

VANADIUM, NIOBIUM AND TANTALUM

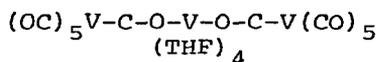
ANNUAL SURVEY COVERING THE YEAR 1977 *

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CARBONYL AND DINITROGEN COMPLEXES

The electronic spectra of $V(CO)_6$ and $V(N_2)_6$, generated by matrix isolation, have been examined, and indicate that CO is both a better σ -donor and π -acceptor than N_2 (1). The ^{51}V NMR of $V(CO)_6^-$ has been recorded and the shift compared to the calculated value (2). $V(CO)_6$ undergoes disproportionation in THF to V^{2+} and $V(CO)_6^-$; a crystal structure of the product obtained after recrystallization from CH_2Cl_2 shows it to be $[V(THF)_4][V(CO)_6]_2$ with linear V-C-O-V bridges:

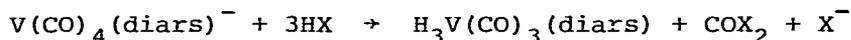


Surprisingly, this bridging has no effect on the C-O distance or the IR: a single ν_{CO} (1859 cm^{-1}) is observed. The V-C distance for the bridging CO is significantly shortened (3).

Irradiation of $V(CO)_6^-$ in the presence of $PhP(CH_2CH_2PPh_2)_2$ (tp) causes sequential replacement of CO's, leading to $V(CO)_5(tp)^-$ (not isolated), cis- $V(CO)_4(tp)^-$, and mer- $V(CO)_3(tp)^-$. Similarly, $CpV(CO)_4$ gives mono- and disubstituted products (4). $V(CO)_6^-$ with Ph_2PPPPh_2 gives dimeric species, formulated by IR and NMR (^{31}P and ^{51}V) evidence as $[(OC)_4V(\mu-Ph_2PPPPh_2)_2V(CO)_4]^{2-}$ and $[(OC)_5V(\mu-Ph_2PPPPh_2)V(CO)_5]^{2-}$; $CpV(CO)_4$ gives mostly

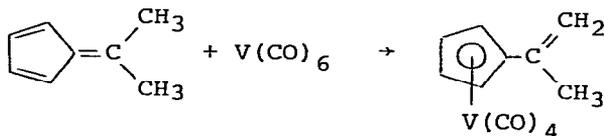
*Annual Survey covering the year 1976 see J. Organometal. Chem., Vol. 138 (1977)p.211-228.

$\text{CpV}(\text{CO})_3(\text{Ph}_2\text{PPPh}_2)$ (5). $\text{MeN}(\text{PF}_2)_2$ reacts with $\text{CpV}(\text{CO})_4$ to yield both $\text{CpV}(\text{CO})_2((\text{PF}_2)_2\text{NMe})$ and $\text{CpV}((\text{PF}_2)_2\text{NMe})_2$; both are highly air-sensitive, in contrast to the parent carbonyl (6). Protonation of $\text{V}(\text{CO})_4(\text{diars})^-$ does not give the corresponding monohydride, but a trihydride:



The trihydride is air-stable, and shows an NMR peak at unexpectedly low field, 8.86 τ . Irradiation under CO gives H_2 loss and formation of $\text{HV}(\text{CO})_4(\text{diars})$ (7).

Compounds $\text{Cp}'\text{V}(\text{CO})_4$ with substituted Cp rings have been prepared from $\text{V}(\text{CO})_6$ and fulvenes. Fulvenes with β -hydrogens give alkenyl groups, e.g.:



while unsubstituted fulvene gives $(\text{MeCp})\text{V}(\text{CO})_4$, and diphenylfulvene gives a complex analyzing as $(\text{C}_5\text{H}_4\text{CPh}_2)_2\text{V}(\text{CO})_4$ (8).

Reduction of TaCl_5 in the presence of $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (dmpe) and CO leads to $(\text{dmpe})_2\text{Ta}(\text{CO})_2\text{Cl}$ which can be further reduced to $(\text{dmpe})_2\text{Ta}(\text{CO})_2^-$. This anion can be protonated with HX or methylated with MeI. Spectral studies indicate that the 7-coordinate Cl and Me complexes have monocapped trigonal prismatic geometry, in contrast to the hydride which has previously been shown (by X-ray crystallography) to be a monocapped octahedron (9). An analogous Nb compound, $(\text{dmpe})_2\text{Nb}(\text{CO})_2\text{H}$, was prepared by reaction of CO with $(\text{dmpe})_2\text{NbH}_5$ (obtained by hydrogenolysis of $(\text{dmpe})\text{NbMe}_5$ in the presence of excess dmpe), and appears to be isostructural (10).

