VANADIUM, NIOBIUM AND TANTALUM

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Crystal Structures

Crystal and molecular structures of $Cp_2V_2(CO)_5$* (1), $Cp(PH_3)Nb[HC(C_6H_5)(CC_6H_5)_3C(=NH)CH_3]$ (2), $[Cp(C_5H_4)NbH]_2$ ("niobocene") (3) and $(CH_3)_3TaCl_2\cdot$bipy (4) have been determined by X-ray diffraction. The vanadium carbonyl complex can be regarded as two parts, $CpV(CO)_3$ and $CpV(CO)_2$, joined by a V-V bond and two unsymmetrical bridging CO groups. The first niobium complex contains an unusual hexahapto-azaallylallylic system (as a 6-electron donor) formed by reaction of acetonitrile with a bis-tolan complex. Niobocene has terminal hydrides and Cp ligands and bridging C_5H_4 ligands (see later).

Details of these structures will be found elsewhere in Annual Surveys in the review "Organometallic Structures - Transition Metals".

Hydrido, Alkyl and Aryl derivatives (see also Niobocene and Cp_2TaH_3 under Cyclopentadienyl derivatives).

A pentahydride of tantalum has been isolated as a complex with two molecules of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ (DMPE) (5). Two methods of preparation were successful,

$$\begin{array}{l} TaCl_5 + K \\ \quad \text{or} \\ [Ta(C_6H_5)_6][Li(THF)_4] \end{array} \xrightarrow[\text{DMPE}]{H_2} H_5Ta(DMPE)_2$$

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* Cp = π-cyclopentadienyl

The Ta-H stretch was found at 1544cm^{-1} in the infrared. On exposure of the white crystalline pentahydride to CO at 1500 psi and 80° in benzene, orange $HTa(CO)_2(DMPE)_2$ was obtained in 58% yield.

The monomethyl derivatives CH_3NbCl_4, CH_3NbBr_4 and CH_3TaCl_4 have been prepared from the pentahalides and dimethylmercury or tetramethyltin in CH_2Cl_2 at -35°. No further substitution was observed at this temperature in the presence of an excess of the alkylating agent. The chlorides were found to be thermally stable, although highly reactive, at room temperature and could be stored indefinitely while the bromide was less stable. All formed 1:1 complexes with a range of phosphines, amines and phosphine oxides, which in the case of $CH_3NbCl_4 \cdot P(C_6H_5)_3$, was monomeric and therefore six-coordinate (6).

Complexes of CH_3NbCl_4 with sulphur-containing ligands and CCl_3CN have been isolated by Fowles _et al._ (7). In this paper alkylation of tantalum pentachloride was also investigated following the corresponding reaction with niobium pentachloride published earlier by the same authors (8). In pentane at room temperature PMR showed that an equilibrium was set up in which mixtures of CH_3TaCl_4, $(CH_3)_2TaCl_3$ and $(CH_3)_3TaCl_2$ were present, the proportions varying with the stoichiometry. By using a $TaCl_5$:$Zn(CH_3)_2$ ratio of 1:1.58, pure $(CH_3)_3TaCl_2$ was obtained. Holliday and coworkers have reported (9) that with bis(cyclopentadienyl)lead, the trimethyltantalum dichloride formed $CpTaCl(CH_3)_3$ which is only the second example of a monocyclopentadienyltantalum derivative.

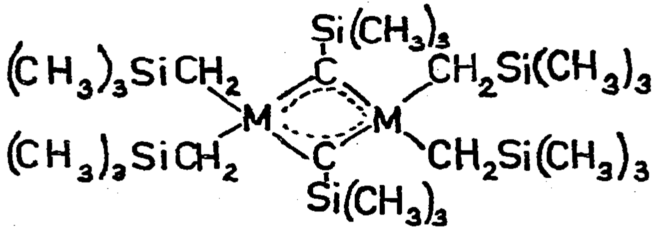
Under suitable conditions a range of complexes of these methyltantalum halides could be formed with THF, dioxan, dithian, CCl_3CN, sulphides, phosphines and phosphine sulphides (7). In most of these complexes the metal appears to be six-coordinate. A weak signal at τ 9.15 in the PMR spectrum of $CH_3TaCl_4 \cdot NCCCl_3$ could be interpreted as evidence for some addition across the triple CN bond forming $Cl_4TaN{=}C(CH_3)CCl_3$.

