# VANADIUM, NIOBIUM AND TANTALUM

## ANNUAL SURVEY COVERING THE YEAR 1975

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The number of publications in this area has remained fairly constant, with a great deal of attention being paid to cyclopentadienyl derivatives. A review on the organometallic chemistry of each metal has been published in Russian (1).

## CRYSTAL STRUCTURES

The crystal and molecular structures of seven complexes have been determined, six by X-ray diffraction and one by electron diffraction. The structures of $(\eta^5\text{-MeC}_5H_4)_2VCl_2$ and of the corresponding titanium derivative have been investigated in order to delineate the bonding description of the unpaired electron in $Cp_2VL_2$* compounds, when L is changed. This is one of three significant papers by Dahl and collaborators which give a new outlook on bonding in $Cp_2M$ complexes. They will be described more fully in the section on cyclopentadienyl derivatives.

$Cp_2NbBH_4$ has been found to be structurally analogous to the corresponding titanium compound, with a double hydride bridge between niobium and boron (3). In $[Nb(C_8H_8)_3]\,[AsPh_4]$, two COT ligands are $\eta^3$- bonded while the other is closer to $\eta^4$- bonded (4).

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*Cp = $\eta^5$- cyclopentadienyl

Vanadium, Niobium and Tantalum, Annual Survey covering the year 1974 see J. Organometal. Chem., 95(1975)317-335.

In the complex, $Cp_2Nb(C_2H_4)(C_2H_5)$, the symmetrically bound ethylene and σ- bonded ethyl ligands lie in the plane between the Cp rings (5), the Nb-C bond lengths being surprisingly similar (2·3Å). The methylene complex, $Cp_2Ta\ Me(CH_2)$ has eclipsed Cp rings, the plane of the $CH_2$ being perpendicular to the C-Ta-C plane. This orientation, coupled with a high barrier to rotation, suggests a full double bond between Ta and $CH_2$ (6), the bond length being 2.026Å.

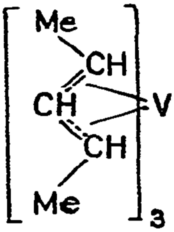
The structure of $CpNb(CO)(Ph_3GeC{\equiv}CPh)_2$ is similar to that of the corresponding tolan complex, but with shortened triple bonds (7). A gas phase electron diffraction study of $Cp_2V$ showed eclipsed Cp rings. The structure is compared with those of the first row $Cp_2M$ compounds (8). The structure of the tantalum carbyne complex, $[(Me_3CCH_2)_3Ta{\equiv}CCMe_3]Li.dmp$, the preparation of which is described in the next section, has a short Ta-C bond (1.76Å) compared with a Ta-C single bond (2.25Å). The coordination about the tantalum is essentially tetrahedral, the lithium lying between the carbyne ligand and the amine and possibly weakly associated with one neopentyl group (9).

ALKYL AND ARYL DERIVATIVES (see also Cyclopentadienyl)

In an attempt to effect insertion of a nitrile group into Nb-C and Ta-C bonds the action of organic nitriles on $MeNbCl_4$, $Me_2NbCl_3$ and $MeTaCl_4$ has been studied (10). 1:1 Complexes were obtained with $C_6F_5CN$, $ICH_2CN$, $ClCH_2CN$ and acrylonitrile ($CH_2{=}CHCN$). No addition to the unsaturated system took place except in the case of tetracyanoethylene to which the halides, $Me_xMCl_{5-x}$, where M=Nb or Ta, appeared to add 1,4.

Insertion of isonitriles, RNC, where R=Me or t-Bu, into the halides of vanadium (also titanium, zirconium and hafnium) occurred readily, apparently via an intermediate adduct. Multiple insertion may occur for R=Me, but only single insertion for R=t-Bu, probably for steric reasons. The compounds obtained, of type $[MCl_3\{C(Cl)=NBu\}(CNBu)]_2$ or $M\{C(Cl)=NMe\}_4$, are poorly soluble and at least dimeric, probably with imino-nitrogen bridges (11).