Reduction of VCl_4 with Mg under N_2 gives a black compound with 1 atom of nitrogen per V. This reacts with CO_2 to give an apparent isocyanate, analyzing as $\text{V}(\text{NCO})\text{OMg}_2\text{Cl}_2(\text{THF})_3$ (11).

ALKYL, ARYL AND ALKYLIDENE COMPLEXES

Compounds Cp_2VR_2 ($\text{R} = \text{Me}, \text{Et}, \text{PhCH}_2$) were prepared from the room-temperature reaction of Cp_2V and R_2Cd ; they were identified by ESR. Only the methyl compound is stable; the others decompose to Cp_2VR (12). Analogs with the heavier metals, Cp_2NbMe_2 and $(\text{MeCp})_2\text{TaMe}_2$, have also been prepared, and their ESR and magnetic moments reported; decomposition of the Nb complex gives methane and traces of ethylene (13). Reaction of Cp_2VCl_2 with $\text{LiCH}(\text{SiMe}_3)_2$ gave $\text{Cp}_2\text{V}(\text{CH}(\text{SiMe}_3)_2)_2$; a similar reaction with LiCHPh_2 gave only vanadocene and tetraphenylethane (14).

The reaction of Cp_2NbCl_2 with BuLi under argon containing traces of O_2 and N_2 , gives a blue, paramagnetic compound which analyzes as $(\text{Cp}_2\text{NbBu})_2\text{O}_2\text{N}_2$. No structure was proposed; an IR peak at 1740 cm^{-1} was assigned to N-N stretching (15). In a separate paper, the same reaction was found to give $(\text{Cp}_2\text{NbBu})_2\text{O}$, for which a crystal structure was determined (16).

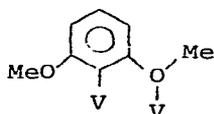
Reaction of VCl_3 with 1 equivalent of ArMgX gives $\text{ArVCl}_2 \cdot 2\text{THF}$ for $\text{Ar} = 2,6\text{-dimethylphenyl}, \text{mesityl}, \text{or penta-methylphenyl}$ (17). If excess ArLi is used, Ar_3V is formed, which could be isolated for the methyl-substituted aryls. Ph_3V is stable only below -40° but reacts with chelating ligands to give $\text{VPh}(\text{acac})_2 \cdot \text{THF}$ and $\text{VPh bipy}_2 \cdot \text{THF}$; $\text{V}(\text{mesityl})_3$ gives adducts $\text{V}(\text{mes})_3 \cdot \text{pyridine}$ and $\text{V}(\text{mes})_3 \cdot \text{bipy}$ (18). $\text{V}(\text{mes})_3$ reacts rapidly with O_2 to give a product analyzing for 1 O per V, suggested to be $(\text{mes})_3\text{V-O-O-V}(\text{mes})_3$. In a subsequent slower reaction a product formulated as $(\text{mes-O})_3\text{VO}$ forms (19).

Mixed alkyl-alkoxy vanadium compounds have been made by two routes. Reaction of $\text{VO}(\text{OR})_3$ with ZnMe_2 gives $\text{MeVO}(\text{OR})_2$, which is relatively stable for bulky R. A similar reaction with $\text{V}(\text{OR})_4$ gives $\text{MeV}(\text{OR})_3$ which are much less stable (20).

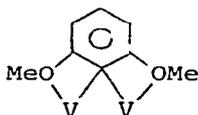
Treatment of R_4V with $R'OH$ gives $R_nV(OR')_{4-n}$, which again are most stable for large R' such as Bu^t (21). Reaction of $V(OBu^t)_4$ with R_3Al gives a compound whose ESR suggests $V(II)$, proposed to be $V(R_2AlR_2)_2$ (22).

Reaction of MX_5 ($M = Nb, Ta; X = Cl, Br$) with RNC ($R = Me, Bu^t$) gives insertion products, $MX_4(CNR)(CX=NR)$ and (for $R = Me$ only) $MX_3(CNR)(CX=NR)_2$; a di-inserted species $MX_3(PPh_3)(CCl=NMe)_2$ was also prepared. Molecular weight determinations suggest these are dimeric, probably bridged through nitrogen (23).

