VANADIUM, NIOBIUM AND TANTALUM

ANNUAL SURVEY COVERING THE YEAR 1972

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I. Organometallic derivatives of vanadium

Thiele in his main lecture at the Vth Organometallic Chemistry Symposium has reported [1] preparations and properties of some vanadium(V) and vanadium(IV) organometallic derivatives. Oxydichlorophenylvanadium(V), $VOCl_2Ph$, can be prepared in large quantities by operating at low temperatures and in hydrocarbon solvents:

$$2\ VOCl_3 + ZnPh_2 \rightarrow 2\ VOCl_2Ph + ZnCl_2$$

The reaction can be similarly carried out with diphenylmercury as arylating agent. The vanadium(V) organometallic is a deep red crystalline substance, soluble in hydrocarbons, and decomposing thermally to give diphenyl, chlorobenzene and benzene in small amounts.

Unsuccessful attempts have been made [1] to prepare a binary tetraalkylvanadium(IV). By treating VCl_4 with alkylborons in diethyl ether, however, vanadium trichloride was formed. Similar results were obtained in an inert solvent such as hexane at −50°C. When dimethylzinc was the alkylating agent, formation of $VCl_2(CH_3)_2$ took place:

$$VCl_4 + Zn(CH_3)_2 \rightarrow VCl_2(CH_3)_2 + ZnCl_2$$

The dimethyl derivative could not be isolated in a pure form, since it contained small amounts of $ZnCl_2$ and diethyl ether which was used for the removal of $ZnCl_2$. By addition of oxygen or nitrogen donors, compounds such as $VCl_2(CH_3)_2 \cdot 2$ pyridine (violet) and $VCl_2(CH_3)_2 \cdot THF$ (μ_{eff} 1.98 BM, green) could be isolated in a pure state. Dichlorodimethylvanadium(IV) was further treated with dimethylzinc in order to synthesize tetramethylvanadium(IV). However, adducts were obtained, rather than the desired product:

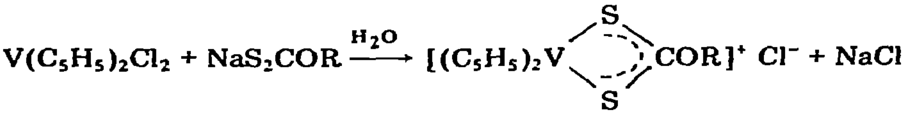
$$VCl_2(CH_3)_2 \xrightarrow[Et_2O]{Zn(CH_3)_2} Zn[V(CH_3)_4Cl_2] \cdot Et_2O$$

The isolation of a binary aryl derivative of vanadium(IV) in a pure form has been successful [2] by the reaction of VCl_4 with pentafluorophenyllithium:

$$VCl_4 + 4\ LiC_6F_5 \xrightarrow{-70°C} 4\ LiCl + V(C_6F_5)_4$$

The vanadium(IV) derivative is a violet crystalline substance, very sensitive to moisture.

Xanthato complexes of vanadium(IV) have been synthesized [3] from $V(C_5H_5)_2Cl_2$ and sodium xanthates in aqueous solutions:



$(R = CH_3, C_2H_5, (CH_3)_2CH, n\text{-}C_4H_9, C_6H_{11})$

The cationic complexes were isolated from the reaction mixtures as the tetrafluoroborates. All the complexes have magnetic moments around 1.65 BM and show an eight-line EPR spectrum consistent with the coupling of the unpaired electrons with ^{51}V, $I = 7/2$. No hyperfine structure was observed, as it might have been expected for further coupling with the ten protons. This was taken as evidence that the electron is not extensively delocalized into the cyclopentadienyl rings.

Dicyclopentadienyldichlorovanadium(IV) reacts [4] with $NOPF_6$ in acetonitrile as solvent leading to halide displacement and formation of a vanadium(IV) acetonitrile cationic complex:

$$V(C_5H_5)_2Cl_2 \xrightarrow[CH_3CN]{NOPF_6} [V(C_5H_5)_2(CH_3CN)_2][PF_6]_2$$

The vanadium(IV) complex has μ_{eff} 1.69 BM in agreement with the d^1 configuration of the central metal atom.