The anionic vanadium species, $[V(CO)_4.DIARS]^-$, where DIARS = o-phenylenebis(dimethylarsine), has been formed by photolysis of $[Et_4N][V(CO)_6]$ in the presence of the arsine. The tetracarbonyl dianion was shown to react with $CF_3I$, $BrMn(CO)_5$ and $Ph_4AsHCl$, among other halides, to form compounds of type $RV(CO)_4.DIARS$, where R=Me, $Mn(CO)_5$ or H, and with allyl chloride to give $h^3$-$C_3H_5V(CO)_3.DIARS$. Infrared, $^1$H-NMR and chemical properties are described (12). Tris-π-pentenylvanadium was prepared from pentenylmagnesium chloride and $VCl_4$ at -30° in ether,



The red-violet compound was stable at 0° but could not be completely purified. The splitting of the 460 $cm^{-1}$ band in the infrared spectrum indicated non-equivalence of the pentenyl ligands (13). Ethylvanadiumtris(diethylamide) has been obtained from $ClV(NEt_2)_3$ and EtLi in heptane at -20°, as a green oil, b.p. 71-73°/ 0.001 mm, stable to about 115° under inert gas, and with $\mu_{eff}$ 1.54BM (14).

Measurement of the He(I) and He(II) photoelectron spectra of $WMe_6$ showed three distinct ionizations from W-C bonding orbitals (< 11 eV) and substantial splitting of the methyl C-H bonding region (11 - 16 eV) indicating steric interaction between methyl groups. The spectrum is consistent with octahedral symmetry. The pentamethyltantalum spectrum showed four bands due to Ta-C and a smearing out in the methyl C-H region due to lower symmetry ($D_{3h}$) resulting in only one band of indistinct structure (15). The explosive nature of $TaMe_5$, $WMe_6$ and $ReMe_6$ has been emphasized by Wilkinson (16).

In the carbenoid complex, $Ta(CH_2CMe_3)_3(CHCMe_3)$, reported last year, treatment with BuLi removed the carbene α-hydrogen. In the presence of coordinating ligands, $Ta(CH_2CMe_3)_3[(CCMe_3)(LiL)]$ was formed, where L=N,N'-dimethylpiperazine (dmp),$(THF)_2$,N,N,N',N'-tetramethylethylenediamine, $(p\text{-dioxan})_2$ or 1,2-dimethoxyethane (8). The crystal structure determination of the dmp complex, described in the first section, showed that the complex is best formulated as a "carbyne", $[(Me_3CCH_2)_3Ta{\equiv}CCMe_3]Li.dmp$.

Displacement of benzyl groups as toluene occurred when $(PhCH_2)_4V$ was treated with acetylene and with cyclopentadiene. With diphenylacetylene, bis(hexaphenylbenzene)vanadium was formed as one of the products. The ESR spectra of $(PhCH_2)_4V$ and its decomposition products in the temperature range -178° to +20° were also described (17).

Only one aryl derivative has been described. Phenylvanadium dichloride complexed with $ZnCl_2$ was obtained by the reaction of $VCl_4$ with $ZnPh_2$ in pentane at room temperature. The air-sensitive violet solid was stable to 110° but attempts to remove the $ZnCl_2$ by complexation with ether or THF resulted in breakdown of the vanadium compound. On the basis of its reflectance spectrum the complex was assigned an octahedral structure (18).

CYCLOPENTADIENYL COMPOUNDS

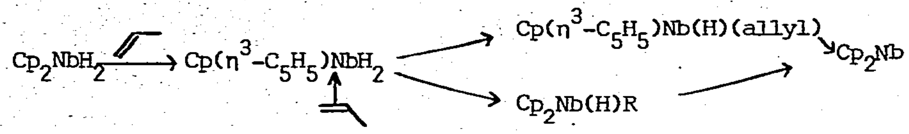
A dilute single crystal electron paramagnetic resonance study of $Cp_2VS_5$, doped in the crystal lattice of diamagnetic $Cp_2TiS_5$ has provided the first quantitative determination of the relative metal orbital character and the directional properties of the unpaired electron in $Cp_2Vl_2$ compounds. The unpaired electron resides primarily on the vanadium atoms in an $a_1$-type molecular orbital composed of $3d_z2$ with a small but significant amount of $3d_{x^2-y^2}$ and virtually no 4s character. These results were taken as evidence for the non-validity of the Ballhausen-Dahl model for $d^1$ and $d^2$ bis(cyclopentadienyl)metal derivatives, and for the inadequacy of the Alcock model (19).

