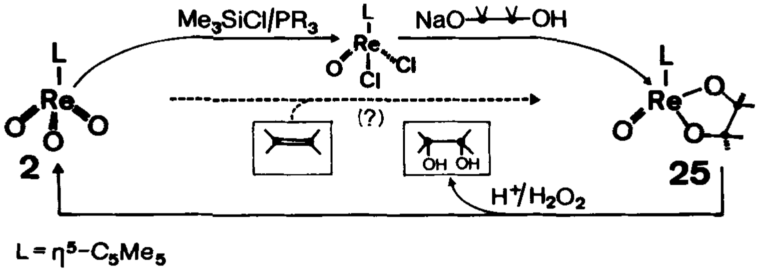


SCHEME 7

VIII. ORGANOMETAL OXIDES FOR OLEFIN OXIDATION?

Formation of furanes from rhenium(V)-pyrane intermediates constitutes an oxidative carbon–carbon coupling process during which the metal stays in oxidation state +5 (Scheme 5). Redox-neutral rhenium–oxygen bond cleavages occur when the five-membered metallocycles of type **25** are treated with protic acids such as HBF_4 according to Scheme 8.[60]

The metallocycles **25** (Fig. 9) may alternatively be viewed as *O*, *O*-glycolate complexes like those known from Sharpless' osmium work on *cis* hydroxylation of olefins to 1.2-glycols.[61] In spite of the fact that osmium tetroxide used in these catalytic reactions is a very harmful chemical, no better replacement has yet been found. This is a result of the generally rather crude knowledge about hydrocarbon chemistry occuring at high-valent transition metals.



SCHEME 8

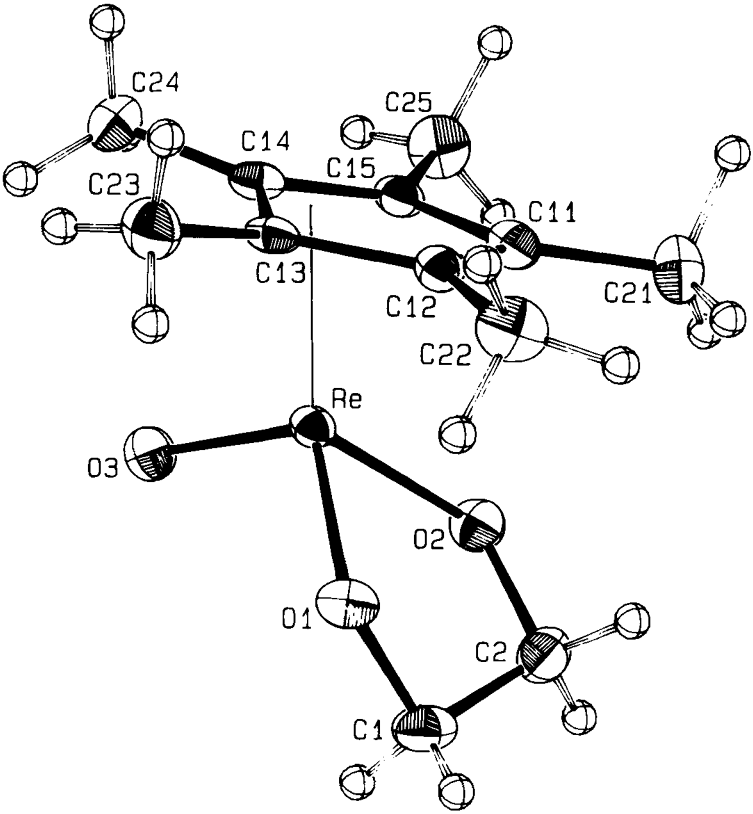


FIGURE 9 ORTEP drawing of the rhenium(V) glycolate complex **25** (Ref. 60).

It may certainly be true that metals other than Os^{+8} are inferior in oxidation power, but a "tune up" towards the right potentials and intermediates seems possible by virtue of tailored auxiliary ligands. In this important area of metal-mediated oxidation chemistry, a rather analogous development as the one that occurred in low-valent coordination compounds for hydroformylation, olefin hydrogenation, etc., can be thought of. Instead of the "soft" phosphane ligands useful for these latter processes, the oxo, alkoxide, and imido ligands should yield step-by-step improvements at the higher oxidation states of transition metals.

We have synthesized a number of rhenium(V) glycolates as well as their *O,N*, *O,S*, and *S,S* congeners.[61,62] Apart from a few exceptions, these compounds are generally thermally quite robust, but heating above the melting points effects selective oxygen–carbon bond breaking in case of the glycolate compounds, with formation of the corresponding olefins. Since H^+/H_2O_2 treatment, on the other hand, cleanly gives glycols and the rhenium(VII) oxide **2** (Scheme 8), the only missing link in a catalytic cycle is direct cycloaddition of the olefins to the oxide **2**. Since activated carbon–carbon bonds like those in ketenes undergo clean [3 + 2] and [2 + 2] cycloaddition reactions with $(\eta^5\text{-}C_5Me_5)ReO_3$ and $(\eta^5\text{-}C_5Me_5)_2Re_2O_4$, respectively,[37] it appears just a matter of enhancing the ReO_3 core reactivity, e.g., replacement of more electron-withdrawing ligands for the π-system C_5Me_5, in order to reach the penultimate goal of removing the question mark from Scheme 8 and replacing the model compounds by a catalytic cycle.

