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Review

Organometallics of Groups 4 and 5: Oxidation States II and lower

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Abstract

The most recent results obtained on organometallic derivatives of Ti-Zr-Hf and V-Nb-Ta in low oxidation states, especially with CO and arene ligands, are reviewed. The primary reaction products in the $MX_n/Al/AlX_3$/arene system, have been shown to contain the η^6-arene metal complexes in the oxidation state (I) (vanadium) or (II) (niobium, zirconium, hafnium). Stoicheiometric and catalytic reactions of the η^6-arene complexes of titanium and zirconium with disubstituted acetylenes have been studied: the zirconium(II)-tetrachloroaluminato complex $Zr(\eta^6\text{-benzene})(AlCl_4)_2$ was shown to catalyze the trimerization of butyne-2 to hexamethyl-dewar-benzene initially, followed by its isomerization to hexamethylbenzene.

Introduction

The organometallic chemistry of Groups 4 (Ti, Zr, Hf) and 5 (V, Nb, Ta) elements in low oxidation states has some interesting unique features which will be outlined here.

Our attention will be mainly concentrated on carbon monoxide and unsaturated carbocycles as ligands. With both these types of ligand, the binary compounds of the zerovalent metals have not been synthesized yet, or else they represent a rather recent acquisition, or they show some atypical features, as compared to the corresponding compound of other transition metals of Group 6 and beyond. Thus, for example, the well-known dimer-monomer alternation for binary metal carbonyls along the 3d transition series, corresponding to the stabilization of metal-metal bonded dimers for elements with an odd atomic number, breaks down at vanadium. However, this "anomaly", which first appeared when hexacarbonylvanadium(0) was discovered [1] in 1959, is now quite well understandable with the acquired knowledge about the energy of single metal-metal bonds for 3d systems [2] : it is well recognized that single metal-metal bonds of 3d elements are rather weak and therefore other factors, such as steric bulkiness and interligand repulsion can disfavour dimer formation.

Appropriate to this discussion is the well-established notion that within typical transition metals, the metal-metal bond energy normally increases on descending a vertical sequence of elements. The sublimation energies shown in Table 1 for Group 4 and 5 elements [2a], in comparison with the corresponding parameters for the Group 6 elements (with a typical transition behaviour) lead to some conclusions. Firstly, the quite high sublimation energies for Group 4 and 5 elements will not favour the formation of binary organometallics; in the case of metal carbonyls, a further unfavourable factor is represented by the quite elevated positive entropy change of the decomposition process. Secondly, the increase of metal-metal bond energy on descending Groups 4 and 5, suggested by the data of Table 1 and by some other peripheral information [3], may determine the stabilization of dimeric species such as $Nb_2(CO)_{12}$ and $Ta_2(CO)_{12}$ which, however, have not yet been isolated.

Ti	V	Cr
113	123	95
Zr	Nb	Mo
146	185	157.5
Hf	Ta	W
168	186.8	200

Table 1. Sublimation enthalpies (kcal/mol) of some transition elements [2a].

The dimeric species of vanadium, $V_2(CO)_{12}$, is stable at very low temperature only [4a], and hexacarbonylvanadium(0) is a 17-electron long-lived radical. It has a high tendency to undergo one-electron reduction to the stable 18-electron species $[V(CO)_6]^-$, and the conversion of equation 1 is therefore not further complicated by the dimerization of the neutral species $\{Mn_2(CO)_{10}/[Mn(CO)_5]^-$; $Co_2(CO)_8/[Co(CO)_4]^-\}$. The exceptionally high substitutional kinetic lability of $V(CO)_6$ has been attributed [4b,4c] to the radical behaviour of this compound.

$$V(CO)_6 + e^- \longrightarrow [V(CO)_6]^- \qquad 1$$

Hexacarbonylvanadium(0) behaves as an electron acceptor vis-à-vis several reducing agents, namely bismesitylenevanadium(0) [5], bis cyclopentadienylvanadium(II) in the presence of carbon monoxide [6], biscyclopentadienylcobalt(II) [7] and several carbonylmetalates [7]. Moreover, hexacarbonylvanadium(0) reduces 9,10-phenanthrenequinone [8] and metallocenes [7] .

In contrast to the well-established chemical and physical properties of $V(CO)_6$, no experimental evidence for the stable hexacarbonyl species of niobium(0) and tantalum(0) has been reported yet [9]. The hexacarbonylniobate(-I), $[Nb(CO)_6]^-$, and hexacarbonyltantalate(-I), $[Ta(CO)_6]^-$, anions are well established and considerable improvements have recently been made in their preparative procedures [10]. $NaNb(CO)_6$ Can now be prepared without any particular difficulty by operating at atmospheric pressure of carbon monoxide and at room temperature. On the other hand, the preparation of $[Ta(CO)_6]^-$ is still not completely satisfactory: to reach low oxidation states is frequently difficult with 5d elements, and, in this connection, it may be recalled that low yields of $HfCp_2(CO)_2$ are obtained [11a], under the conditions usually providing satisfactory yields of the corresponding titanium(II) and zirconium(II) species [11b].

