VANADIUM, NIOBIUM AND TANTALUM *

ANNUAL SURVEY COVERING THE YEAR 1971

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1. Organometallic derivatives of vanadium

Tetrabenzylvanadium(IV) was reported[1] to be the product of the following reaction:

$$VCl_4 + 2\,Mg(CH_2C_6H_5)_2 \rightarrow 2\,MgCl_2 + V(CH_2C_6H_5)_4 \qquad (1)$$

The reaction was carried out at −20° in pentane containing a small amount of diethyl ether. The reaction resulted in the formation of a green complex dissolving in pentane with a deep-green color. However, apparently the compound was not isolated and analyzed. Its formula was assigned on the basis of: (1) formation of four mole of toluene per vanadium on methanolysis, and (2) high resolution ESR of its pentane solution suggesting the coupling of the unpaired spin with eight equivalent protons. The solutions were reported to be stable under nitrogen up to 60°, so it seems worthwhile to attempt the isolation of the compound.

Pentasulfide and pentaselenide dicyclopentadienyl derivatives of vanadium(IV) were obtained[2] by the following reaction:

$$V(C_5H_5)_2Cl_2 + X_5^{2-} \rightarrow 2\,Cl^- + V(C_5H_5)_2X_5 \qquad (2)$$

$(X = S, Se)$

These compounds are believed to contain a VX_5 six-membered ring. The substances are black and stable in air in the solid state. In agreement with their formulation as derivatives of vanadium(IV), these d^1 systems showed ESR signals with $g = 1.976$ $(X = S)$ and $g = 2.006$ $(X = Se)$.

The X-ray structure of the trifluoroacetato complex of vanadium(III), $[V(C_5H_5)(O_2CCF_3)_2]_2$, and the magnetic susceptibility data for this complex and its acetato analogue, have been published[3]. The molecular structure of the trifluoroacetato complex is schematically shown in Fig. 1. The molecule is dimeric, the two vanadium atoms being joined by the bridging trifluoroacetato groups. The vanadium–vanadium distance is quite large (3.7 Å), which suggests that the direct interaction between the d^2 centers is probably not very important. The magnetic susceptibilities for the

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* The matter is arranged according to decreasing oxidation number if the central metal atom.

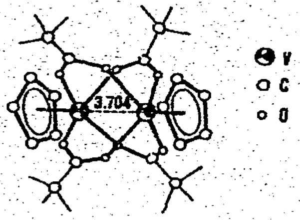


Fig. 1. Molecular structure of $[V(C_5H_5)(O_2CCF_3)_2]_2$ schematically drawn. (Adapted from G.M. Larin, V.T. Kallinikov, G.G. Aleksandrov, Yu.T. Struchkov, A.A. Pasnskii and N.E. Kolobova, *J. Organometal. Chem.*, 27 (1971) 53.)

trifluoroacetato and the acetato complexes are similar; they do not obey the Curie law and the magnetic moments decrease at decreasing temperature. The data were interpreted on the basis of superexchange through the carboxylato bridges.

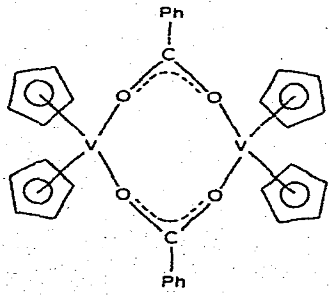
The infrared spectra of the following compounds were reported:

$V(C_5H_5)_2(O_2CR)_2$ $[V(C_5H_5)_2(O_2CC_6H_5)]_2$

(I), $R = CH_3$, $p\text{-}C_6H_4NO_2$ (II)

$[V(C_5H_5)(O_2CCH_3)_2]_2$

It has been suggested that compound (II) has the following dimeric structure.



(II)

Thermochemical data have been reported for dicyclopentadienylvanadium(II). From combustion and vapour pressure data, the mean dissociation energy for the $V-C_5H_5$ bond was estimated to be 88 kcal/mole[5,6].