We have also seen organometallic glycolate complexes with other metals of relevance to oxidation processes. Thus the vanadium(V) species $(\eta^5\text{-}C_5Me_5)VOCl_2$ (**26**) forms the dinuclear compound **27** (Fig. 10).[63]

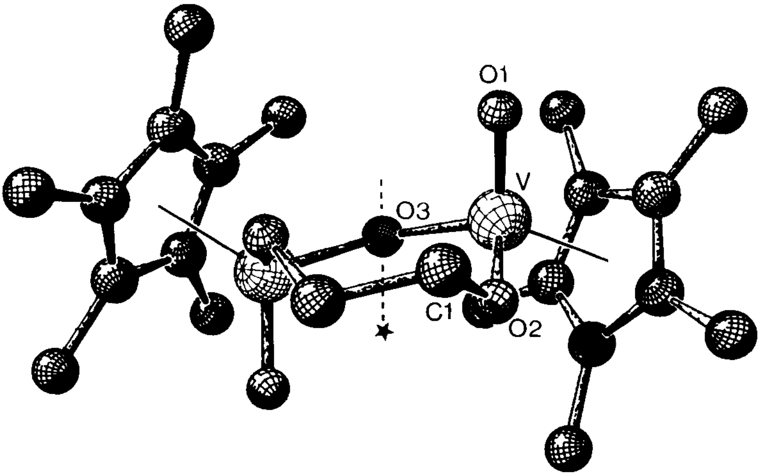


FIGURE 10 Structure of the dinuclear oxo vanadium(V) complex **27**. The compound crystallized from methylene chloride in the monoclinic space group C2/c (Int. Tab. Nr. 15).

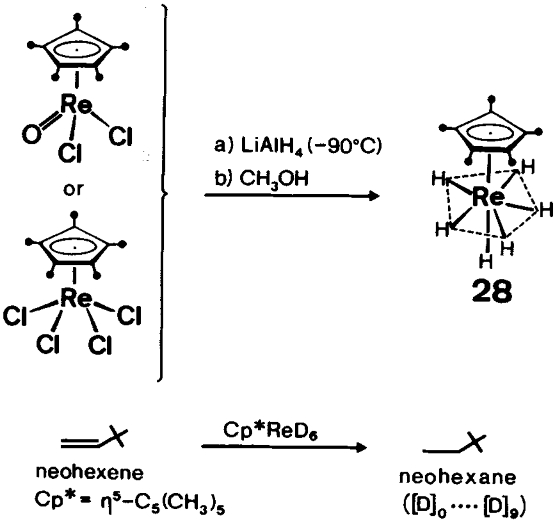
Apart from catalytic perspectives (amine oxidation), the *N,O*-metallocycles promise easy access to imido (NR) complexes.

Inorganic oxo anions can be attached to rhenium(V) in place of the glycolate ligands, some examples being the carbonate, sulfate and sulfite complexes $(\eta^5\text{-}C_5Me_5)ReO(\eta^2\text{-}O_2CO)$, $(\eta^5\text{-}C_5Me_5)ReO(\eta^2\text{-}O_2SO_2)$, and $[(\eta^5\text{-}C_5Me_5)Re(\mu\text{-}O)(\eta^2\text{-}O_2SO)]_2$, respectively.[64,65] Oxometallates and silanoles as oxo-bound ligands are on the way.

IX. NEW POLYHYDRIDES OF RHENIUM

In spite of the uniqueness of our two title compounds $(\eta^5\text{-}C_5Me_5)ReO_3$ (**2**) and CH_3ReO_3 (**4**), rhenium chemistry in general resembles that of molybdenum and tungsten much more than the chemistry of any other element. For example, it is only these three elements that catalyze olefin metathesis at an industrially acceptable extent. Beyond that "catalysis bracket," there are numerous analogous compounds, with the reader just being reminded of metal–metal multiple bonded compounds comprising a major part of these elements' chemistry.[16] One less obvious similarity is hydride chemistry. Rhenium is compatible with hydrogen across the entire oxidation state range. Suffice it to come up again with the textbook example of enneahydrido rhenate(VII), $[ReH_9]^{2-}$, having no authentic counterpart for any other metal in the periodic table. Hydrogen atoms attached to rhenium are also encountered in low oxidation states, with typical examples being $HRe(CO)_5$ and $H_3Re_3(CO)_{12}$. Redox versatility of hydridorhenium species is a great advantage of Felkin's carbon–hydrogen activation catalysts of the type L_2ReH_7 ($L = PR_3$),[66] although there is still demand for further improvement of catalyst activity and selectivity.

The neutral novel rhenium(VII) hydride **28**—air-stable, sublimable, thermally robust up to the melting point at 192°C!—can be made in 75% yield when either $(\eta^5\text{-}C_5Me_5)ReCl_4$ or $(\eta^5\text{-}C_5Me_5)ReOCl_2$ is treated with lithium aluminum hydride in tetrahydrofuran at low temperatures with subsequent methanolysis (Scheme 9).[67] This synthesis is mechanistically not fully understood; it is tempting to assume that the Re^{+5} precursor compounds are first converted to something like (solvated) "$(\eta^5\text{-}C_5Me_5)ReH_4$"



SCHEME 9

which undergoes successive oxidative addition of dihydrogen (from LiAlH$_4$/CH$_3$OH).