Concerning zerovalent complexes of unsaturated carbocyclic ligands, significant differences exist between vanadium on one hand and niobium and tantalum on the other hand. As a matter of fact, while the zerovalent $V(arene)_2$ complexes have been known for many years [5,12], the corresponding zerovalent systems of niobium and tantalum have been prepared only recently [13] by the metal vaporization technique. Some years ago [5,12] it had been established that the so-called reductive Friedel-Crafts reaction (*i.e.*, the $MCl_n/Al/AlCl_3/arene$ system, first used by Fischer and Hafner [14]), as applied to VCl_n, is able to reduce vanadium to the I oxidation state, which undergoes further reduction to the zerovalent state in aqueous solution [12], or disproportionation to vanadium(0) and vanadium(II) + vanadium(III) [5,15]. The most recent work from these laboratories has clarified the behaviour of niobium under the conditions normally used for vanadium, and this point will be discussed.

Coming now to the Group 4 elements, much effort appears to be necessary in order to acquire a satisfactory knowledge of low-valent organometallic compounds in this area of the Periodic Table. At the beginning of our studies in this field, no binary carbonyl derivatives of titanium, zirconium or hafnium [16] were known. While our work was in progress, Ellis and coworkers in the United States reported the preparation of the hexacarbonylzirconate(-II) anion, $[Zr(CO)_6]^{2-}$, as the 15-crown-5 stabilized potassium derivative [17a]. The corresponding titanium species can be obtained [17b] in a similar way (reaction 2), while the formation of the $[Hf(CO)_6]^{2-}$ anion [18], requires the use of a tetracarbonyltridentate-tertiaryphosphine complex, $Hf(CO)_4(trmpe)$, trmpe = $H_3CC(CH_2PMe_2)_3$, for its preparation (reaction 3).

$$MCl_4(ether)_n \xrightarrow[\text{15-crown-5, CO}]{KC_{10}H_8} [K(\text{15-crown-5})_2]_2[M(CO)_6] \qquad 2$$

M = Ti, Zr; ether = THF, n=2; ether = DME, n=1

$$M(CO)_4(trmpe) \xrightarrow[\text{Cryptand 2.2.2, CO}]{KC_{10}H_8} [K(cryptand)]_2[M(CO)_6] \qquad 3$$

M = Ti, Zr, Hf

As far as the arene as ligand for Group 4 metals is concerned, after the original discovery [19] of the titanium(II) derivatives $Ti(\eta^6\text{-arene})[(\mu\text{-}Cl)_2(AlCl_2)]_2$, obtained by reaction 4, the corresponding zirconium(II) and hafnium(II) complexes had not been reported in the literature at the biginning of our study, although a bonding arrangement similar to that crystallographically established for titanium [20] would be possible also for zirconium

$$3\ TiCl_4 + 2\ Al + 4\ AlCl_3 + 3\ \text{arene} \longrightarrow 3\ Ti(\eta^6\text{-arene})[(\mu\text{-}Cl)_2(AlCl_2)]_2 \qquad 4$$

and hafnium. At any rate, the use of the $MX_4/Al/AlX_3$/arene system with the zirconium(IV) and the hafnium(IV) halides appeared to be an interesting entry to low-valent organometallics of these two metals.

This review-article updates the previous one appeared in this journal in 1986 [21].

Organometallics of Group 5 elements

A) Carbonyl derivatives

The search for zerovalent binary derivatives of niobium and tantalum has been extensive. The first attempts aimed at obtaining zerovalent complexes of niobium dealt with the oxidation of the $[Nb(CO)_6]^-$ anion. By analogy with the corresponding vanadium system, which undergoes a one-electron transfer to proton [22,23], with H_2 formation, several attempts were made to treat a suspension of $NaNb(CO)_6$ with dry HCl in a hydrocarbon solvent. Under these conditions, however, the dimeric anion of niobium(I), $[Nb_2(\mu\text{-}Cl)_3(CO)_8]^-$, was formed, which was structurally characterized as the protonated-thf derivative $C_4H_8OH\,[Nb_2(\mu\text{-}Cl)_3(CO)_8]\cdot C_4H_8O$.