Similar addition across methyl isonitrile, CH_3NC, occurred with $NbCl_5$ and $TaCl_5$ (10)

$$TaCl_5 + 2CNCH_3 \xrightarrow[48h,20^{\circ}]{ether} TaCl_4[C(Cl){=}N(CH_3)]\cdot CNCH_3$$
$$\big\downarrow {\scriptstyle CNCH_3}$$
$$TaCl_3[C(Cl){=}N(CH_3)]_2\cdot CNCH_3$$

The compounds have bands in the infrared at 1600-1700 cm^{-1} (assigned to C=N) and 2200-2280 cm^{-1} (due to coordinated $CNCH_3$). The latter could be displaced from the first complex by triphenylphosphine.

Details of the preparation of the carbene-bridged dimeric species (M=.Nb or Ta)



from $NbCl_5$ or $TaCl_5$ and $(CH_3)_3SiCH_2MgCl$ have been reported (11). The crystal structure of the niobium compound was described earlier (12). Both the niobium and the tantalum derivatives were found to be air and moisture-sensitive and soluble in ether, petroleum and benzene, but decomposing in chlorinated solvents. They did not sublime and with dry oxygen they formed mixtures of alkoxy compounds.

When trimethylsilylmethylzinc was used as alkylating agent, di- and trialkyl chloro species were produced; i.e. $[(CH_3)_3SiCH_2]_3NbCl_2$ (orange), $[(CH_3)_3SiCH_2]_3TaCl_2$ (yellow) and $[(CH_3)_3SiCH_2]_2TaCl_3$ (pale yellow) after 30 min in ether at room temperature (13). There was no evidence of alkylation beyond the dichloride even with excess zinc alkyl at 80°. The di- and trialkyls could be purified by sublimation at $50^{\circ}/10^{-4}$mm.

Addition of $NbCl_5$ or $TaCl_5$ to an excess of neopentylmagnesium halide produced a mixture of many species. With three equivalents of Grignard reagent the trisalkyl dichloro compound, $[(CH_3)_3CCH_2]_3TaCl_2$, was obtained in a relatively clean reaction as pale yellow crystals, sensitive towards moisture but stable to oxygen and remarkably stable to heat (11). In the same paper attempted preparation of neopentylvanadium compounds was described. As with other alkylvanadium derivatives the neopentyls were less stable than the corresponding niobium or tantalum compounds and could not be isolated.

Similarly benzylvanadium chlorides, $(C_6H_5CH_2)_nVCl_{4-n}$, could not be isolated because of rapid decomposition. Alkylation of VCl_4 with benzylmagnesium chloride, dibenzylmagnesium or dibenzylzinc has been studied under a variety of reaction conditions (14). When two equivalents of Grignard reagent were used, or one equivalent of either $(C_6H_5CH_2)_2Mg$ or $(C_6H_5CH_2)_2Zn$, the VCl_4 was smoothly reduced to VCl_2. With four equivalents of the Grignard reagent, tetrabenzylvanadium was obtained but the yield did not exceed 10% due to the formation of lower valent vanadium derivatives,

$$VCl_4 + (C_6H_5CH_2)_2M \xrightarrow[-MCl_2]{-18^{\circ}} [(C_6H_5CH_2)_2VCl_2] \longrightarrow VCl_2 + (C_6H_5CH_2)_2$$

The most satisfactory synthesis of tetrabenzylvanadium was from VCl_4 and $(C_6H_5CH_2)_2Mg$ (1:2) in ether at -18°. The product was isolated as the black crystalline etherate, $(C_6H_5CH_2)_4V\cdot(C_2H_5)_2O$, which was stable only below 0° and was pyrophoric in air.