Neohexene is hydrogenated by **28** at higher temperatures. When Cp*ReD$_6$ is used, a mixture of neohexane isotopomers (Scheme 9) is observed by GC/MS.[68] Thermal (>200°C) hydrogen elimination (+15°C) of **28** yields the red-colored, air-stable dinuclear rhenium(IV) hydride {(η^5-C$_5$Me$_5$)ReH$_3$}$_2$ (**29**). According to a low-temperature X-ray diffraction study, two terminal and two bridging hydrogen atoms are present at each rhenium.[68] Photolysis of **28** in the presence of trimethylphosphane, however, gives the derivative (η^5-C$_5$Me$_5$)Re(H)$_2$(PMe$_3$)$_2$ (**30a**; Re^{+3}) while thermal reaction with CCl$_4$ yields the chloro complex {(η^5-C$_5$Me$_5$)Re(μ-H)Cl$_2$}$_2$ (**30b**; Re^{+4}) in a radical-type reaction.[68]

X. SULFUR FOR OXYGEN?

The sulfur compound (η^5-C$_5$Me$_5$)ReS$_3$ is still unknown, having resisted synthesis via various sources of sulfur, e.g., S(SiMe$_3$)$_2$.

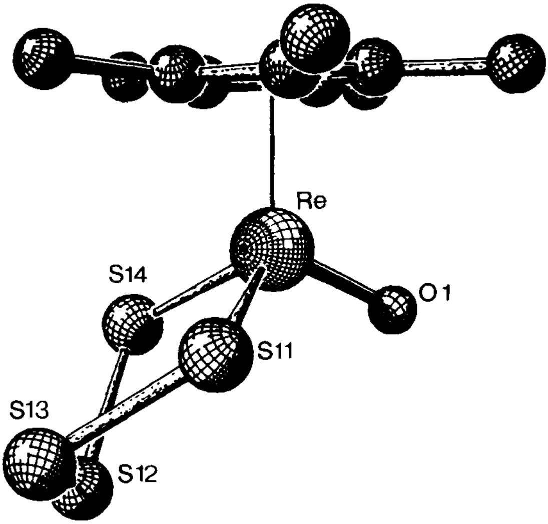
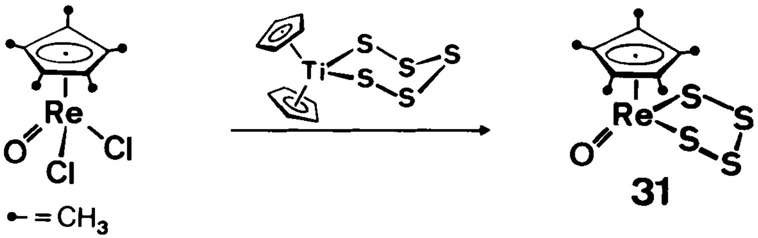


FIGURE 11 Structure of the ReS_4 metallacycle **31** (SCHAKAL drawing). The compound crystallizes from toluene at −25°C in the triclinic space group P1 (Int. Tab. No. 2). Selected bond distances (pm): Re-O1 171.8(3), Re-S11 226.4(1), Re-S14 224.4(2), S11-S13 214.2(2), S12-S13 199.3(3), S12-S14 215.3(2).

Only dinuclear products containing sulfido bridges are accessible, for example the dimer of composition $(\eta^5\text{-}C_5Me_5)_2Re_2S_4$.[68] The five-membered metallacycle **31** (Fig. 11) is available in good yields by means of the TiS_5 compound shown in Scheme 10.[51] It is interesting that only *four* out of five sulfur atoms get transferred to



SCHEME 10

rhenium. This last-named example further demonstrates the much higher catenation tendency of sulfur over oxygen.

XI. FROM SMALL TO LARGE SIZE ORGANOMETAL OXIDES

In summarizing the first harvest of organorhenium oxide chemistry, some notable aspects along the borderline between homogeneous and heterogeneous catalysis become evident. Most support materials in heterogeneous catalytic processes are oxidic in nature, while at the same time hardly anything is known on the chemistry and structural details of catalyst-to-support interactions. This lack of knowledge is mainly due to the fact that there is no direct chemical means of investigating such "oxide anchoring" at catalytically active surfaces. Tailored model compounds consisting of a lipophilic catalyst component (e.g., $(\eta^5\text{-}C_5Me_5)ReO_x$ or CH_3ReO_x units) and typical "inorganic" backbone oxides such as oxometallates or heteropolyoxide ions promise a more basic understanding of such interlinkages. On the other hand, structurally defined organometal oxides may be polymerized at the organic groups. Immobilized catalysts for epoxidation, hydroxylation, and metathesis of olefins could be accessible along these lines. Figure 12 shows two possible general approaches to polymeric organorhenium oxides.