Several other oxidizing agents were tried in the attempt to promote the one-electron transfer from $[Nb(CO)_6]^-$, such as Cu(I), Cu(II), Ag(I), Fe(III) and others. In all these cases, the dimeric $[Nb_2(\mu\text{-}X)_3(CO)_8]^-$ was the oxidation product [7], the dimeric halide-bridged anion being apparently our thermodynamic sink in the presence of oxidizing metal halides. In order to establish the conditions for a one-electron transfer process to occur from $[Nb(CO)_6]^-$ to give a zerovalent niobium carbonyl complex, some oxidations were attempted with silver(I) salts containing poorly coordinating anions. The reactions of AgX (X = NO_2, BF_4) with $[M(CO)_6]^-$, led to the formation of the mixed silver-niobium (or tantalum) carbonyl clusters, which, however, could not be completely characterized, in view of their low stability at room temperature [24]. On the other hand, by using the tertiary-phosphine substituted complexes $NEt_4[M(CO)_4dmpe]$ [dmpe = 1,2-bis(dimethylphosphino) ethane], the mixed silver-niobium (or tantalum) carbonyl complexes shown in equation 5 were prepared, isolated and studied crystallographically [25].

The single crystal X-ray diffractometric experiments carried out on the $Ag_3M_3(CO)_{12}(dmpe)_3$ complexes have established that the Group 5 metals and the

$$3\,NEt_4[M(CO)_4(dmpe)] + 3\,AgX \longrightarrow Ag_3M_3(CO)_{12}(dmpe)_3 + 3\,NEt_4X \qquad 5$$

$$(M{=}Nb,Ta;\ X{=}NO_2,BF_4)$$

silver atoms constitute a planar hexanuclear heterobimetallic raft (see Figure 1). Concerning the assignment of an oxidation state to niobium and tantalum in these complexes, which is a relevant point in the discussion, the following experimental observations are to be taken into consideration. a) The IR $\tilde{\nu}_{CO}$'s are observed at 1930m-s and 1842 vs cm^{-1} (M=Nb), or at 1928m-s and 1843vs cm^{-1} (M=Ta) in tetrahydrofuran as solvent. This spectrum agrees with that expected for a local C_{4v} symmetry of the carbonyl groups (A_1+ E), thus showing that the solid-state structure is maintained in solution. These IR data should be compared with those of the tertiary-phosphine substituted carbonylmetalates(-I) NEt_4

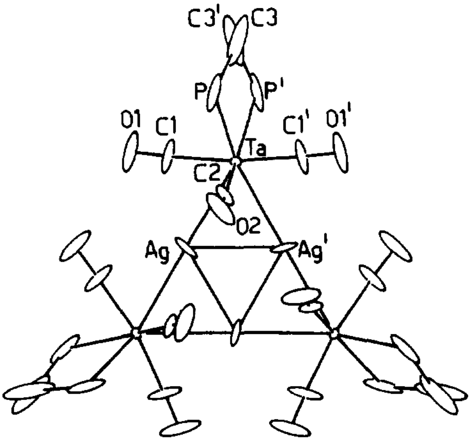


Figure 1. Molecular structure of $Ag_3M_3(CO)_{12}(dmpe)_3$ [25]. Two of the carbonyl groups have been omitted for clarity.

[$M(CO)_4(dmpe)$] showing $\tilde{\nu}_{CO}$'s at 1898s, 1760vs and 1735sh cm^{-1} (M=Nb) or at 1892s, 1775vs and 1740sh cm^{-1} (M=Ta) in the same solvent. This comparison suggests that on going from the anionic precursor to the uncharged silver-containing products, a considerable decrease of the electronic charge on niobium (or tantalum) has occurred, which is what one would expect as the consequence of an increased oxidation state. b) The Ag-Ag distance in the hexanuclear cluster [2.8424(5) Å (M=Nb) and 2.818(8) Å (M=Ta)] is similar to that in the metal (2.883 Å) [26], whereas a significantly shorter one would be expected if the bonding situation in the system favoured an electronic delocalization onto the Group 5 metal. c) Silver slowly separates from solutions of the cluster, which incidentally requires the IR spectra to be measured on freshly prepared solutions. d) The reaction of the hexanuclear cluster with HI, as shown in equation 6, produces silver metal, molecular hydrogen and the iodo niobium(I) or tantalum(I) species $MI(CO)_4dmpe$. An electron delocalization towards the metal M in the cluster would presumably induce the formation of the products of the alternative, not observed, reaction 7. In this connection, it is important to realize

$$Ag_3M_3(CO)_{12}(dmpe)_3 + 3\,HI \longrightarrow 3\,Ag + 3\,MI(CO)_4(dmpe) + 3/2\,H_2 \tag{6}$$

$$Ag_3M_3(CO)_{12}(dmpe)_3 + 3\,HI \not\longrightarrow AgI + 3\,MH(CO)_4(dmpe) \tag{7}$$

that the hydrido complexes $MH(CO)_4(dmpe)$ are well established [27]. We therefore suggest that the reaction represented in equation 6 is triggered by a concerted attack by the two components of HI oriented as shown in Figure 2.

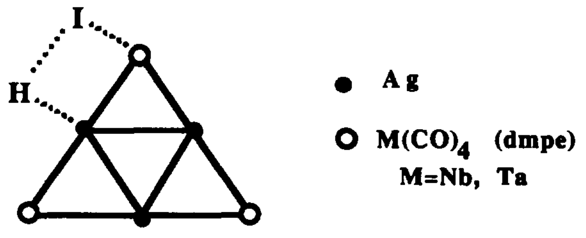


Figure 2. Attack of HI to the $Ag_3M_3(CO)_{12}(dmpe)_3$ complexes.