Similar EPR measurements carried out on $(\eta^5\text{-MeC}_5H_4)_2VCl_2$ diluted in the analogous titanium compound, support the premise that the metal orbital characters of the unpaired electron are not strongly dependent on the nature of the ligands, L. The anisotropy in the $^{51}V$ hyperfine coupling interaction arises primarily from the different vanadium orbital character of $3d_z2$ and $3d_{x^2-y^2}$ atomic orbitals. Determination of the structures of the vanadium and titanium chlorides by X-ray diffraction showed that the principal differences between them are:- the Cl-V-Cl bond angle of 87.1° is 6° smaller than the Cl-Ti-Cl bond angle, and the V-Cl bond length of 2.398Å is 0.04Å longer than the Ti-Cl bond length. These bond length differences were in harmony with the unpaired electron in the vanadium(IV) complex occupying a molecular orbital which is antibonding with respect to the V-L bonds. Since most of the spin density on the metal is localized in the xz plane, a significant interaction with the Cl ligands is possible, from which was rationalized both the decrease in the L-M-L angle and the antibonding effect on the M-L bond distance as the number of electrons occupying this MO is increased (2).

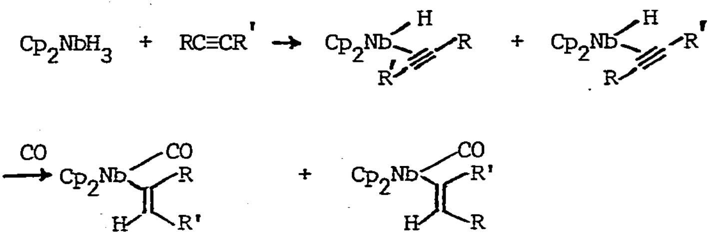
Data from molecular orbital calculations and photoelectron spectra obtained for $d^0$,$d^1$ and $d^2$ titanium and vanadium compounds of type, $Cp_2ML_2$ were found to support the above interpretation from the EPR and crystallographic data regarding the relative contributions of the $d_{z^2}$ and $d_{x^2-y^2}$ atomic orbitals to the molecular orbital composition. Photoelectron spectra of $Cp_2MCl_2$ and $(\eta^5\text{-}MeC_5H_4)_2MCl_2$ were measured and interpreted using the approximate molecular orbital calculations (20). Other authors have recorded the photoelectron spectra of bent bis(cyclopentadienyl) metal complexes containing hydride, methyl, olefin, allyl and carbonyl ligands, including $Cp_2Nb(\eta\text{-}C_3H_5)$ and $Cp_2TaH_3$ during a study of the nature of metal-ligand bonding. The bands were assigned with reference to the molecular orbital structures of the molecules, and substantiate the bonding scheme proposed earlier. The contribution of $d_{x^2-y^2}$ and $d_{z^2}$ orbitals to the upper $a_1$ orbital is also considered (21).

Replacement of $Cl^-$ in $Cp_2VCl$ by non-coordinating $BPh_4^-$ led to $Cp_2V^+$ which coordinated ligands readily giving 16-electron species, $[Cp_2VL]^+[BPh_4]^-$, where L=$Me_2CO$ or pyridine. Displacement of acetone (and also of water from the monoaquo cation) by CO occurred readily giving $[Cp_2V(CO)_2][BPh_4]$, while similar complexes formed with $2C_6H_{11}NC$ and $Ph_2PCH_2CH_2PPh_2$. Mixed ligand complexes, $[Cp_2V(CO)L][BPh_4]$, where L=py, $PEt_3$ or $PBu_3$, were also obtained (22).

In the reaction between $Cp_2NbH_2$ and isobutylene, propylene and ethylene, temperature modulated electron spin resonance studies have indicated the presence of transient paramagnetic niobium(IV)-olefin complexes. On the basis of hyperfine splittings and g factors, the reaction sequence is believed to involve coordination, rearrangement and reductive elimination; e.g.

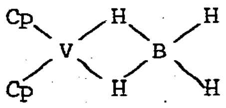


The niobium hydrides have g factors larger than those of the corresponding dialkyl species, roughly in proportion to the number of hydrido ligands present (23). The niobium trihydride, $Cp_2NbH_3$, was prepared from $Cp_2NbCl_2$ reduced with "Vitride" followed by hydrolysis. With dialkylacetylenes, complexes were obtained (two isomers in the case of unsymmetrical acetylenes) which formed alkenylniobium carbonyl derivatives with CO,



Acid hydrolysis then gave cis-olefins, while $MeOSO_2F$ formed methyl olefins (24).