Intermediate-size metal oxide clusters occasionally show up in the literature. Figure 13 presents a few prominent examples. The cubane-type cluster compound of composition $(\eta^5\text{-}C_5H_5)_4Cr_4O_4$ was published by Fischer *et al.* as early as 1960 as an accidental result in chromocene chemistry.[69] The sulphur and selenium analogues resembling this very structural type are also known.[70,71] The group around Bottomley has tackled some synthetic and structural problems in the field of organovanadium oxides in a systematic way. By using dinitrogen oxide as a mild, selective oxidant, they have opened another synthetic strategy that promises broad applicability; the pentanuclear cluster of composition $(\eta^5\text{-}C_5H_5)_5V_5O_6$ may be cited as one typical example.[72] Finally, hexanuclear titanium oxides of general composition $[(\eta^5\text{-}C_5H_5)_6Ti_6O_{8-n}]^{n+}$ (n = 0, 2, 4) are known from Caulton's and Floriani's work.[72] Figure

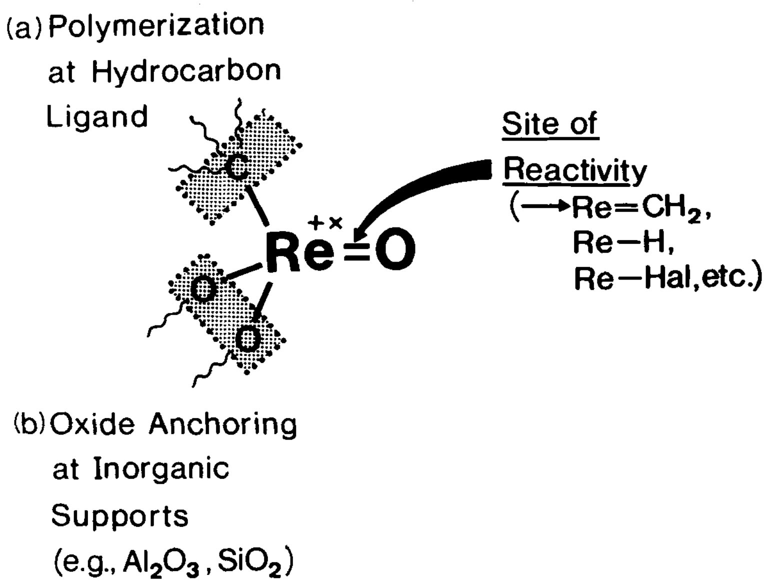


FIGURE 12 Possible ways of immobilizing organorhenium compounds via polymerization at the hydrocarbon ligands or anchoring at inorganic supports.

13 unfolds a simple structural prinicple in that the metal/oxide ratio seems to govern both stoichiometry and structures of such compounds, while the metals involved do not care too much about their formal oxidation states. However, a clear-cut clue to composition versus structures of organometal oxides has not yet been found. Thus another organotitanium oxide of composition $(\eta^5\text{-}C_5Me_5)_4Ti_4O_6$ adopts an adamantane-type structure.[73] Suffice it to say that the chemistry of all these materials is still unexplored.

On the way towards a convergence of organometallic and inorganic chemistry, even bigger oxides containing organic groups have been synthesized and structurally characterized. Klemperer's "goliath" of Fig. 14 may be considered a highlight in this area. Five norbornadienerhodium units are linked together by two heteropolyion aggregates $Nb_2W_4O_{19}$.[74] These compounds, which are easier to make than it appears, should help us to understand the above-mentioned catalyst/support interactions since they are accessible to the standard analytical methods such as NMR, X-ray, etc.

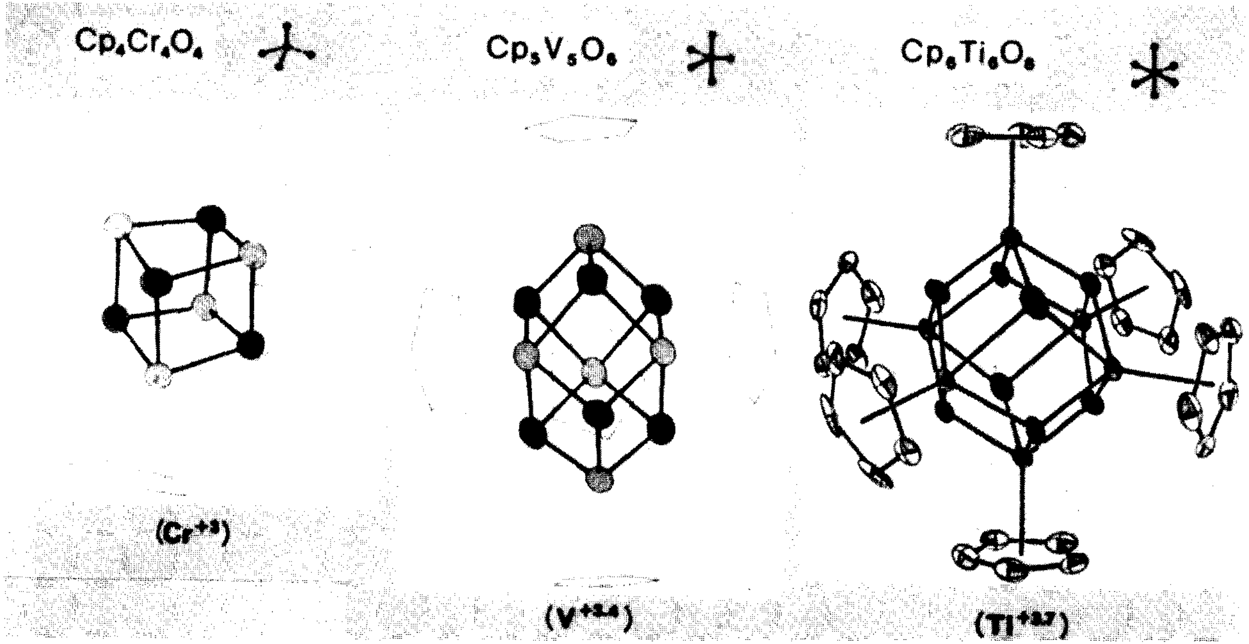


FIGURE 13 Three typical organometal oxide clusters (taken from Refs. 69b, 73a, and 73b).