We conclude that the structural, spectroscopic and chemical data are best explained by assuming that the hexanuclear cluster of niobium or tantalum contains the zerovalent Group 5 metal and bare silver atoms.

B) Arene derivatives

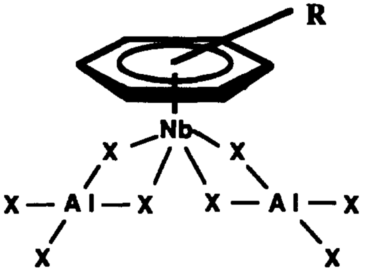
Earlier chemical evidence [5,12] had indicated that a bis(mesitylene) vanadium(I) compound was produced under the conditions of the Fischer-Hafner synthesis ($VCl_n/Al/AlCl_3$/mes; mes = 1,3,5-trimethylbenzene); however, the exact nature of this product had not completely elucidated. The tetrachloroaluminato derivative of the bis-mesitylene vanadium(I) cation has now been isolated and structurally characterized [28a]. The structure consists of discrete $[Vmes_2]^+$ cations and $AlCl_4^-$ anions. The cation contains symmetrically bonded, substantially parallel 1,3,5-trimethylbenzene rings in an eclipsed conformation. Thus, vanadium(I) in this system is reluctant to expand its coordination number by covalently bonding a bridging chloride from the $AlCl_4$ moiety.

We also recently turned our attention to the η^6-arene complexes of niobium and tantalum. Several years ago, Fischer and Röhrscheid [28b] reported the reaction of $NbCl_5$ with the reducing system $Al/AlCl_3$ in the presence of hexamethylbenzene (HMB) and isolated a trinuclear niobium complex $[Nb_3Cl_6(\eta^6\text{-HMB})_3]^+$ and the dimeric compound $Nb_2Cl_4(\eta^6\text{-HMB})_2$ from the reaction mixture **after treatment with water** at low temperature. Our recent work [29] has established the nature of the primary products of the reaction in the $NbX_5/Al/AlX_3$/arene system and the likely connection of the new data with the earlier findings by Fischer and Röhrscheid. The products obtained from the reduction of NbX_5 with the Al/AlX_3 system are represented as reactions 8 and 9. Single crystals of the products of reaction 8 could not be obtained and therefore their structure could not be established conclusively. However, it is be-

$$NbX_5 + Al + AlX_3 + HMB \longrightarrow \underset{X = Cl,\ Br}{(\eta^6\text{-HMB})Nb(AlX_4)_2} \tag{8}$$

$$2\,(\eta^6\text{-HMB})Nb(AlBr_4)_2 \xrightarrow[\text{Room temperature}]{\text{THF}} Nb_2Br_4(\eta^6\text{-HMB})_2 + 2\,AlBr_3 \tag{9}$$

lieved that the tetrahaloaluminato complexes of equation 8 should contain a symmetrically bonded arene ligand and bridging halides, similar to what already found [20] for the corresponding titanium(II) complexes. The niobium(II) complex is paramagnetic for one unpaired electron [30], as required for a monomeric formulation. In the case of the HMB-bromo derivative, decomplexation of the AlX_3 moiety occurred with tetrahydrofuran, the $Nb_2Br_4(\eta^6\text{-HMB})_2$ compound being isolated under these conditions. The latter was studied by X-ray diffractometry and found [29] to have a centrosymmetric molecular structure, i.e. with four bridging bromides and one HMB ligand *per* niobium atom. The niobium atoms are 2.760(2) Å apart. The literature [31] reports a few dimeric niobium(II) complexes (a metal centre of d^3 configuration) and the available structural parameters span quite a large range of values, depending on the nature of the ligand. The presence of a single niobium-niobium bond in our compound is in agreement with a total counting of 18 valence electrons for the central metal atom and with the diamagnetism of the chloride analogue, as reported by Fischer and Röhrscheid [28b].



In their pioneering work on the $NbCl_5$ / Al / $AlCl_3$ / HMB system, Fischer and Röhrscheid [28b] reported a product of the same stoicheiometry as that of equation 9, obtained in low yields after treating the crude reaction mixture with water at 0 °C, the major component being the trinuclear compound $[Nb_3Cl_6(\eta^6\text{-HMB})_3]$ Cl. Our work, carried out on the bromide derivative, is relevant to their findings. We could confirm that the low-temperature treatment with water of the supposedly mononuclear compound of niobium(II), led to the evolution of molecular hydrogen and to the formation of the trinuclear complex $[Nb_3Br_6(\eta^6\text{-HMB})_3]$ Br (reaction 10). On the other hand, the dimeric complex of equation 9 is unaffected by water at low temperature over short periods of time. We therefore conclude that the original reaction mixture obtained by Fischer and Röhrscheid

$$3\ Nb(\eta^6\text{-HMB})(AlX_4)_2 + H^+ \longrightarrow [Nb_3X_6(\eta^6\text{-HMB})_3]^+ + 1/2\ H_2 + 6\ AlX_3 \qquad 10$$

contained the tetrachloroaluminato derivative of niobium(II), which underwent partial $AlCl_3$ decomplexation in the presence of water and extensive oxidation to the trinuclear Nb(II)-Nb(II)-Nb(III) complex in the presence of the strongly acidic medium arising from the hydrolysis of $AlCl_3$.