In contrast to other metal tetrahydroborates, bridge-terminal hydrogen exchange in $Cp_2VBH_4$ can be slowed on the NMR time scale sufficiently to observe bridging H at τ 34. Terminal H resonance, although obscured by solvent, was calculated to be at τ 5 for a bidentate geometry,



The vibrational spectra indicate weakening of B-H and strengthening of V-H bonds, leading to shifts in the infrared spectral bands due to bridging hydride to 1745 and 1650 $cm^{-1}$ (25).

The acylation of $Cp_2NbBH_4$ with $CF_3CO_2H$ and $PhCO_2H$ gave $Cp_2Nb(O_2CCF_3)_2$ and $CpNb(O_2CPh)_3$ respectively (26).

The first example of a simple methylene complex, $Cp_2TaMe(CH_2)$, has been prepared by the scheme,

$$Cp_2TaMe_3 \xrightarrow[-CPh_3Me]{+[CPh_3]^+BF_4^-} [Cp_2TaMe_2]^+BF_4^- \xrightarrow{base} Cp_2TaMe(CH_2)$$

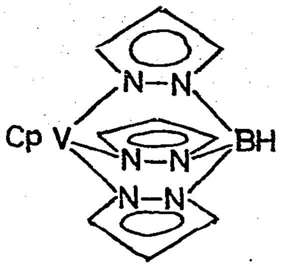
base = $Me_3P(CH_2)$, $LiN(SiMe_3)_2$ or NaOMe

The monomeric buff-coloured crystalline complex was moderately stable in air in the solid state for a short time but quite sensitive in solution. Decomposition over 1-2 days in $C_6D_6$ at 25° gave 50% yield of $Cp_2Ta(Me)(CH_2CH_2)$ while in the presence of ethylene, this was the only detectable product. These and other reactions suggest that cleavage of a doubly methylene-bridged dimer may be involved (27). The X-ray crystal structure determination of the methylene complex has been discussed in the first section (6). In this paper the variable temperature NMR spectrum is discussed together with those of the related complexes, $Cp(\eta^5\text{-}MeC_5H_4)TaMe(CH_2)$, $Cp_2TaCl(CHCMe_3)$ and $Cp_2TaCH_2Ph(CHPh)$.

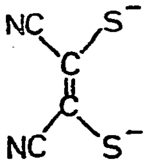
The metal-metal bonded compounds, $Cp_2VGeR_3$, where R=Et or Ph, were obtained by reaction of $Cp_2V$ with $(R_3Ge)_2Cd$, metallic cadmium being eliminated. The diamagnetic, dark violet compounds are monomeric and sensitive to oxygen. Treatment with HCl or AcOH gave $Cp_2VCl$ or $CpV(OAc)_2$ together with $Ph_3GeH$ (28).

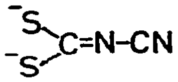
A series of polypyrazolylborate complexes of titanium and vanadium has been prepared. From the reaction between $Cp_2VCl$ and

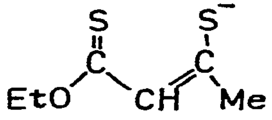
$KHBPz_3$, where Pz = pyrazolyl, the green paramagnetic complex below was isolated (29),

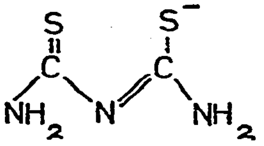


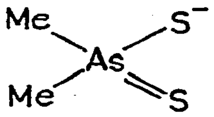
The complex oxidized only slowly in air and showed $\mu_{eff}$3.59BM. Organochalcogen derivatives have received some attention. Complexes of $Cp_2V^{IV}$ with dithiochelates forming 4-, 5- and 6- membered rings have been prepared from $Cp_2VCl_2$ and salts of the following ligands,



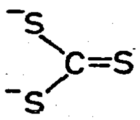


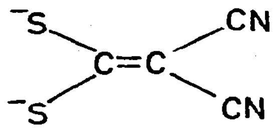


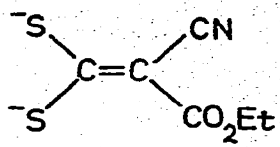


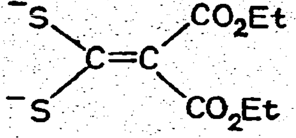


Complexes of monovalent ligands were precipitated as $BF_4^-$, $PF_6^-$ or $BPh_4^-$ salts. The results of conductance and magnetic measurements and of infrared, electronic and ESR spectra were interpreted in terms of the expected monomeric structures (30). Similar four-membered ring dithiolates were made by other workers (30a) using the ligands,









as well as $(S_2CNCN)^{2-}$ and $[S_2C_2(CN)_2]^{2-}$. The complexes were characterized by molecular weight, electrical conductance and magnetic measurements.