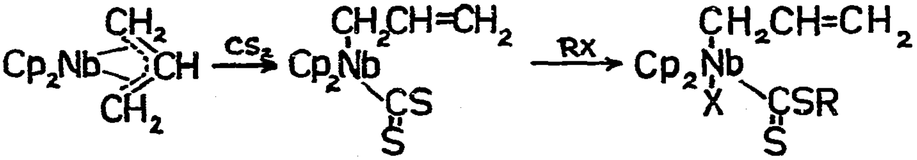
<u>Cyclopentadienyl derivatives</u> [see above for $CpTaCl(CH_3)_3$]

By treatment of Cp_2TaH_3 with $(CH_3)_3Sn\ N(CH_3)_2$ in boiling THF Lappert and coworkers have prepared a white tantalum-tin compound by elimination of amine (15)

$$Cp_2TaH_3 + (CH_3)_2N\ Sn(CH_3)_3 \longrightarrow Cp_2TaH_2{\cdot}Sn(CH_3)_3 + (CH_3)_2NH$$

Only one hydrido atom could be replaced even under forcing conditions. The bimetallic complex could be safely manipulated in air and was more thermally stable than the trihydride precursor.

Reaction of CS_2 with the alkylniobium compound, $Cp_2Nb(\pi\text{-allyl})$, has been shown to involve a π- to σ-rearrangement of the allyl group and the formation of a Nb-C bonded compound with the CS_2. Further reactions occurred with alkyl iodides leading to dithioester derivatives. Ethyl bromide (but not chloride) behaved similarly under more forcing conditions (16). The last-formed compounds were remarkably stable in the solid state for compounds containing a Nb-C bond and could be exposed to the atmosphere for several weeks without detectable change.

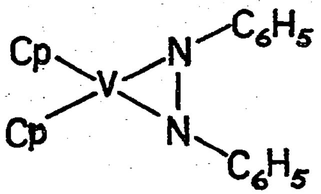


E.S.R. spectra of glasses containing the tetrahedral compounds Cp_2VX_2 and Cp_2NbX_2, where X=Cl, SCN, OCN or CN, have been recorded at 77 and 290 K and analyzed in detail (17). π-Electrons of the cyclopentadienyl rings and σ-bonding electrons from the other ligands X are almost completely delocalized, π-bonding to the Cp residue being stronger than σ-bonding to the X ligands. The position of the unpaired electrons was also calculated.

^{13}C NMR spectra of $CpV(CO)_4$ and $[CpNb(CO)(C_6H_5C{\equiv}CC_6H_5)]_2$ have been measured and the factors influencing the shielding of the ligand nuclei discussed (18).

The vanadium(IV) dithiocarbamates, $[Cp_2V(S_2CNR_2)][B(C_6H_5)_4]$ where $R=CH_3$, C_2H_5, iso-C_3H_7 or C_4H_9, exhibited two one-electron polarographic reduction waves in the potential range + 0.75 to -2.2 V relative to a Ag-AgCl (acetone) reference electrode. The first reduction, which was fully reversible, gave a neutral vanadium(III) complex extremely sensitive to oxygen (19).

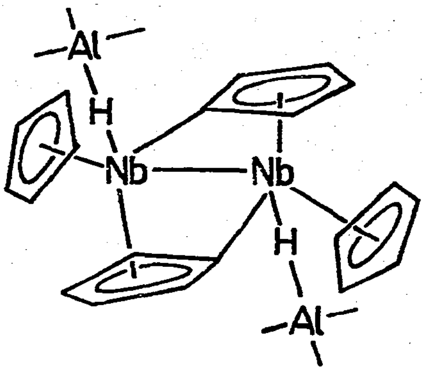
With azobenzene, vanadocene was found to undergo an oxidative addition reaction in toluene at room temperature over one day giving red-black crystals of



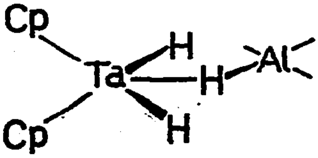
in 80% yield (20). This is the analogue of the titanium compound formed from $Cp_2Ti(CO)_2$ and azobenzene. The vanadium derivative was paramagnetic (μ_{eff} 1.77 BM) and thermally stable. Hydrolysis gave hydrazobenzene and with acetylene dicarboxylic ester, azobenzene was displaced giving the known compound $Cp_2V(CH_3O_2\dot{C}=\dot{C}CO_2CH_3)$.