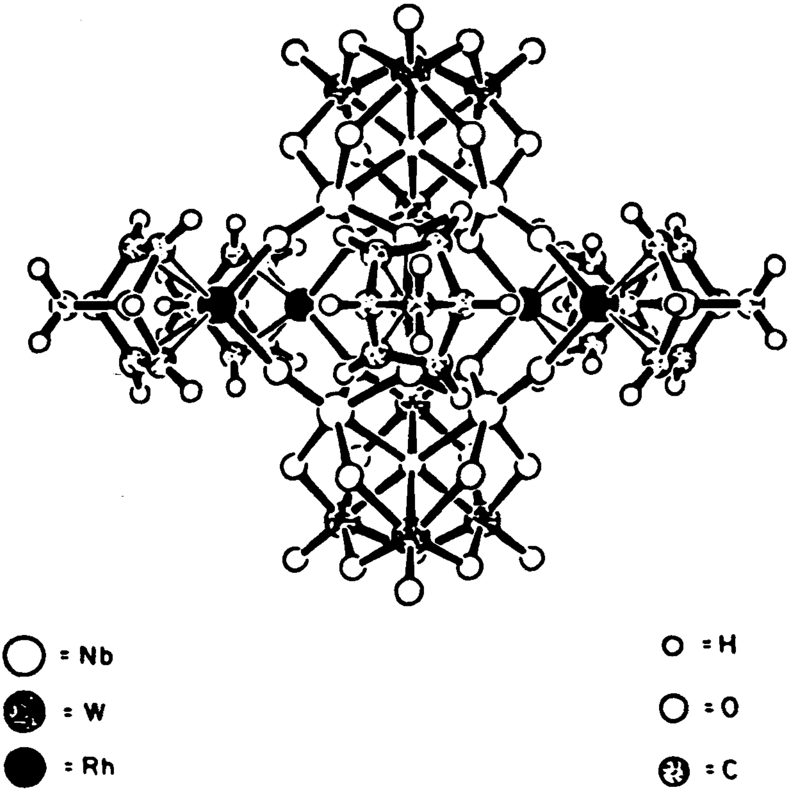


FIGURE 14 PLUTO drawing of the C_{2v} structure of the organometallic oxide $[\{(\eta^5\text{-}C_7H_8)Rh\}_5(cis\text{-}Nb_2W_4O_{19})_2]^{3-}$ (taken from Ref. 74).

XII. INORGANIC CHEMISTRY TODAY

We should realize that our particular discipline of organometallic chemistry is going to head for new ventures in the near future.[17] Figure 15 demonstrates that there are enough attractive topics for organometallic research, ranging from physics and engineering-related fields to organic chemistry, biochemistry, and biology. Organometallic compounds will certainly play a further major role in organic synthesis. As a matter of fact, most modern approaches to carbon–carbon bond linkage reactions (including natural prod-

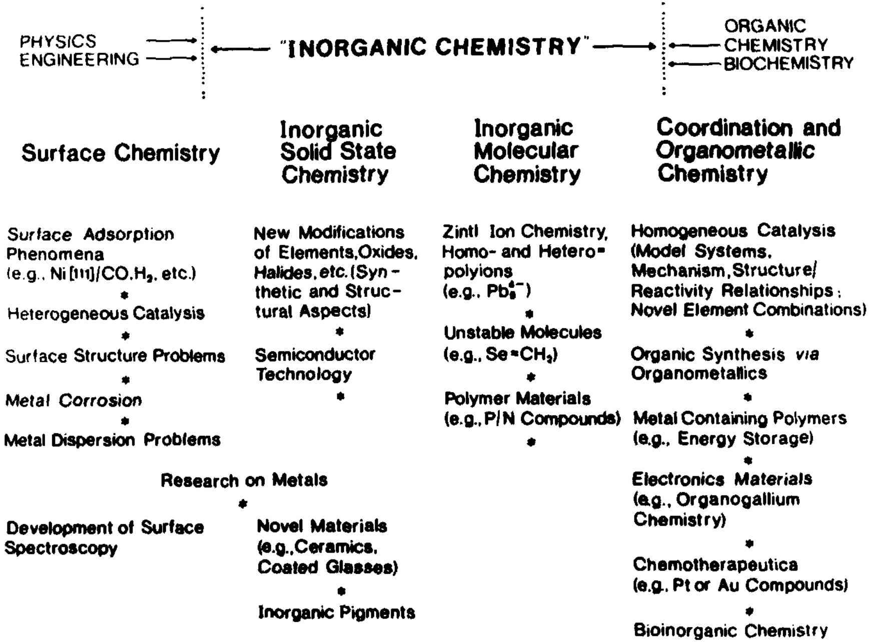


FIGURE 15 Some areas of present day inorganic chemistry (see text).

ucts syntheses) employ transition metals. However, organometallic compounds have been used much less to approach metal-containing polymers, electronic materials (semi- and superconductors), medical drugs (chemotherapeutica), and bioinorganic chemistry (e.g., models for the interactions of transition metals with peptides or enzymes). The more classical areas of inorganic research—inorganic solid state chemistry and inorganic molecular chemistry—have hardly been involved in organometallics. For example, Zintl ion chemistry almost exclusively remained a matter for inorganic chemists, although the combination of homo- and heteropolyions with organometal fragments should yield a plethora of new element-to-element combinations from which we should learn more about aggregation phenomena in general. Heterogeneous catalysis, on the other end of the spectrum (Fig. 15), may enjoy a better molecular understanding in the near future through high-valent organometallic species attached to oxidic and sulphidic compounds. It is hoped that organometallic chemistry will take these chances and opportunities that have been missing during the past three decades to quite a large extent.