EPR measurements have been carried out [5] of dicyclopentadienyldichlorovanadium(IV) of d^1 configuration. The results suggest that the unpaired electron is largely localized on the metal.

Similarly, EPR results [6] have been obtained for $V(C_8H_8)_2$, which also has one unpaired electron. The experimental parameters suggest that the electron is residing in an orbital which has predominant d_{z^2} character.

The reactions to obtain cyclopentadienylbiscarboxylato complexes of vanadium(III) have been announced [7]. They consist of treating $V(C_5H_5)(CO)_4$ with the proper carboxylic acid in boiling toluene. The complexes obtained, of formula $[V(C_5H_5)(OOCR)_2]_2$ are dimeric, as shown by the X-ray structural data obtained for the compounds with $R = CF_3$ and furanyl. A magnetic investigation [8] has shown that these compounds are antiferromagnetic. The compounds studied were those with $R = H, CF_3, CCl_3, CH_3$, furanyl, thiofuranyl, C_6H_5, $m\text{-}C_6H_4OCH_3$, $m\text{-}C_6H_4F$. In view of the fact that, according to X-ray results, the vanadium atoms are in $[V(C_5H_5)(OOCCF_3)_2]_2$ at nonbonding distance (3.7 Å), the antiferromagnetic behavior has been attributed to a superexchange mechanism through the organic ligands. The X-ray results obtained on the furancarboxylato

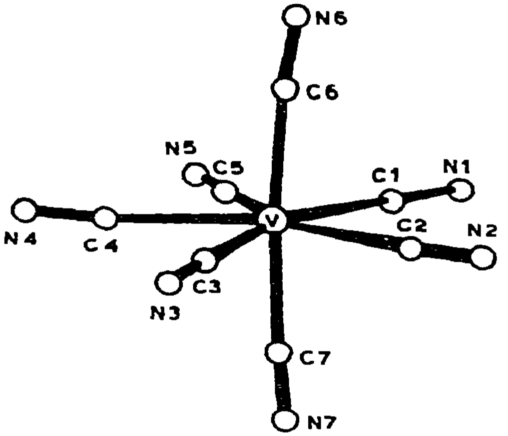


Fig. 1. Molecular structure of $[V(CN)_7]^{4-}$. (From R.L.R. Thomas and R.A. Levenson, J. Amer. Chem. Soc., 94 (1972) 4345.)

complex also show a nonbonding distance (3.65 Å) between the two vanadium atoms.

The molecular structure of the $[V(CN)_7]^{4-}$ anion has been solved [9] and found to consist of a distorted pentagonal bipyramid of the cyanide groups around the central metal atom, as indicated in Fig. 1. The distorsion is especially evident in the axial CN groups.

The hydrido- and the iodo-vanadium(I) complexes $V(CO)_4H(dppe)$ and $V(CO)_4I(dppe)$ (dppe = 1,2-diphenylphosphinoethane) have been prepared [10]. The syntheses are:

$$[V(CO)_4(dppe)]^- \xrightarrow{H^+} V(CO)_4H(dppe)$$

$$[V(CO)_4(dppe)]^- + I_2 \rightarrow I^- + V(CO)_4I(dppe)$$

The hydrido species is moderately stable in air, but decomposes slowly at room temperature to give $V(CO)_4(dppe)$. The latter was prepared by the following reaction:

$$[NEt_4][V(CO)_4(dppe)] + C_7H_7BF_4 \rightarrow \tfrac{1}{2}(C_7H_7)_2 + [NEt_4][BF_4] + V(CO)_4(dppe)$$