Cyano complexes of vanadium(III), vanadium(II) and vanadium(I) have been obtained under anhydrous conditions[7]. The following reactions were carried out:

$$V(O_2CCH_3)_3 + 7\,KCN \xrightarrow{CH_3OH} \underset{\text{(III)}}{K_4[V(CN)_7]} + 3\,KO_2CCH_3 \qquad (3)$$

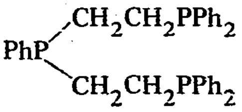
$$V(O_2CCH_3)_3 + 6\,NaCN \xrightarrow{\text{liq.}NH_3} \underset{\text{(IV)}}{Na_3[V(CN)_6]} + 3\,NaO_2CCH_3 \tag{4}$$

$$K_4[V(CN)_7] + K \xrightarrow{\text{liq.}NH_3} \underset{\text{(V)}}{K_4[V(CN)_6]} + KCN \tag{5}$$

$$K_4[V(CN)_7] + 2K \xrightarrow{\text{liq.}NH_3} \underset{\text{(VI)}}{K_5[V(CN)_6]} + KCN \tag{6}$$

The heptacyanovanadate has a room temperature magnetic moment $\mu = 2.7$ BM, roughly corresponding to two unpaired electrons which is consistent with the d^2 configuration of this system. The infrared spectrum shows two CN stretching vibrations at 2096 and 2073 cm^{-1} and consequently a pentagonal bipyramidal structure may be proposed for the $[V(CN)_7]^{4-}$ anion.

The reaction of $V(C_5H_5)(CO)_4$ with the tri-tertiary phosphine



$$PhP(CH_2CH_2PPh_2)_2$$

(P–P–P)

led to the formation of the disubstitution product:

$$V(C_5H_5)(CO)_4 + PPP \rightarrow 2\,CO + V(C_5H_5)(CO)_2(PPP) \tag{7}$$

Evidently the phosphine acts in the case as a bidentate ligand[8].

Reactions of $V(C_5H_5)(CO)_4$ with diphenylacetylene, some of them already reported in earlier publications[9], have been reviewed[10].

The $[V(CO)_6]^-$ anion is very resistant to thermal substitution reactions. It has been reported[11] that Group V hexacarbonylmetallate anions can be recovered unchanged from molten triphenylphosphine. Carbon monoxide substitution has now[11] been achieved photolytically. The following representative reactions were carried out, using $[Na(diglyme)_2][V(CO)_6]$ as starting material:

$$[V(CO)_6]^- + Ph_2PCH_2CH_2PPh_2 \xrightarrow[10.5\ h]{h\nu,\,THF} 2\,CO + [V(CO)_4(PCH_2CH_2PPh_2)]^- \tag{8}$$

$$[V(CO)_6]^- + PPh_3 \xrightarrow[11\ h]{h\nu,\ THF} CO + [V(CO)_5PPh_3]^- \tag{9}$$

Similar reactions were carried out also with triphenylstibine and triphenylarsine and the anions were isolated as tetraalkylammonium salts. The pentacarbonylvanadate of reaction (9) had been obtained earlier by a different route[12].

Experimental conditions are apparently very important in determining the course of reactions (8) and (9). In fact it has been reported[13] that no reaction between $[V(CO)_6]^-$ and triphenylphosphine took place in a sealed infrared cell under irradiation with a mercury lamp in methyltetrahydrofuran as solvent. On the other hand, when carbon monoxide was allowed to escape from the reaction vessel, less than one CO per vanadium was evolved and intractable products were reported[13] to be formed. Also to be noticed that the same paper[13] reports the formation of a species believed to be $[V(CO)_5(Me{-}THF)]^-$ upon irradiation of a Me–THF solution of the hexacarbonylvanadate anion at about 90 K. The starting anion was regenerated upon warming to room temperature.

Solution contact shift data for $[V(C_6H_6)_2]^+$, $[V(C_6H_5Me)_2]^+$ and $[V(C_6H_3Me_3)_2]^+$ and solid state contact shift data for $V(C_6H_6)_2$ and $V(C_6Me_6)_2$ have been reported[13a]. The vanadium(I) cations are suggested to have the electronic configuration $(e_{2g})^3(a_{1g})^1$. Large downfield shifts were observed for both the ring protons and the methyl protons for the vanadium(I) species. On the other hand, the vanadium(0) species, for which the electronic configuration $(e_{2g})^4(a_{1g})^1$ was suggested, shown an anomalous upfield shift of the methyl resonance. This was explained with a polarization effect by the unpaired spin.