The monomeric niobium(II) tetrahaloaluminato complexes arising from the $NbCl_5/Al/AlCl_3$/mes system can be further reduced by the excess aluminium still present in the crude reaction mixture, simply by addition of an ethereal solvent (tetrahydrofuran or 1,2-dimethoxyethane). This finally leads to the zerovalent bis-mesitylene complex, $Nb(mes)_2$ [29], which represents the first example of a zerovalent organometallic compound of niobium not requiring the use of the metal vapour technique for its preparation.

Quite interesting is the chemistry of $Nb(mes)_2$ towards CO. A smooth reaction occurs at room temperature and atmospheric pressure, more readily at pressures of CO above atmospheric. The reaction of equation 11 is formally similar to that observed with $V(mes)_2$, except that the redox carbonylation of niobium(0) occurs more readily. In comparative experiments carried out at room temperature and at 5 atm of CO pressure, the vanadium system is substantially unaffected by CO. The ionic $[V(mes)_2]\ [V(CO)_6]$ [32] can therefore be obtained only under more drastic conditions.

$$Nb(mes)_2 + 7\ CO \longrightarrow [Nb(mes)_2CO]\ [Nb(CO)_6] + 2\ mes \qquad 11$$

The different behaviour between $V(mes)_2$ and $Nb(mes)_2$ in their reaction with CO can be compared with the reductive carbonylation systems of vanadium and niobium, **A** and **B**, respectively, shown below. While vanadium requires high temperatures and pressures to be reductively carbonylated to $[V(CO)_6]^-$, $NbCl_5$ is converted to $[Nb(CO)_6]^-$ under much milder conditions (room temperature and atmospheric pressure). The systems **A** and **B** operate on different metal

A [23a]: $VCl_3/Mg/Zn/pyridine/CO \longrightarrow [V(CO)_6]^-$

B [13a,13b]: $NbCl_5/Mg/Zn/pyridine/CO \longrightarrow [Nb(CO)_6]^-$

substrates and therefore cannot be directly compared. Different rates may in fact be involved in the preliminary redox steps of the reaction. On the other hand, the just mentioned results obtained with the η^6-arene complexes of vanadium(0) and niobium(0) suggest that low-valent niobium has generally easier kinetic pathways for the access of carbon monoxide to its coordination sphere. This is a further example of the well-established [33] kinetic lability of the 4d transition metal systems with respect to their 3d analogues. The behaviour of $Ta(mes)_2$ toward CO is not yet known. The extension of this work to tantalum should provide this information: however, it is predictable that $Ta(mes)_2$ will resemble $V(mes)_2$ rather than $Nb(mes)_2$.

The products of equation 11 are believed to be formed by gradual substitution of the arene ligand from the coordination sphere of niobium, followed by the electron transfer between a carbonyl-containing zerovalent niobium complex as electron acceptor and $Nb(mes)_2$ still present in solution. In view of the already mentioned unavailability of the carbonyl derivative of niobium(0), this suggestion could not be validated. However, it has been shown that $V(CO)_6$ does in fact react with $Nb(mes)_2$ as expected, namely according to equation 12.

$$V(CO)_6 + Nb(mes)_2 + CO \longrightarrow [Nb(mes)_2CO]\,[V(CO)_6] \qquad 12$$

The bis-mesitylenecarbonyl niobium(I) cation has a carbonyl stretching vibration (THF) at 1990 cm^{-1}, consistent with the oxidation number +I for the metal and a structure with bent arene ligands to leave the appropriate room for the carbonyl group [29b].

Work in the field of the carbonyl derivatives of Group 5 elements is presently carried out aimed at two main objectives: a) the isolation of other niobium(0) and tantalum(0) carbonyl derivatives, in addition to the silver hexanuclear clusters already acquired; b) improving the preparative procedures for low-valent tantalum organometallics, which appear to be the most elusive one. The metal-vapour technique, which is very helpful in detecting new species and in studying their behaviour (especially the thermal behaviour) has some limitation for large-scale preparations, particularly when elevated ΔH's of sublimation are involved, as in the case of niobium and tantalum.