Bisarylseleno and -telluro derivatives of vanadium and niobium have been isolated and characterized; viz. $Cp_2V(ER)_2$, where ER=SePh or $SC_6H_4Me$-o, and $Cp_2Nb(ER)_2$, where ER=SePh or TePh. The green paramagnetic complexes were unstable in air (31).

Organochalcogen-bridged binuclear complexes of niobium and iron or cobalt of type,  $Cp_2Nb\langle{}^{ER}_{ER}\rangle M\langle{}^{CO}_{L}$, where M=Fe or Co; ER=SPh, SePh or TePh; L=NO (for Fe) or CO(for Co), have been prepared from $Cp_2Nb(ER)_2$ and $Hg[Fe(CO)_3NO]_2$ or $Hg[Co(CO)_4]_2$ in acetone at room temperature. The complexes proved to be more stable than the $Cp_2Nb(ER)_2$, but decomposed in solution in air. The $^1H$ NMR spectra are discussed with reference to the geometrical isomers present (32).

With $Me_3CO_2H$, vanadocene gave $CpVO_2$ in 85% yield, which was converted to $CpVOCl_2$ by $SOCl_2$. Similarly vanadocene gave 66% yield of $CpV(O_2CPh)_2$ when treated with $Me_3CO_2(O)CPh$ (33).

The rest of the papers mentioned in this section report the results of physical measurements carried out on known compounds. The formation of ion-molecule reaction products as well as binuclear secondary ions in the mass spectrum of $CpV(C_7H_7)$ has been noted and their fragmentation discussed (34). Comparisons are made with $CpCr(C_7H_7)$, $CpCr(C_6H_6)$ and $CpMn(C_6H_6)$. X-ray photoelectron spectroscopy has been used to determine the vapour phase core electron binding energies for severel vanadium compounds (35) including $CpV(C_7H_7)$, $CpV(CO)_4$ and $(C_7H_7)V(CO)_3$.

The He(I) photoelectron spectrum of $CpNb(C_7H_7)$ has been measured and compared with those of the corresponding zirconium and molybdenum derivatives and with the 3d analogues. Molecular orbital considerations are discussed (36). $^{13}C$ Pulse Fourier Transform NMR spectra have been recorded for a range of ring-substituted metallocenes including $(EtC_5H_4)_2V$. Off-resonance experiments as well as selective proton decoupling were used to confirm formerly ambiguous assignments (37).

Fragmentation patterns in the mass spectra of the carboxylates, $[CpV(O_2CR)_2]_2$, where R=H,Me,$CCl_3$,$CF_3$,Ph, m-$FC_6H_4$, α-furyl or α-thienyl, have been studied (38). The variation of magnetic susceptibility with temperature for three of these dimeric carboxylates, R=Me, Ph or α-furyl, have been measured, and the exchange coupling constants for the S=1 vanadium (III) ions are given as -227, -197 and -185 $cm^{-1}$ respectively. The EPR spectra also reflect the exchange coupling (39).

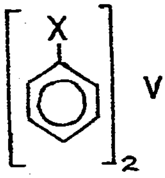
Exchange of Cp ligands between $(Cp_2TiCl)_2$ and $[(d_5\text{-}Cp)_2TiCl]_2$, and between $(\eta^5\text{-}MeC_5H_4)_2VCl_2$ and $Cp_2VCl_2$ has been observed in benzene under photolysis at 313 nm. The rates of exchange were monitored by mass spectral measurements (40). Comparison of the high resolution infrared spectra of $CpV(CO)_4$ and $(\eta^5\text{-}CH_3COC_5H_4)V(CO)_4$ has confirmed that interpretation of these spectra by the method of local symmetry (MLS) is applicable "until the molecular orbitals of the carbonyl become deformed enough to produce observable spectroscopic differences" (41).

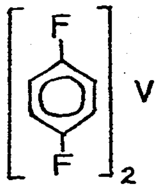
By observing the shift in the infrared frequencies of the carbonyl bands, the formation of complexes between $AlCl_3$ and various arene and cyclopentadienylmetal carbonyls has been studied (42), including $CpV(CO)_4$, $CpV(CO)_3PPh_3$ and $CpNb(CO)_4$.