Thermal decomposition of $(\pi\text{-}C_5D_5)_2VC_6H_5$ in the solid state at 150° gave C_6H_5D (60-65%), biphenyl (10-13%) and perdeuterovanadocene, $(\pi\text{-}C_5D_5)_2V$ (80-90%) together with a residue containing only vanadium and carbon (ca. 4%). Removal of all deuterium atoms from some cyclopentadienyl rings was therefore complete, leading to the formation of benzene and the high yield of vanadocene (21).

Tebbe has studied the reaction of cyclopentadienylniobium and -tantalum hydrides with alkyls of aluminium, gallium, zinc, cadmium and hafnium (22). The products were either simple Lewis acid-base adducts or compounds formed by alkane elimination from these adducts. Triethylaluminium formed strong adducts; e.g. $[Cp(C_5H_4)NbHAl(C_2H_5)_3]_2$, $Cp_2Nb(L)HAl(C_2H_5)_3$, where $L=C_2H_4$, CO or $P(CH_3)_3$, and $Cp_2TaH_3Al(C_2H_5)_3$. The niobocene complex probably contained Nb-H-Al bonds,

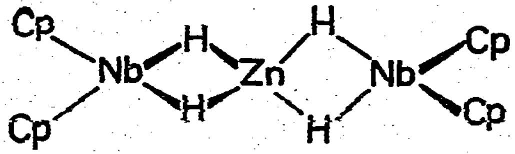


From the hydride shift in the PMR spectra, similar hydride bridges could exist in the C_2H_4, CO and $P(CH_3)_3$ complexes. In the tantalum complex, since only the A portion of the AB_2 hydride PMR spectrum was affected by coordination, selective interaction at the central hydrogen was proposed



The $Ga(C_2H_5)_3$-tantalum adduct was analogues to this but $Zn(C_2H_5)_2$ and $Cd(C_2H_5)_2$ formed weaker adducts, apparently in equilibrium with their components.

Complexes of these alkyls with Cp_2NbH_3 were detected by PMR at -20° to -50° but alkane elimination occurred at room temperature giving $Cp_2NbH_2Al(C_2H_5)_2$ and $(Cp_2NbH_2)_2Zn$ while $Hf(CH_2C_6H_5)_4$ formed $Cp_2MH_2Hf(CH_2C_6H_5)_3$, where M=Nb or Ta. The niobium-zinc compound was formulated with two double hydride bridges



The ultraviolet light induced exchange of carbon monoxide in the vanadium compound $CpV(CO)_4$ has been studied using ^{13}C and ^{18}O enriched CO in hexane or carbon disulphide (23). All of the infrared active CO stretching absorptions present during the reactions were assigned to modes of the all-$^{12}C^{16}O$ molecules and the isotopically enriched species produced in the reactions. The method of local symmetry was used to predict the spectra of the isotopically substituted derivatives.

Protonation of cyclopentadienylvanadium and -niobium carbonyls by CF_3CO_2H in CH_2Cl_2 has been studied by Lokshin et. al. using the shift to higher frequency of the carbonyl absorption on protonation to monitor the reactions (24). $CpV(CO)_4$ was not protonated whereas $CpNb(CO)_4$ was, indicating a higher basicity of the niobium atom. In the phosphine complexes protonation of both occurred but again more readily with the niobium compound.

The ability of lower valent vanadium compounds to remove halogens from organic halides has been explored by Cooper (25). Vanadocene reacted rapidly with aralkyl halides, RX, giving coupled products, RR, and no RH. With vic-dihalides the corresponding olefins were also formed (RX=$C_6H_5CH_2Br$, $C_6H_5CHBr_2$, $(C_6H_5)_2CHCl$ or $C_6H_5CCl_3$).

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