Organometallics of Group 4 elements

After the pioneering work carried out about thirty years ago on the titanium(II) η^6-arene complexes of formula $Ti(\eta^6\text{-arene})[(\mu\text{-}Cl)_2(AlCl_2)]_2$, these systems have been investigated mainly from the viewpoint of their interest as polymerization catalytic precursors [19,34].

Our most recent work in this field has dealt mainly with: a) studying the effect of the halide ligand on the structure and properties of the titanium(II)-arene complexes; b) extending the synthesis of the η^6-arene complexes to other Group 4 elements; c) investigating the interaction of these systems with triply bonded molecules such as carbon monoxide and substituted acetylenes. We shall briefly describe the most relevant results of these studies.

Preliminary to point a) was the search for appropriate preparative methods for the tetrahalides of titanium, zirconium and hafnium. In the case of titanium, a solution to this problem was already available in the literature and we limited ourselves to quantifying the results. $TiCl_4$ Was found [35] to rapidly undergo exchange with HBr or HI in heptane, to yield $TiBr_4$ or TiI_4, respectively, in good yields and in excellent chemical purity. The driving force of the exchange reaction 13 originates from the formation of HCl in solution. A simple calculation based on the $\Delta G°_f$ [36] shows that the $\Delta G°$ of the exchange reaction is -4.7 kcal/mol (X=Br) or -5.4 kcal/mol (X=I). Accordingly, we found that substantially quantitative yields of the required product are obtained through the exchange

$$TiCl_4 + 4\,HX \longrightarrow TiX_4 + 4\,HCl \qquad 13$$

reaction. These reactions and the equally successful one with $TiCp_2Cl_2$ [35], occur readily: mechanistically, they are believed to proceed *via* the preliminary coordination of HX to the metal, followed by proton shift to the adjacent position occupied by Cl and by the elimination of HCl; see figure 3 for the suggested intermediate in the $TiCp_2X_2$/HX exchange. This interpretation is supported by the reported isolation [37a] of unstable complexes of HX with the pentacarbonyltungsten(0) fragment; also relevant to this point is the recent preparation of metal complexes of halogenated hydrocarbons [37a]. A spectroscopic study [38] of the $TiCp_2F_2$-HCl system at low temperature has suggested a hydrogen-bond interaction with the metal-coordinated fluoride. Although this is also a possibility, we prefer the associative mechanism of Figure

3: in this connection, it is relevant that $ZrCp_2H_2$ and $HfCp_2H_2$ are known [39] to coordinate CO at low temperature.

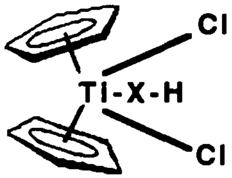


Figure 3: Possible intermediate in the reaction of $TiCp_2Cl_2$ and HX.

The $TiX_4/Al/AlX_3$/arene, X=Br,I, system gave the expected Ti(η^6-arene)$(AlX_4)_2$ complexes. The reasoning behind the search for these compounds is that the Ti-X bond is believed to decrease its energy in the Cl > Br > I sequence, while, on the other hand, hydrolysis of this bond is expected to become less important in the same sequence. Thus, the bromo- and the iodo-η^6-arene complexes of titanium(II) were expected to be more easily obtained from TiX_4, and less prone to undergo hydrolysis, thus allowing the isolation of new products to be carried out.

Several bromo- and iodo derivatives of titanium(II) of general formula Ti(η^6-arene)$[(\mu\text{-}X)_2(AlX_2)]_2$ were prepared through the usual $TiX_4/Al/AlX_3/$ arene system run at room temperature, followed, in the case of the bromo derivative only, by a short period of time at the reflux temperature of the reaction mixture. The electronic spectra of these compounds, measured in the parent hydrocarbon as solvent, show a three-band pattern with a shift to lower wavelengths in the sequence I > Br > Cl: this is in agreement with the usual relative position of the halide in the spectrochemical series [40].

The titanium(II) complexes react with CO in the parent hydrocarbon as solvent at about -20 °C to give red-brown precipitates of analytical composition $Ti(arene)_2(CO)_2\,(AlX_4)_2$, X = Br,I. On the contrary, intractable oils or solids with hardly reproducible analytical data, characterized by an exceedingly low stability to air and moisture, were obtained from the chloro derivative Ti(η^6-arene)$[(\mu\text{-}Cl)_2(AlCl_2)]_2$ and CO under similar conditions. The bromo derivatives were studied with special care and, on the basis of the spectroscopic data (the $\tilde{\nu}_{CO}$'s depend on the nature of both the halide and the arene ligand), the structure shown in Figure 4 was suggested for these compounds. If the structural assignment is correct, this amounts to saying that CO is capable of displacing two of the four halide ligands from the coordination sphere of titanium, the second arene moiety, analytically detected, being probably incorporated within the crystal lattice. Since it is unlikely that the Ti-CO bond energy is higher than that of the Ti-Br bond, it is believed that the driving force to the formation of the carbonyl complexes of titanium(II) originates mainly from the lattice energy of the new ionic solid [a] .