Reactions of $VC_5H_5(CO)_4$ and $V(CO)_6$ with ring-substituted cycloheptatrienes have been reported [11]. With $VC_5H_5(CO)_4$, the reactions were carried out in refluxing $(n\text{-}C_4H_9)_2O$ for 9 hours. Under these conditions, two main reaction pathways were observed:

$$VC_5H_5(CO)_4 + C_7H_7X \begin{array}{l} \xrightarrow{-X\cdot} VC_5H_5(C_7H_7) \qquad \text{(a)} \\[2ex] \xrightarrow{-H\cdot} VC_5H_5(C_7H_6X) \qquad \text{(b)} \end{array}$$

Reaction a is particularly important for 7-C_7H_7CN and 7-$C_7H_7C_7H_7$, while reaction b predominates with 3-$OCH_3C_7H_7$, 3-$OC_2H_5C_7H_7$ and $C_2H_5CO_2C_7H_7$ (mixture of several positional isomers). The reactions of $V(CO)_6$ with several substituted cycloheptatriene derivatives in refluxing hexane resulted in the preparation of the tricarbonylvanadium(—I) tropylium derivatives:

$$V(CO)_6 + C_7H_7X \xrightarrow{\text{refl. hexane}} V(C_7H_6X)(CO)_3$$

$$(X = H,\ 3\text{-}OCH_3,\ 3\text{-}OC_2H_5,\ 3\text{-}OC_3H_7,\ CO_2C_2H_5,\ 7\text{-}CH_3,\ 7\text{-}C_6H_5)$$

Mass-spectrometric measurements of the various complexes have been reported.

The reaction of the isopropyl Grignard reagent with VCl_4 in the presence of C_7H_8 under specified conditions resulted in the formation of dicycloheptatrienevanadium(0) [12]:

$$VCl_4 \xrightarrow[\text{diethyl ether}]{i\text{-}C_3H_7MgBr,\ C_7H_8} V(C_7H_8)_2$$

The mass spectrum shows, besides the molecular ion, the ions arising from hydrogen abstraction, namely $V(C_7H_7)(C_7H_8)^+$ and $V(C_7H_7)_2^+$. Facile hydride abstractions have been successfully carried out chemically with $[Ph_3C][BF_4]$, the already known $[V(C_7H_8)(C_7H_7)]^+$ cation [13] and $[V(C_7H_7)_2]^{2+}$ were isolated as the tetrafluoroborate derivatives.

The following intermetallic derivatives of vanadium were reported [14]: $Ph_3SnV(CO)_6$, $Ph_3SnV(CO)_5PPh_3$, $Ph_3SnV(CO)_5P\text{-}n\text{-}Bu_3$, $EtHgV(CO)_6$, and $EtHgV(CO)_5PPh_3$. The first compound was prepared by the following reaction:

$$[Na(diglyme)_2][V(CO)_6] \xrightarrow[CH_2Cl_2]{Ph_3SnCl} Ph_3SnV(CO)_6$$

The photolytic behavior of hexacarbonylvanadate (—I) solutions has been examined [15]. It has been found that photolysis in the presence of cyanides gives carbonyl substitution in liquid ammonia:

$$[V(CO)_6]^- \xrightarrow[-50\ -\ -60^\circ]{h\nu,\ NaCN,\ NH_{3(l)}} [V(CO)_5CN]^-$$

On the other hand, treatment of $[Et_4N][V(CO)_6]$ with NEt_4CN at room temperature under irradiation leads to carbonyl substitution and oxidation to vanadium(0) (the reaction is carried out in the presence of 2,2'-dipyridyl):

$$[Et_4N][V(CO)_6] \xrightarrow[\text{dipy, room temp.}]{h\nu,\ Et_4NCN,\ CH_3CN} [Et_4N]_4[V_2(CO)_8(CN)_4]$$