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References

1. *Essays on Organometallic Chemistry*, Part 1. This series of papers to be continued with Part 2 in Angew. Chem. (October 1988) is to outline both general trends and special topics in present day organometallic chemistry. For this reason, no specific class of compounds is going to be discussed in full detail.

2. L. C. Cadet de Gassicourt, Mem. Math. Phys. 3, 623 (1760).
3. An excellent analysis of Lavoisier's influence upon the development of paradigms in science has been performed by the German historican Elisabeth Ströker, cf. E. Ströker, *Theorienwandel in der Wissenschaftsgeschichte—Chemie im 18. Jahrhundert* (Vittorio Klostermann, Frankfurt am Main, 1982).
4. G. R. (R. W.) Bunsen, Pogg. Ann. Chem. Pharm. **24**, 270 (1837).
5. E. Frankland, J. Chem. Soc. **2**, 263 (1849); *ibid.* **2**, 297 (1849).
6. One of the few comprehensive contributions covering the history of organometallic chemistry has been given by J. S. Thayer, Advan. Organometal. Chem. **13**, 1 (1975); see also W. A. Herrmann, J. Organometal. Chem. **250**, 319 (1983); *ibid.* **300**, 111 (1980).
7. (a) W. C. Zeise, Pogg. Ann. **21**, 497 (1831); *ibid.* **23**, 1 (1854); (b) J. Liebig, Ann. Chem. **9**, 1 (1834); *ibid.* **23**, 12 (1837).
8. (a) K. Birnbaum, Ann. Chem. **145**, 67 (1868); J. Prakt. Chem. **104** (1868); (b) Structure of Zeise's salt $KPtCl_3(C_2H_4)\cdot H_2O$: R. A. Love, T. F. Koetzle, G. J. B. Williams, L. C. Andrews and R. Bau, Inorg. Chem. **14**, 2653 (1975).
9. L. Mond, C. Langer and F. Quincke, J. Chem. Soc. **57**, 749 (1890).
10. Hieber's achievements in metal carbonyl chemistry are described in one comprehensive article and in a necrology: (a) W. Hieber, Advan. Organometal. Chem. **8**, 1 (1970); (b) E. O. Fischer, Chem. Ber. **112**, XXI (1979).
11. (a) S. A. Miller, J. A. Tebboth and J. Tremaine, J. Chem. Soc. [London] **1952**, 632; (b) T. J. Kealy and P. L. Pauson, Nature **168**, 1039 (1951); (c) P. L. Pauson, Pure Appl. Chem. **49**, 839 (1977).
12. According to a personal communication by G. W. Parshall, ferrocene had already been made (but not recognized as such) by chemists at DuPont in the early fourties.
13. Structure of ferrocene: (a) E. O. Fischer and W. Pfab, Z. Naturforsch. **7B**, 377 (1952); (b) G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, J. Amer. Chem. Soc. **74**, 2125 (1952); (c) G. Wilkinson, J. Organometal. Chem. **100**, 273 (1975).
14. E. O. Fischer and W. Hafner, Z. Naturforsch. **10B**, 665 (1955).
15. Important steps in early transition metal chemistry of hydrocarbons are the recognition of arylchromium compounds in 1919 (F. Hein), the discovery of the so-called oxo synthesis in 1938, using cobalt catalysts (hydroformylation; O. Roelen), alkyne coupling reactions at nickel centers (W. Reppe), and K. Ziegler's work on organolithium and aluminium compounds. For original communications and/or leading references, see (a) F. Hein, Ber. Dtsch. Chem. Ges. **52**, 195 (1919); E. O. Fischer and D. Seus, Chem. Ber. **89**, 1809 (1956); (b) R. L. Pruett, Advan. Organometal. Chem. **17**, 1 (1979); (c) W. Reppe, *Neuere Entwicklungen auf dem Gebiete der Chemie des Acetylens und Kohlenoxids* (Springer-Verlag, Berlin, New York, 1949); K. P. C. Vollhardt, Acc. Chem. Res. **10**, 1 (1977); (d) K. Ziegler, Advan. Organometal. Chem. **6**, 1 (1968).
16. Recent textbooks: (a) A. Yamamoto, *Organotransition Metal Chemistry-Fundamental Concepts and Applications* (Wiley, New York, 1986); (b) Ch. Elschenbroich and A. Salzer, *Organometallchemie* (Teubner-Verlag, Stuttgart, 1986); (c) J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, 2nd Edition (California University Books, Mill Valley, California, USA, 1987).
17. G. W. Parshall, Organometallics **6**, 687 (1987).
18. Monographs on organotransition metal catalysis: (a) G. W. Parshall, *Homogeneous Catalysis* (Wiley, New York, 1980); (b) C. Masters, *Homogeneous Transition Metal Catalysis—A Gentle Art* (Chapman and Hall, London, 1981).