II. Organometallic derivatives of niobium and tantalum

A binary organometallic derivative of niobium(V) was reported by Wilkinson and co-workers[14]. It was prepared by the reaction of $NbCl_5$ with $MgCl(CH_2SiMe_3)$ in diethyl ether. The product has the formula $[Nb(CSiMe_3)(CH_2SiMe_3)_2]_2$ and its structure, as it results from an X-ray diffraction study, is shown in Fig. 2. The important feature of the structure is the absence of hydrogen attached to the bridging $(CSiMe_3)$ groups, as suggested by structural and chemical evidence. The Nb–Nb distance is 2.90 Å. A tantalum analogue was also prepared, which is isostructural with the niobium complex.

Dicyclopentadienyltrihydridoniobium(V) has been prepared[15] by the reaction of niobium pentachloride with sodium cyclopentadienide and $NaBH_4$ under hydrogen pressure (800 atm) in toluene as solvent. The trihydrido derivative has a niobium–hydrogen stretching vibration at 1710 cm^{-1} and shows two resonances in the ^1H NMR spectrum at τ12.73 and τ13.72 in toluene-d_8. This suggests that the trihydride has structure (VII) similar to that proposed for the corresponding tantalum derivative[16]. The niobium–hydrido species

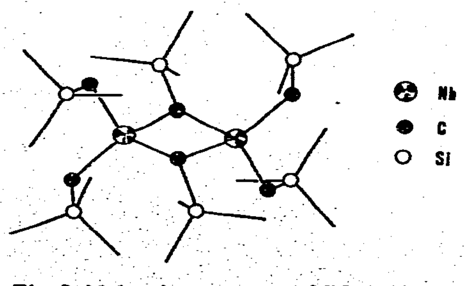
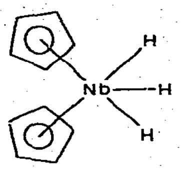


Fig. 2. Molecular structure of $[Nb(CSiMe_3)(CH_2SiMe_3)_2]_2$. (From F. Huq, W. Mowat, A.C. Skapski and G. Wilkinson, *Chem. Commun.*, (1971) 1477.)



(VII)

has a reactivity much higher than $Ta(C_5H_5)_2H_3$. The following reactions were observed:

$$Nb(C_5H_5)_2H_3 \rightleftharpoons \tfrac{3}{2} H_2 + \underset{\text{(VIII)}}{C_{10}H_{10}Nb} \tag{10}$$

$$C_{10}H_{10}Nb + \tfrac{1}{2} H_2 \rightleftharpoons \tfrac{1}{2}[Nb(C_5H_5)_2H]_2 \tag{11}$$

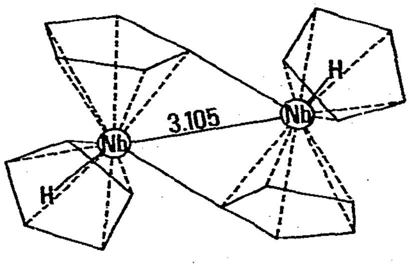
$$\tfrac{1}{2}[Nb(C_5H_5)_2H]_2 + C_2H_4 \rightleftharpoons \underset{\text{(IX)}}{Nb(C_5H_5)_2H(C_2H_4)} \tag{12}$$

$$C_2H_4 + Nb(C_5H_5)_2H(C_2H_4) \rightleftharpoons \underset{\text{(X)}}{Nb(C_5H_5)_2C_2H_5(C_2H_4)} \tag{13}$$

The compounds (VIII)–(X) were isolated and characterized by spectral and analytical data. It is also noteworthy that $Nb(C_5H_5)_2H_3$ catalyzes the C_6H_6–D_2 exchange at 80°. Compound (VIII) was shown by X-ray diffraction methods[17] to have the structure shown in Fig. 3. The molecule contains bridging C_5H_4 units and terminal hydrido groups; its formula is therefore $[Nb(C_5H_5)H(C_5H_4)]_2$. The niobium–niobium distance is 3.10 Å, which suggests the presence of a niobium–niobium bond. As it has been already reported in the Titanium, Zirconium, Hafnium section of these AS, the suggestion was also made[15] that the structure of the corresponding titanium compound is similar.