The fact that the vanadium(0)—cyanide complex is diamagnetic led the author to suggest a dimeric formulation for it. Finally, $Na[V(CO)_6]$ gives carbonyl substitution under irradiation in liquid ammonia:

$$NaV(CO)_6 \xrightarrow[-60^\circ]{h\nu,\ NH_{3(l)}} Na[V(CO)_5(NH_3)]$$

II. Organometallic derivatives of niobium and tantalum

The reactions of niobium pentachloride with dimethylzinc have been studied [16]. Equimolar quantities or nearly so of the two reagents gave $NbCl_3(CH_3)_2$:

$$NbCl_5 + Zn(CH_3)_2 \rightarrow NbCl_3(CH_3)_2 + ZnCl_2$$

Attempts to isolate $NbCl_4(CH_3)$ by using the same reagents in a 2/1 ratio, resulted in a mixture of chloroniobium(V) complexes in various degrees of alkylation. However, adducts of the tetrachloromethyl complex with dioxane and 1,2-diphenylthioethane have been obtained, e.g.:

$$NbCl_4(CH_3) \xrightarrow{\text{dioxane}} [NbCl_4(CH_3)]_2 \cdot \text{dioxane} \xrightarrow{\text{dioxane}} NbCl_4(CH_3) \cdot \text{dioxane}$$

Adducts of $NbCl_3(CH_3)_2$ were similarly reported.

The preparation of $TaH_3(C_5H_4CH_3)_2$ was described [17]. The synthesis consists of treating tantalum pentachloride with lithium–methylcyclopentadienide in tetrahydrofuran/benzene followed by addition of $LiAlH_4$ and hydrolysis. The trihydrido complex is a white substance, m.p. 89.5-91°C. Exchange reactions between benzene and deuterium were found to be catalysed by the trihydrido and by other niobium and tantalum complexes, namely $NbH_3(C_5H_5)_2$, $[NbH(C_5H_5)(\mu\text{-}C_5H_4)]_2$ (the "niobocene dimer"), and $TaH_3(C_5H_5)_2$. The activities of the two niobium complexes and the catalytic activity of the two tantalum(V) complexes are all very similar. By using $NbH_3(C_5H_5)_2$ as catalyst, several aromatic compounds were tested for exchange of the ring hydrogens with D_2. The reactivity was found to decrease in the order: $p\text{-}C_6H_4F_2 > C_6H_5F > C_6H_6 > C_6H_5OCH_3 > C_6H_5CH_3 > p\text{-}C_6H_4(CH_3)_2$.

Dicyclopentadienyl derivatives of niobium(V) and niobium(IV), and some intermetallic compounds containing the $Nb(C_5H_5)_2$ unit have been described [18]. It was found that treatment of $NbCl_5$ with TlC_5H_5 in dimethoxyethane, further working up in air and reduction with $SnCl_2$ resulted in the formation of $Nb(C_5H_5)_2Cl_2$. Oxidative treatment of the latter gave the μ-oxy dinuclear complex:

$$Nb(C_5H_5)_2Cl_2 \xrightarrow{\text{air, } HBF_4} [(Nb(C_5H_5)_2Cl)_2O][(BF_4)_2]$$

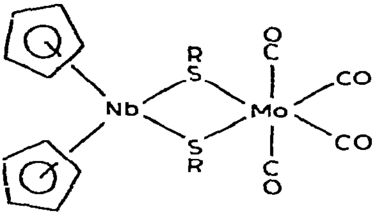
The chloro groups of $Nb(C_5H_5)_2Cl_2$ can undergo substitution reactions:

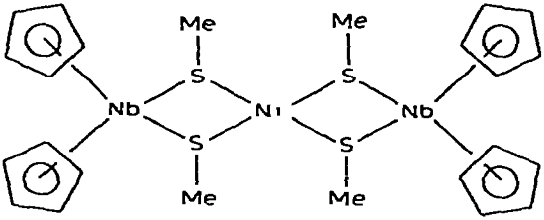
$$Nb(C_5H_5)_2Cl_2 + 2\,SR^- \rightarrow 2Cl^- + Nb(C_5H_5)_2(SR)_2$$

The niobium(IV) complex obtained by the above reaction can be oxidized by iodine:

$$Nb(C_5H_5)_2(SR)_2 \xrightarrow{I_2,\ CH_2Cl_2} [Nb(C_5H_5)_2(SR)_2]I$$

Intermetallic derivatives were obtained from $Nb(C_5H_5)_2(SR)_2$ by treatment either with $Mo(CO)_4(C_7H_8)$ or with chloronickel and chloropalladium complexes.