19. G. W. Parshall and R. E. Putscher, J. Chem. Educ. **63**, 189 (1986).
20. Review: H. Sinn and W. Kaminsky, Advan. Organometal. Chem. **18**, 99 (1980).
21. (a) W. S. Knowles, Acc. Chem. Res. **16**, 106 (1983); (b) B. Bosnich, Chem. in Britain **21**, 808 (1984); (c) H. Brunner, J. Organometal. Chem. **300**, 39 (1986); (d) J. Halpern, Pure Appl. Chem. **55**, 99 (1983).
22. Reviews: (a) C. Masters, Advan. Organometal. Chem. **17**, 61 (1979); (b) W. A. Herrmann, Advan. Organometal. Chem. **20**, 159 (1982); (c) W. A. Herrmann, Angew. Chem. **94**, 118 (1982); Angew. Chem. Internat. Edit. Engl. **21**, 117 (1982).
23. Monograph: K. J. Ivin, *Olefin Metathesis* (Academic Press, London, 1983).
24. Applications of organometallic compounds: (a) F. R. Hartley and S. Patai, *The Chemistry of the Metal–Carbon Bond* (Wiley, New York, (since 1981)); (b) S. G. Davies, *Organotransition Metal Chemistry: Applications to Organic Synthesis* (Pergamon Press, Oxford, 1982).
25. (a) F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th edit. (Wiley & Sons, New York, 1980); (b) I. Haiduc and J. J. Zuckerman, *Basic Organometallic Chemistry* (Walter de Gruyter, Berlin, 1985).
26. J. Buckingham (Ed.), *Dictionary of Organometallic Chemistry* (Chapman and Hill, London, 1984).
27. G. Wilkinson, F. G. A. Stone and E. Abel (Ed.), *Comprehensive Organometallic Chemistry* (Pergamon Press, Oxford, 1982).
28. Cf. N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements* (Pergamon Press, Oxford, 1984).
29. Reviews: (a) E. O. Fischer (Nobel Lecture), Angew. Chem. **86**, 651 (1974); Advan. Organometal. Chem. **14**, 1 (1976); (b) J. E. Hahn, Progr. Inorg. Chem. **31**, 205 (1984); (c) E. O. Fischer and U. Schubert, J. Organometal. Chem. **100**, 59 (1975); (d) K.-H. Dötz (Ed.), *Transition Metal Carbene Complexes* (Verlag Chemie, Weinheim, 1984).
30. (a) K. Mertis, D. H. Williamson and G. Wilkinson, J. Chem. Soc. Dalton **1975**, 607; (b) P. G. Edwards, G. Wilkinson, K. M. A. Malik and M. B. Hursthouse, *ibid.* **1980**, 2467, and references quoted therein; (c) Review: G. Wilkinson (Nobel Lecture), Angew. Chem. **86**, 664 (1974); Science **185**, 109 (1974).
31. (a) R. R. Schrock, J. Organometal. Chem. **300**, 249 (1986); (b) R. R. Schrock, Acc. Chem. Res. **19**, 342 (1986); (c) R. R. Schrock and G. W. Parshall, Chem. Rev. **76**, 243 (1976).
32. K. Mertis, L. Galyer and G. Wilkinson, J. Organometal. Chem. **97**, C65 (1975).
33. (a) H. A. Skinner, J. Chem. Thermodyn. **10**, 314 (1978); (b) J. A. Connor, Top. Curr. Chem. **71**, 71 (1977); (c) J. Halpern, Acc. Chem. Res. **15**, 238 (1982).
34. R. Taube, Z. Chem. **18**, 425 (1978).
35. R. Dagani, Chem. Eng. News **62**, No. 30, p. 28 (1984).
36. W. A. Herrmann, E. Voss and M. Flöel, J. Organometal. Chem. **297**, C5 (1985).
37. Previous reviews on the chemistry of trioxo(η^5-pentamethylcyclopentadienyl)rhenium(VII): (a) W. A. Herrmann, J. Organometal. Chem. **300**, 111 (1986); (b) W. A. Herrmann and J. Okuda, J. Mol. Catal. 109 (1987); (c) W. A. Herrmann, E. Herdtweck, M. Flöel, J. Kulpe, U. Küsthardt and J. Okuda, Polyhedron **6**, 1165 (1987); (d) W. A. Herrmann, in *Organic Synthesis with Organometallic Compounds*, eds. A. deMeijere and H. tom Dieck (Springer-Verlag, Berlin, 1987).
38. W. A. Herrmann, R. Serrano and H. Bock, Angew. Chem. **96**, 364 (1984); Angew. Chem. Internat. Edit. Engl. **23**, 383 (1984).