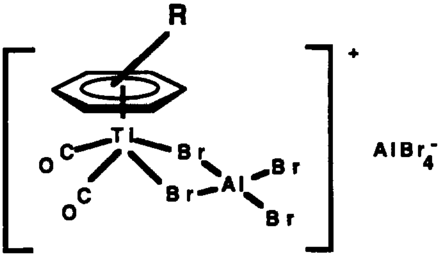


Figure 4. Suggested structure for the products of the reaction between Ti(η^6-arene)[(μ-Br)$_2$AlBr$_2$]$_2$ and carbon monoxide.

It is interesting to note that the alternative formulation of these compounds as containing the still unknown [Ti(η^6-arene)$_2$(CO)$_2$]$^+$ cation, is not justified by the experimental data. This cation would be isoelectronic with the stable species TiCp$_2$(CO)$_2$ [41] and [VCp$_2$(CO)$_2$]$^+$ [42]. From this viewpoint, the isolation of the isoelectronic (as far as the valence electrons are concerned) niobium(I) species, [Nb(mes)$_2$(CO)]$^+$, acquires some specific relevance, since the presence of two arene ligands *per* metal atom with CO as additional ligand is a rather rare event

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[a] It is noteworthy that in the course of these studies, particularly concentrated on the toluene-bromo derivative, Ti(η^6-toluene)[(μ-Br)$_2$AlBr$_2$]$_2$, as reference compound, a parasitic absorption of CO subsequent to the formation of the titanium-carbonyl species was observed. This was shown to be due to the formation of p-tolualdehyde [actually, as the AlBr$_3$ adduct, AlBr$_3$·(p-MeC$_6$H$_4$CHO)]: AlBr$_3$, but not AlCl$_3$ or AlI$_3$, was found to promote the carbonylation of toluene at room temperature and at atmospheric pressure.

$$AlBr_3 + CO + C_6H_5Me \longrightarrow AlBr_3\cdot(p\text{-}MeC_6H_4CHO)$$

and is mostly limited to early transition elements [43] for obvious reasons of electron counting.

The extension of this chemistry to zirconium and hafnium was straightforward, with some difficulties again with the 5d element in terms of reduction and isolation of the products. The $MX_4/Al/AlX_3$/arene system [44], M=Zr, was studied in some detail [45] and our new data, obtained under rigorous exclusion of water, allowed the earlier report [28b] on the $ZrCl_4/Al/AlCl_3$/HMB system (treated in a subsequent step with water at low temperature) to be interpreted under an unified concept.

The primary products of the reaction are again the zirconium(II)-arene complexes of formula $Zr(\eta^6\text{-arene})(AlX_4)_2$. In the case of the symmetric benzene and HMB, the corresponding solid products could be isolated and analyzed. The identification of the other compounds, including those of hafnium, was based on spectroscopic data. Definite proof of the oxidation state II for zirconium in these systems came from the syn-proportionation reaction between $ZrBr_4$ and $Zr(\eta^6\text{-benzene})(AlBr_4)_2$ giving $ZrBr_3$ in good yields, according to the stoicheiometry of equation 14.

$$Zr(\eta^6\text{-benzene})(AlBr_4)_2 + ZrBr_4 \longrightarrow 2\,ZrBr_3 + \text{benzene} + 2\,AlBr_3 \qquad 14$$

In addition to the reactions with CO, already mentioned for the titanium(II)-arene system, those with substituted acetylenes was studied for the η^6-arene derivatives of titanium(II) and zirconium(II).

The titanium(II) compound, $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2AlBr_2]_2$ reacts with butyne-2 to give a ligand synthesis reaction (*via* trimerization), followed by an arene exchange, according to equation 15. This reaction probably occurs through the intermediacy of another complex, very likely containing a tetramethylcyclobutadiene complex of formula $Ti(\eta^4\text{-}C_4Me_4)[(\mu\text{-}Br)_2AlBr_2]_2$.

$$Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2AlBr_2]_2 + 3\,C_2Me_2 \longrightarrow Ti(\eta^6\text{-HMB})[(\mu\text{-}Br)_2AlBr_2]_2 + C_6H_5Me \qquad 15$$

The reaction of $Ti(\eta^6\text{-toluene})[(\mu\text{-}Br)_2AlBr_2]_2$ with C_2Ph_2 did not proceed beyond the stage of the 1:2 molar ratio and the tetraphenylcyclobutadiene complex of formula $Ti(\eta^4\text{-}C_4Ph_4)[(\mu\text{-}Br)_2AlBr_2]_2$ was isolated and structurally characterized [46].