The crystal and molecular structure of dicyclopentadienylhydridocarbonylniobium(III) has been published [19]. The preparation [20] of the compound involves the preliminary formation of $Nb(C_5H_5)(C_5H_6)(CO)_2$, followed by thermal decomposition of the latter (with hydrogen migration to the metal):

$$Nb(C_5H_5)(CO)_4 \xrightarrow{h\nu,\ C_5H_6} 2\ CO + Nb(C_5H_5)(C_5H_6)(CO)_2$$

$$Nb(C_5H_5)(C_5H_6)(CO)_2 \rightarrow Nb(C_5H_5)_2H(CO)$$

The molecular structure of the hydrido-carbonyl is shown in Fig. 2. The two cyclopentadienyl rings are bent and eclipsed. It has been pointed out [19] that the analogous vanadium complex, $V(C_5H_5)_2H(CO)$ has not been prepared until now.

Hydrido derivatives of dicyclopentadienylniobium(III) with tertiary phosphines have been synthesized [21] by treating $Nb(C_5H_5)_2Cl_2$ with $NaBH_4$, followed by treatment with the phosphine:

$$Nb(C_5H_5)_2Cl_2 \xrightarrow[THF]{NaBH_4,\ PR_3} Nb(C_5H_5)_2H(PR_3)$$

The hydride has basic properties; it reacts with aqueous HCl to give the protonated species $[Nb(C_5H_5)_2H_2(PR_3)]^+$ which was isolated as the tetrafluoroborate and the hexafluorophosphate.

Oxidations of the cationic complex $[M_3(HMB)_3Cl_6]^+$ (HMB = hexamethylbenzene) have been reported [22]:

$$[M_3(HMB)_3Cl_6]^+ \xrightarrow{Ce^{IV}} [Me_3(HMB)_3Cl_6]^{2+}$$

$$(M = Nb, Ta)$$

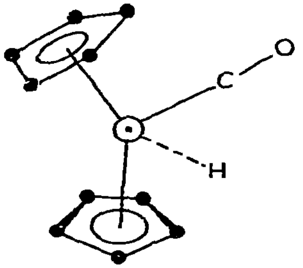


Fig. 2. Molecular structure of $Nb(C_5H_5)_2H(CO)$. (From N.I. Kirillova, A.I. Gusev and Yu. T. Struchkov, Zh. Strukt. Khim., 13 (1972) 473.)

The cationic complexes resulting from the oxidation were isolated as hexafluorophosphates or thiocyanates. These compounds were found to be diamagnetic. In order to account for the diamagnetism of these complexes formally containing one niobium(II) ion of d^3 configuration out of three, the complexes were suggested to be hexanuclear, i.e. $[M_6(HMB)_6Cl_{12}]^{4+}$.

The following intermetallic compounds of niobium and tantalum were reported [14]: $Ph_3SnM(CO)_6$, $Ph_3SnM(CO)_5PPh_3$, $Ph_3SnM(CO)_4(dppe)$, $Ph_3SnTa(CO)_5P(OPh)_3$, $PPh_3AuM(CO)_6$, $[(PPh_3)_3Au][Ta(CO)_6]$, $PPh_3AuM(CO)_5$-PPh_3, $EtHgNb(CO)_6$ and $EtHgM(CO)_5PPh_3$ (M = Nb, Ta). The first compound in the list was, for example, prepared by the following reaction:

$$[K(diglyme)_3][Ta(CO)_6] \xrightarrow[CH_2Cl_2, 0°C]{Ph_3SnCl} Ph_3SnTa(CO)_6$$

It is interesting to note that treatment of $PPh_3AuTa(CO)_6$ with triphenylphosphine resulted in the formation of the ionic product of the hexacarbonyltantalate anion:

$$PPh_3AuTa(CO)_6 \xrightarrow{PPh_3} [(PPh_3)_3Au][Ta(CO)_6]$$

The expected carbonyl substitution was not observed.

Acknowledgment

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