39. J. Okuda, E. Herdtweck and W. A. Herrmann, Inorg. Chem. (in press).
40. (a) P. Hofmann and N. Rösch, J. Chem. Soc. Chem. Commun. **1986**, 843; (b) P. Hofmann, N. Rösch and H. R. Schmidt, Inorg. Chem. **25**, 4470 (1986).
41. U. Küsthardt, Ph.D. Thesis, Technische Universität München, 1986.
42. V. Latyaeva, V. Pereshein and A. Lineva, Tr. Khim. Khim. Tkhnol. **4**, 32 (1974) [Chem. Abstr. **83**, 179261z (1975)].
43. F. Bottomley and L. Sutin, J. Chem. Soc. Chem. Commun. **1987**, 1112.
44. I. R. Beattie and P. J. Jones, Inorg. Chem. **18**, 2318 (1979).
45. J. Kuchler, Diploma Thesis, Technische Universität München, 1987.
46. W. A. Herrmann, J. Kuchler, J. K. Felixberger, E. Herdtweck and W. Wagner, Angew Chem., in press (1988).
47. H. Schmidbaur and D. Koth, Chem.-Ztg. **100**, 290 (1976).
48. (a) R. H. A. Bosma, G. C. N. van den Aardweg and J. C. Mol, H. Organometal. Chem. **255**, 159 (1983); (b) X. Xiaoding and J. C. Mol, J. Chem. Soc. Chem. Commun. **1985**, 631; (c) G. C. N. van den Aardweg, R. H. A. Bosma and J. C. Mol., *ibid.* **1983**, 262.
49. B. E. Bursten and R. H. Cayton, Organometallics **6**, 2004 (1987).
50. W. A. Herrmann and J. K. Felixberger, unpublished results (1987).
51. W. A. Herrmann, J. Kulpe, M. Flöel and E. Herdtweck, unpublished results (1986).
52. W. A. Herrmann, J. K. Felixberger, E. Herdtweck, A. Schäfer and J. Okuda, Angew. Chem. **99**, 466 (1987); Angew. Chem. Internat. Edit. Engl. **26**, 466 (1987).
53. M. Flöel, E. Herdtweck, W. Wagner, J. Kulpe, P. Härter and W. A. Herrmann, Angew. Chem. **99**, 787 (1987); Angew. Chem. Internat. Edit. Engl. **26**, 787 (1987).
54. E. J. M. deBoer, J. deWith and G. Orpen, J. Amer. Chem. Soc. **108**, 8271 (1986).
55. H. Bönnemann and W. Brijoux, Nouv. J. Chim. **11**, 549 (1987) (Figure 27 and Reference 24).
56. (a) J. M. Mayer and T. H. Tulip, J. Amer. Chem. Soc. **106**, 3878 (1984); (b) J. M. Mayer, D. L. Thorn and T. H. Tulip, *ibid.* **107**, 7454 (1985).
57. W. A. Herrmann, R. A. Fischer and E. Herdtweck, J. Organometal. Chem. **329**, Cl (1987).
58. W. A. Herrmann, R. A. Fischer and E. Herdtweck, unpublished results (1987).
59. W. A. Herrmann, R. A. Fischer and E. Herdtweck, Angew. Chem. **99** (1987); Angew. Chem. Internat. Edit. Engl. **26** (1987).
60. W. A. Herrmann, D. Marz, E. Herdtweck, A. Schäfer, W. Wagner and H.-J. Kneuper, Angew. Chem. **89**, 462 (1987); Angew. Chem. Internat. Edit. Engl. **26**, 462 (1987).
61. Review: M. Schröder, Chem. Rev. **80**, 187 (1980).
62. W. A. Herrmann and D. Marz, unpublished results (1986/87).
63. W. A. Herrmann, E. Herdtweck and G. Weichselbaumer, unpublished results (1987).
64. W. A. Herrmann, K. A. Jung, A. Schäfer and H.-J. Kneuper, Angew. Chem. **99**, 464 (1987); Angew. Chem. Internat. Edit. Engl. **26**, 464 (1987).
65. W. A. Herrmann and K. A. Jung, unpublished results (1987).
66. (a) D. Baudry, M. Ephritikhine, H. Felkin and R. Holmes-Smith, J. Chem. Soc. Chem. Commun. **1983**, 788; (b) D. Baudry, M. Ephritikhine, H. Felkin and J. Zakrzewski, Tetrahedron Lett. **25**, 1283 (1984).
67. W. A. Herrmann and J. Okuda, Angew. Chem. **98**, 1109 (1986); Angew. Chem. Internat. Edit. Engl. **25**, 1092 (1986).
68. W. A. Herrmann, H. Theiler, W. Wagner and E. Herdtweck, unpublished results (1987).

69. (a) E. O. Fischer, K. Ulm and H. P. Fritz, Chem. Ber. **93**, 2167 (1960); (b) F. Bottomley, D. E. Paez and P. S. White, J. Amer. Chem. Soc. **103**, 5581 (1981); *ibid.* **104**, 5651 (1982).
70. H. Brunner, H. Kauermann and J. Wachter, J. Organometal. Chem. **265**, 189 (1984).
71. (a) J. Rohrmann, W. A. Herrmann, E. Herdtweck, J. Riede, M. L. Ziegler and G. Sergeson, Chem. Ber. **119**, 3544 (1987); (b) J. Rohrmann, Ph.D. Thesis, Technische Universität München, 1986.
72. (a) J. Huffman, J. Stone, W. Krusell and K. G. Caulton, J. Amer. Chem. Soc. **99**, 5829 (1977); (b) A. Roth, C. Floriani, A. Chiesi-Villa and C. Guastini, *ibid.* **108**, 6823 (1986).
73. L. M. Babcock, V. W. Day and W. G. Klemperer, J. Chem. Soc. Chem. Commun. **1987**, 858.
74. C. J. Besecker, W. G. Klemperer and V. W. Day, J. Amer. Chem. Soc. **104**, 6158 (1982).