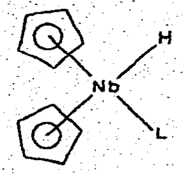
The ethylene–hydrido complex (IX) is one of the members of a class of compounds of general formula $Nb(C_5H_5)_2H(L)$, in which L is a σ-donor with π-acid character. The structure indicated below has been suggested for it.

Bimetallic derivatives of niobium with nickel, palladium and platinum have been re-



$Nb_2(C_5H_5)_2H_2(C_5H_4)_2$

Fig. 3. Molecular structure of the niobocene dimer schematically drawn. (From L.J. Guggenberger and F.N. Tebbe, *J. Amer. Chem. Soc.*, 93 (1971) 5924.)



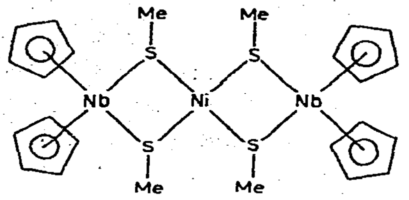
(IX)

ported[18]. The following sequence of reactions was carried out:

$$Nb(C_5H_5)_2Cl_2 + 2\,SMe^- \rightarrow 2\,Cl^- + Nb(C_5H_5)_2(SMe)_2 \tag{14}$$

$$2\,Nb(C_5H_5)_2(SMe)_2 + NiCl_2 \rightarrow \underset{(XI)}{[(C_5H_5)_2Nb(SMe)_2Ni(SMe)_2Nb(C_5H_5)_2]^{2+}} + 2\,Cl^- \tag{15}$$

Cation (XI), which may be formally considered to contain the niobium(V)–nickel(0)–niobium(V) sequence, was shown to have the structure shown below. The coordination around nickel is substantially tetrahedral and the methyl groups attached to sulfur are in a *transoid* conformation. Reactions similar to (15) were also carried out with $PdCl_2(PhCN)_2$ and with $PtCl_2(PhCN)_2$.



(XI)

Vapor pressure measurements[19] of $Nb(C_5H_5)(CO)_4$ have been reported between 98 and 140°. The enthalpy and entropy changes for the vaporization process were found to be 22.45 kcal/mole and 48 e.u., respectively. These values can be compared with these for the corresponding manganese derivative (12.5 kcal/mole and 25.9 e.u.).

An allyltrifluorophosphine derivative of tantalum was obtained[20] by the following reaction:

$$2\,Ta(C_3H_5)_4 + 10\,PF_3 \rightarrow 2\,Ta(C_3H_5)(PF_3)_5 + 3\,C_6H_{10} \tag{16}$$

The reaction was carried out at room temperature with PF_3 under pressure (20 atm). The ruby-red compound is moderately stable at room temperature under nitrogen in the solid state. Attempts to displace all the allyl groups from tetraallyltantalum were unsuccessful.

While the $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ anions and the corresponding substituted species are known (*vide infra*) the neutral binary carbonyls of niobium and tantalum had not been reported as yet. There is now infrared evidence[21] that a series of binary carbonyls of tantalum can be prepared by vaporization of tantalum at 2800 K and subsequent annealing in an argon/CO (200/1) matrix at temperatures between 13 and 35 K. The infrared spectra showed the presence of bands in the 1819–1967 cm^{-1} range, attributed to CO stretching vibrations of $Ta(CO)_n$ species. In particular a band at 1967 cm^{-1} was attributed to monomeric $Ta(CO)_6$. The infrared-active CO stretching vibration of $V(CO)_6$ gives rise to a broad band[22] in the gas phase at about 1990 cm^{-1}.

Photochemical carbonyl substitution reactions, similar to those obtained with $[V(CO)_6]^-$, were also reported[11] for $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$. The substitutions were as follows:

$$[M(CO)_6]^- + PPh_3 \xrightarrow[6\ h,\ 40-60^\circ]{h\nu,\ THF} CO + [M(VO)_5(PPh_3)]^- \tag{17}$$

$$[M(CO)_6]^- + Ph_2PCH_2CH_2PPh_2 \xrightarrow[10.5\ h]{h\nu,\ THF} 2\ CO + [M(CO)_4(PPh_2CH_2CH_2PPh_2)]^- \tag{18}$$

(M=Nb,Ta)

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