The product obtained from VCl_3 and 2,6-dimethoxyphenyllithium is a diamagnetic compound analyzing as VAr_2 ; a dimeric structure with the aryl groups functioning as C-O bridging ligands and a V-V triple bond was proposed (24). An X-ray crystal structure basically confirms this proposal but the bridging arrangement is more complex than expected: in the V_2Ar_4 unit, which resembles $M_2(OAc)_4$ -type structures, two ligands are bidentate:



and two are tridentate:

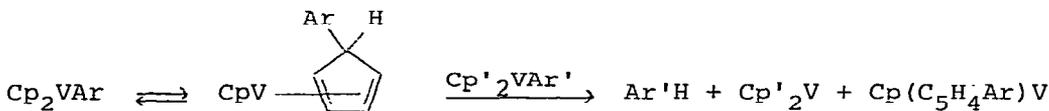


The V-V distance is 2.200 Å (25).

Other chelated alkyl compounds reported are (2-pyrazolylphenyl) $_3V$ (26); (dipivaloylmethanato) $V(C_6H_4-O-CH_2NMe_2)_2$ (27), and $Cp_2V(CH_2C_6H_4-O-NMe_2)$ (28). The first two both have magnetic moments reasonable for $V(III)$ compounds (2.84 and 2.7 B.M., respectively); the last is thermally unstable.

Several studies on thermal decompositions have been reported. Cp_2NbPh_2 decomposes to give benzene (quantitative);

$\text{Cp}_2\text{Nb}(\text{C}_6\text{D}_5)_2$ gives only $\text{C}_6\text{D}_5\text{H}$, indicating the extra hydrogen comes exclusively from Cp rings (in contrast to the Ti analog). Kinetic studies show a first-order reaction with $E_a \sim 35$ Kcal/mole; a deuterium isotope effect was observed for substituting D for H on Ph but not on Cp. A rate-determining step involving homolysis of the Nb-Ph bond leading to a bound phenyl radical was proposed (29). Thermolyses of Cp_2VAr were examined using differential thermal analysis; o-methyl substitution increases stability. Products formed include ArH, Cp_2V and $\text{Cp}(\text{C}_5\text{H}_4\text{Ar})\text{V}$. The mechanism was delineated by means of a labelling study: decomposition of a mixture of $(\text{C}_5\text{H}_5)_2\text{V}(\text{C}_6\text{H}_5)$ and $(\text{C}_5\text{D}_5)_2\text{V}(\text{C}_6\text{D}_5)$ gives C_6D_6 , $\text{C}_6\text{D}_5\text{H}$, C_6H_6 , $\text{C}_6\text{H}_5\text{D}$; $(\text{C}_5\text{H}_5)_2\text{V}$, $(\text{C}_5\text{D}_5)_2\text{V}$; $(\text{C}_5\text{H}_5)-(\text{C}_5\text{H}_4\text{C}_6\text{H}_5)\text{V}$ and $(\text{C}_5\text{D}_5)(\text{C}_5\text{D}_4\text{C}_6\text{D}_5)\text{V}$ but no $(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{C}_6\text{D}_5)\text{V}$. This indicates an intermolecular hydrogen abstraction but an intramolecular migration, e.g. (30):



Cp_2VMe and Cp_2VMe_2 give mostly methane on decomposition; some ring-methylated products were obtained (31).

The neopentylidene complexes $\text{CpMCl}_2(\text{CHCMe}_3)$ ($\text{M} = \text{Nb}, \text{Ta}$) were prepared from $\text{MCl}_3(\text{CH}_2\text{CMe}_3)_2$ and CpTl . The Ta complex reacts with ethylene to give $\text{Me}_3\text{CCH}_2\text{CHCH}_2$, suggested to arise via a metallocyclobutane intermediate which then undergoes a hydride shift. Although this intermediate is similar to species proposed for the olefin metathesis reaction, no metathesis product ($\text{Me}_3\text{CCHCH}_2$) could be detected. With substituted olefins, the regiospecificity of olefinic products suggests that the alkylidene carbon behaves as a nucleophile in metallocyclobutane formation; thus propylene gives $\text{Me}_3\text{CCH}_2-\text{CMeCH}_2$ and styrene gives $\text{Me}_3\text{CCH}_2\text{CHCHPh}$. The metal-containing

products are metallocyclopentanes, (for C_2H_4) $CpTaCl_2(CH_2)_4$ (32). A patent describing reactions of alkylidenes with carbonyl compounds (reported last year) has been issued (33).

CYCLOPENTADIENYL COMPLEXES

Structural studies on Cp_2MH_3 ($M = Nb$, by X-ray; $M = Ta$, by neutron diffraction) have been reported; these confirm the structure assigned based on NMR, with the three hydrogen atoms and the metal all in a plane. Structural parameters are typical of bent sandwich systems; no significant difference between the terminal and central hydrides in terms of M-H distance was observed (34).