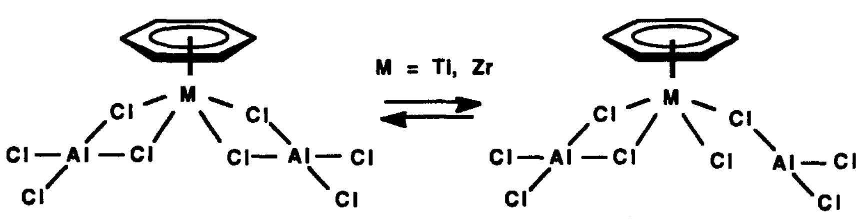
Cyclotrimerization of substituted acetylenes is an interesting reaction and many metal systems are known to carry out this transformation[47]. In the case of butyne-2, it generally leads to hexamethylbenzene (HMB) [48]. To the best of our knowledge, one system only [51] is known to catalyze the trimerization of C_2Me_2 to hexamethyl-dewar-benzene (HMDB), namely $AlCl_3$, as reported by Schäfer some years ago. We have successfully repeated [50] the experiments by Schäfer, mentioned in a preliminary report [51a] and in a review-article [51b]: by operating at 19.8 ± 0.1 °C, C_2Me_2 is converted to HMDB and HMB, the concentration of HMB increasing with time at the expenses of HMDB, thus showing that isomerization is slower than trimerization.

We have also compared $AlCl_3 \cdot C_4Me_4$, and the Ti(II)- and the Zr(II)-tetrachloroaluminato complexes, as far as their ability to cyclotrimerize butyne-2 to HMDB is concerned. The experiments show that the zirconium system appears to be the best catalyst for the formation of HMDB, better than $AlCl_3$ itself or its adduct with C_4Me_4 [52], and much better than the titanium(II) analogue. Particularly significant is the comparison between the zirconium and the titanium systems, which suggests a specific function of the Group 4 element on the mechanism of trimerization. Equilibria 16 could be operating in solution. On the other hand, beside being unrealistic, this hypothesis is ruled out by the

$$Zr(\eta^6\text{-benzene})(AlCl_4)_2 \rightleftharpoons Zr(\eta^6\text{-benzene})Cl(AlCl_4) + AlCl_3 \qquad \text{16a}$$

$$Zr(\eta^6\text{-benzene})(AlCl_4)_2 \rightleftharpoons Zr(\eta^6\text{-benzene})Cl_2 + 2\ AlCl_3 \qquad \text{16b}$$

time dependence of both HMDB and HMB formation, showing that there is a specific role of the Group 4 element in this reaction. We believe that an equilibrium of the type 17 is operative and that the vacant coordination position



(17)

at aluminium becoming available at the right-hand side of equilibrium 17 may be responsible for the trimerization of C_2Me_2 to HMDB, while the Group 4 element may become important in the subsequent isomerization.

Relevant to the latter suggestion is the product which has been isolated from the reaction of C_2Ph_2 with the zirconium(II) complex $\mathrm{Zr(\eta^6\text{-}benzene)(AlCl_4)_2}$. This compound, $\overline{\mathrm{Zr(CPh(CPh)_4CPh}}\mathrm{)[(\mu\text{-}Cl)_2(AlCl_2)]_2}$, is a rather rare example of a seven-membered carbocyclic structure including zirconium [50], arising from the trimerization of diphenylacetylene. The seven-membered ring has two sets of C-C distances and possesses the conformation shown in Figure 5.

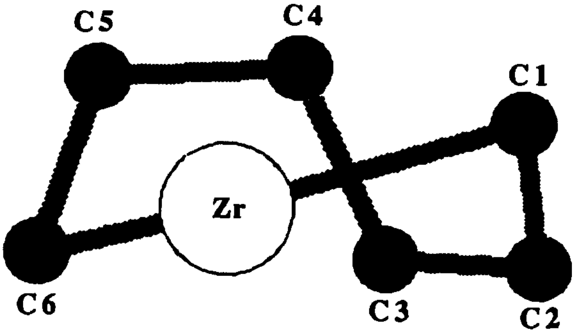


Figure 5. The seven-membered ring of $\overline{\mathrm{Zr(CPh(CPh)_4CPh}}\mathrm{)[(\mu\text{-}Cl)_2(AlCl_2)]_2}$ [50]. Phenyl rings have been omitted for sake of clarity.

Conclusions

The low oxidation states of Group 4 and 5 elements, from II to zero, represent a still largely unexplored field of research. On the other hand, the isolation of low-valent complexes may become particularly relevant for mechanistic studies involving the polymerization of unsaturated substrates. The great affinity of these metals for oxygen-containing substrates and for halides, requires a different approach to the problem of their reduction. The $MX_n/Al/AlX_3/$ arene system is a very appropriate one to reach the oxidation state II for niobium and for Group 4 elements starting from their readily available halides. In this case, a considerable stabilizing effect is played by both the arene ligand and the halidecomplexed AlX_3 moiety.

It is believed that work in this frontier of metals at the borderline between transition and main group elements may become quite important in dealing with low-valent metal complexes of main group elements, a problem which is still at an early stage [53].

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