The $^{13}C$ NMR and $^{1}H$ NMR spectra for the complex, $Cp_2Nb(C_2H_4)(C_2H_5)$, have been recorded and compared with the corresponding spectra of $CpNb(H)(C_2H_4)$. The exchange of the two distinct ends of the ethylene ligand is slow on the NMR time scale at 27° (5). The X-ray structure determination of this complex was mentioned in the first section.

## OTHER π-BONDED COMPLEXES

The syntheses, properties and spectra of a series of bis(arene) complexes of vanadium (and chromium) have been reported. Vanadium vapour, generated by vapourization from a resistively heated tungsten boat, was co-condensed at -196° with >15 fold excess of arene substrates. The products were isolated under inert atmosphere and purified by sublimation. The vanadium complexes are shown below,





X = H, F, Cl, $CF_3$

These halogenated sandwich complexes showed increased air stabilities over bis(benzene)vanadium. In solution they were quite air-sensitive but in crystal-form air could be tolerated for several minutes (43). This work is also contained in a report of lectures by Klabunde (44).

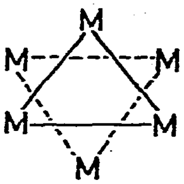
The full paper on the catalytic oligomerization of butadiene using catalysts derived directly from metal atoms or bis(arene) compounds has been published (45). Neither vanadium atoms nor bis(benzene)vanadium alone cause polymerization, but in the presence of alkylaluminium halides, cyclic and linear polymers were obtained in moderate yields. In this paper more attention is paid to titanium.

Reduction of bis(η-benzene)vanadium with a potassium mirror in hexamethylphosphoramide gave the anion, $[(C_6H_6)_2V]^-$, as a blue solution with a single $^1$H NMR resonance at τ 6.72, consistent with an axially symmetric anion. Mild oxidation reformed $(C_6H_6)_2V$ almost quantitatively (46). ESR monitoring of the reduction in the presence of naphthalene, biphenyl and benzene indicated the sequence of decreasing electron affinities, $C_{10}H_8 > (C_6H_5CH_2)_2V > PhPh > C_6H_6$.

Optimum conditions for the preparation of bis(ethylbenzene)vanadium (a mixture of various bis(arene) complexes differing in the number of ethyl groups attached to the benzene rings) have been shown to be; $VCl_3$-$AlCl_3$ (1:1.5) heated in absolute EtPh for 2 hr. at 125° (47). Thermal decomposition of bis(ethylbenzene)vanadium at 350-450° occurred by cleavage of the V-arene bond and dehydrogenation of the ligand. The alkyl radicals then underwent various recombination and alkylation reactions catalyzed by the metallic vanadium film formed on decomposition, leading to gaseous and liquid products ranging from hydrogen and methane to triethylbenzene(48).

Electronic configurations have been proposed for dicyclooctatetraene-titanium and -vanadium complexes on the basis of group theory considerations of symmetry and molecular orbitals. The MO diagram is in agreement with magnetic susceptibility and EPR results obtained for the vanadium complex (49). Anionic cyclooctatetraene complexes of niobium and tantalum of type $[M(C_8H_8)_3]^-$ have been prepared from $K_2C_8H_8$ and $NbCl_5$ in the case of niobium, and from $[Li(THF)_4]^+[TaPh_6]^-$ and $C_8H_8$ in the case of tantalum. Tetraphenylarsonium salts were precipitated (4). The crystal structure determination of $[AsPh_4][Nb(C_8H_8)_3]$ has been mentioned in the first section.

Diamagnetic hexamethylbenzeneniobium and -tantalum cluster compounds, $[(Me_6C_6)_6M_6X_{12}]^{4+}$, where X=Cl or Br, resulted from oxidation of the trimetallic cations, $[(Me_6C_6)_3M_3X_6]^{+}$. Electrochemical studies indicated that oxidation of the chloride complex occurred at potentials around -0.2V and was reversible by triangular voltammetry. Several chemical reagents also brought about oxidation including cerium (IV), N-bromosuccinimide, iodine and even air in acid solution. It was suggested that the structure of the new complexes, isolated as their hexafluorophosphate or thiocyanate salts, could involve two staggered metal triangles (50),



The dianion generated from the closo carboranes, 1,2 $-C_2R_2B_{10}H_{10}$, where R=H or Me, has been shown to react with $VCl_3$, $TiCl_4$ and $ZrCl_4$ to give a series of anionic metallocarboranes formulated as $[M(C_2R_2B_{10}H_{10})_2]^{2-}$, with M in the +2 formal oxidation state, and isolable in good yields as tetraalkylammonium salts (51).

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