The reduction of Cp_2NbCl_2 with a variety of reducing agents (Na, Mg, Zn, Na(Hg), Na naphthalenide) yields a complex claimed to be Cp_2Nb , based on ESR spectroscopy. If correct, this would be the first complex of the heavier metals having a true metallocene structure and fewer than 18 electrons stable enough to detect. Some oxidative reactions were reported: MeI gives $[Cp_2NbIME]^+I^-$, for example, but these reactions might be compatible with other structures as well. The compound could not be isolated (35). Use of only 1 equivalent of reducing agent gives Cp_2NbCl as an isolable, highly soluble, diamagnetic product; it reacts rapidly with air or CO to give Cp_2NbOCl or $Cp_2NbCl(CO)$, respectively (36). Reaction of $TaCl_5$ with $NaCp$ and $LiPPh_2$ gives P_2Ph_4 and an air-sensitive purple compound analyzing as $Cp_4Ta_2Cl_3$; a structure with three bridging chlorides was proposed. The magnetic moment (1.32 B.M.) is compatible with one unpaired electron per dimeric unit (37).

An improved synthesis of vanadocene starts with $VCl_2 \cdot 2THF$, obtained by reducing VCl_3 in THF with zinc; treatment with $NaCp$ gives Cp_2V in 60-70% yield. 1H and ^{13}C NMR of this paramagnetic molecule are reported (38). A cyclic voltammetry study of Cp_2V shows a reversible one-electron reduction, indi-

cating some stability for Cp_2V^- . The oxidation takes place in two one-electron steps, the first reversible and the second irreversible (39). The Raman spectrum of Cp_2V has been determined (40).

Thermolysis of Cp_2V gives mostly CpH and H_2 initially; at later stages degradation of Cp rings to smaller alkanes begins to occur, possibly catalyzed by the metallic vanadium produced (41). Reaction of Cp_2V with alcohols gives CpH and vanadium alkoxide species (42).

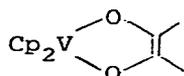
Cp_2MCl_2 ($\text{M} = \text{Nb}, \text{Ta}$) undergoes ring exchange when treated with NaCp' ($\text{Cp}' = \text{C}_5\text{D}_5, \text{C}_5\text{H}_4\text{R}$) followed by HCl ; this method could be used to prepare polymer-supported metallocene dichlorides. Cp_2VCl exchanges with NaC_5D_5 but not $\text{NaC}_5\text{H}_4\text{R}$; anchoring was achieved by reacting polymer-attached Cp^- with Cp_2V (43). Mixtures of Cp_2VCl_x ($x = 0, 1, 2$) with their perdeuterated analogs show ring scrambling on irradiation (44).

An X-ray structure determination for Cp_2VCl shows it to be monomeric, in agreement with earlier solution studies and in contrast to the Ti analog which is dimeric. This was interpreted in terms of an MO picture: the additional electron goes into an orbital (b_2) which would be strongly antibonding in the Cp_2VX_2 -type structure $\text{Cp}_2\text{V}(\mu\text{-Cl})_2\text{VCp}_2$. A general discussion of $d^2 \text{Cp}_2\text{MX}_n$ systems is presented (45).

Two independent groups have reported the use of the unexpected reagent R_3SnCp in synthesis of mono-Cp complexes. Reaction of MX_5 ($\text{M} = \text{Nb}, \text{Ta}; \text{X} = \text{Br}, \text{Cl}$) with Me_3SnCp or Cp_2Mg gives CpNbBr_3 or CpMX_4 (all others) (46). Similarly, Bu_3SnCp was used to make CpMCl_4 as well as ring-substituted analogs. Reaction of NbCl_5 with two equivalents of Bu_3SnCp gives Cp_2NbCl_2 in 80% yield, a highly convenient synthesis of the latter compound (47). Reduction of CpNbCl_4 with EtAlCl_2 in the presence of diphos gives $\text{CpNbCl}_3(\text{diphos})$, whereas

partial hydrolysis of $(\text{MeCp})\text{NbCl}_4$ gives $[\text{MeCpNbCl}_3(\text{OH})]_2\text{O}$; both of these have been characterized by X-ray crystallography. In contrast, reduction of CpTaCl_4 with EtAlCl_2 gives Cp_2TaCl_2 in 40% yield (48).

Reaction of $\text{CpV}(\text{CO})_4$ with PhMH ($\text{M} = \text{S}, \text{Se}$) gives $\text{CpV}(\mu\text{-MPh})_4\text{VCp}$. The sulfur compound is diamagnetic while the selenium shows antiferromagnetic behavior (49). Reaction of Cp_2V with $t\text{-BuSH}$ gives $\text{CpV}(\mu\text{-S})(\mu\text{-SBu}^t)_2\text{VCp}$ which goes on to $(\text{CpVS})_4$ on further heating (50). A series of $[\text{Cp}_2\text{VL}]^+$ complexes, where L is a dithiocarbamate ligand, have been prepared (51). Cp_2V reacts with α -diketones to give products exhibiting ESR typical of $\text{V}(\text{IV})$, formulated as enediolate complexes (52):



Reaction of Cp_2V with RHgCl gives Cp_2VCl , Hg and R_2Hg ; an intermediate suggested to be $\text{Cp}_2\text{VCl}(\text{HgR})$ was observed by ESR (53).

OTHER π -BONDED COMPLEXES

Ethylene reacts with $(\text{dmpe})_2\text{NbH}_5$ to give a complex believed to be $(\text{dmpe})_2\text{NbH}(\text{C}_2\text{H}_4)_2$; NMR data suggest a structure similar to the well-characterized, isoelectronic $(\text{diphos})_2\text{MoH}(\text{C}_2\text{H}_4)_2^+$, although no rapid insertion of C_2H_4 into Nb-H was observed by NMR, in contrast to the Mo complex (10). VCl_3 catalyzes hydrogenation of olefins by LiAlH_4 (54).

A series of substituted allyl complexes $(\eta^3\text{-allyl})\text{V}(\text{CO})_5$ were made by reacting $\text{V}(\text{CO})_6^-$ with allylchlorides and/or $\text{HV}(\text{CO})_6$ with dienes. Also, $\text{V}(\text{CO})_6^-$ reacts with $\text{Ph}_3\text{C}_3^+\text{Br}^-$ to give, after irradiation, $(\text{Ph}_3\text{C}_3)\text{V}(\text{CO})_5$ (55). Irradiation of $\text{V}(\text{CO})_4(\text{diphos})^-$ with allyl chloride gives $(\eta^3\text{-C}_3\text{H}_5)\text{V}(\text{CO})_3(\text{diphos})$ (56); its crystal structure shows a normal η^3 -allyl type bonding (57). A compound formulated as $\text{Cp}_2\text{Nb}(\eta^3\text{-C}_8\text{H}_9)$ was prepared

from $\text{Cp}_2\text{NbCl}_2 + \text{C}_8\text{H}_8 + \text{NaBH}_4 + \underline{i}\text{-PrMgCl}$, or from $\text{Cp}_2\text{NbBH}_4 + \text{C}_8\text{H}_8 + \text{Et}_3\text{N}$ (58).

Reduction of $(\text{dmpe})_2\text{TaCl}_4$ with sodium naphthalenide gives $(\text{dmpe})_2\text{TaCl}(\eta^4\text{-C}_{10}\text{H}_8)$; the bonding of the naphthalene was confirmed by an X-ray structure. Reduction with excess NaNp followed by reaction with ROSO_2F ($\text{R} = \text{H}, \text{Me}$) gives $(\text{dmpe})_2\text{TaR}(\eta^4\text{-C}_{10}\text{H}_8)$. Variable-temperature ^{31}P NMR shows a fluxional rearrangement involving rotation of the naphthalene in the basically pentagonal bipyramidal structure (59). A review of cyclobutadiene complexes includes several examples of group V species (60).

Reaction of the cluster $[(\text{C}_6\text{Me}_6)_3\text{Nb}_3\text{Cl}_6]^+$ with TCNQ gives $[(\text{C}_6\text{Me}_6)_3\text{Nb}_3\text{Cl}_6]^{2+} \text{TCNQ}^{2-}$; the crystal structure shows substantial interactions between TCNQ and hexamethylbenzene groups, resulting in a zig-zag polymeric chain. The cluster geometry differs little from the monocationic species, in agreement with the suggestion that the HOMO in the latter is mainly non-bonding. The ESR shows one unpaired electron residing on the metal cluster; the crystals behave as semiconductors (61).

A crystal structure of $\text{Cp}_2\text{Nb}(\eta^1\text{-allyl})\text{CS}_2$ shows a typical bent sandwich structure with a bent, side-bonded CS_2 group (62). The intercalation of organometallics into TaS_2 has been studied (63).

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