VANADIUM, NIOBIUM AND TANTALUM

ANNUAL SURVEY COVERING THE YEAR 1976

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This survey follows the basic organization scheme used in previous years, with complexes classified according to ligand type. Complexes with more than one class of ligand will be found under the feature of primary interest. The abbreviations Cp (for η^5-cyclopentadienyl) and Cp' (for any ring-substituted cyclopentadienyl group) have been used throughout.

A review emphasizing preparative details of selected group Va organometallic compounds has been published in the Houben-Weyl series (1). A review entitled "Organic Derivatives of Niobium(V) and Tantalum(V)" is primarily concerned with non-organometallic compounds but contains a section on the general organometallic chemistry of these elements as well (2).

CARBONYL COMPLEXES

This area has received a great deal of attention during the past year, especially on studies of neutral and anionic binary carbonyls. Two groups have investigated neutral vanadium carbonyls by means of matrix isolation techniques (3-5). All monomeric species $V(CO)_n$, n = 1-6, were observed

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(4); the hexacarbonyl appears (by IR) to have D_{4h} symmetry, reflecting the expected Jahn-Teller distortion (3,5). In addition, higher concentrations of V give dimeric species, including $V_2(CO)_{12}$ which was assigned a dibridged structure, $(\mu\text{-}CO)_2(V(CO)_5)_2$ (3,5). $V(CO)_6$ was also examined by low-temperature EPR and visible spectroscopy; the results agree with a structure of lower than octahedral symmetry (6).

$[Ph_4As][V(CO)_6]$ has been isolated as a crystalline, moderately air-stable salt (7); the solution IR spectrum shows the expected octahedral symmetry with no ion-pairing. This anion has been silylated with SiH_3I to give $H_3SiV(CO)_6$, which decomposes thermally at room temperature to give, somewhat surprisingly, $(H_3Si)_2O$ (8). The "superreduced" carbonyl anion $[V(CO)_5]^{3-}$ was prepared by reducing $[V(CO)_6]^-$ with sodium in liquid ammonia. The anion is only stable below -20° but can be readily converted to the stable metal-metal bonded species $[(Ph_3M)_2V(CO)_5]^-$ (M = Sn, Pb) and $((Ph_3P)Au)_3V(CO)_5$ (9).

Several photosubstitution studies on carbonyl complexes were reported. $[V(CO)_6]^-$ exhibits highly efficient photosubstitution with CH_3CN or pyridine; spectral studies on $[M(CO)_6]^-$ for all three group Va metals were also reported (10). Photoincorporation of bidentate ligands ($Ph_2P(CH_2)_nPPh_2$, n = 1-4) into $V(CO)_6^-$ and $CpV(CO)_4$ generally gives the disubstituted tetracarbonyl anions, although the monosubstituted intermediates (with only one end of the bidentate ligand coordinated) could be detected by IR (11). ^{51}V NMR data were reported for these compounds. Photolysis of $CpV(CO)_4$ with monodentate phosphines and phosphites yields $CpV(CO)_3L$ (12).

The following non-photochemical route for CO substitution was found to be especially useful for M = Nb or Ta:

$$[M(CO)_6]^- + Ph_3SnCl + PPh_3 \longrightarrow Ph_3SnM(CO)_5(PPh_3) \xrightarrow{Na(Hg)} [M(CO)_5(PPh_3)]^-$$

Disubstituted anions $[M(CO)_4(L_2)]^-$ (L_2 = bidentate phosphine or arsine) were also prepared. For M = V, low yields in the first step make the photochemical method of substitution preferable (13). Preparative details have been given for the salts $A[M(CO)_6]$ where A = $[K(diglyme)_3]^+$ or $[Ph_4As]^+$ and M = Nb or Ta (14).

The dianion $[CpV(CO)_3]^{2-}$ can be generated by reduction of $CpV(CO)_4$ with sodium in HMPA and converted to $[Ph_3SnV(CO)_3Cp]^-$ (15). Treatment of $CpV(CO)_4$ with $K[N(SiMe_3)_2]$ gives the cyano anion $[CpV(CO)_3(CN)]^-$; IR and ^{51}V NMR data are reported (16). $[CpV(CO)_3]^{2-}$ reacts with CN^- under irradiation to give a species of apparent formula $[CpV(CO)_2(CN)]_2^{2-}$ (16).

Electrochemical studies were carried out on $[V(CO)_6]^-$ and $CpV(CO)_3L$ (L = phosphine or phosphite ligand). $[V(CO)_6]^-$ shows a reversible one-electron oxidation in acetone, but $V(CO)_6$ is not stable in acetone, rapidly disproportionating to $[V(acetone)_x]^{2+}$ and $[V(CO)_6]^-$. A second, irreversible oxidation presumably corresponds to formation of highly unstable $[V(CO)_6]^+$ (17). $CpV(CO)_3L$ gives a one-electron oxidation whose potential and reversibility depend upon L; chemical oxidation with $p\text{-}FC_6H_4N_2^+$ or NO^+ gives air-sensitive, paramagnetic cations $[CpV(CO)_3L]^+$ for which EPR data were obtained (12).

ALKYL, ARYL AND ALKYLIDENE COMPLEXES

Two general reviews on transition metal alkyls contain substantial material of relevance to this group: one deals specifically with binary ("homoleptic") metal alkyls, MR_n, emphasizing trends in stability and decomposition mechanisms (18). The other is an extensive review of alkyl and aryl complexes of the "early" transition metals, groups IVa-VIIa (19).

Crystalline, solvent-free $V(CH_2Ph)_4$ has been prepared from VCl_4 and $Mg(CH_2Ph)_2$; its stability appears somewhat greater than the previously reported (see 1973 survey) etherate. EPR and NMR data are reported (20). Similar treatment for $NbCl_4$ gives only reduction products; these contain Nb, Mg and benzyl groups, but it was not established whether any Nb-C bonds were present (21). $TaCl_5$ reacts with dibenzylmagnesium or -zinc in petroleum ether to give $TaCl_{5-x}(CH_2Ph)_x$, x = 1-3 (20). Reaction of VCl_4 with $Zn(CH_3)_2$ leads to a variety of mixed (reduced V-Zn-CH_3-Cl)-containing species, depending upon the ratio of reagents used; some of these may have V-C bonds (22).

Treatment of $V(mes)_3$ (mes = mesityl) with LiAr in THF affords the "ate" complexes $Li[V(mes)_3Ar]\cdot 4THF$ (Ar = mes, Ph); studies on magnetic properties, visible spectra and differential thermal analysis were reported (23). Exposure of $[V(mes)_4]^-$ to air gives the air- and water-stable $V(mes)_4$ in 90% yield (24). Another ate complex, $Li[Ta(p\text{-}tol)_6]\cdot Et_2O$, was obtained from $TaBr_5$ and Li(p-tol) (25). A patent reports the hydrogenolysis of $Li[TaPh_6]$ or $NbPh_4\cdot 2LiPh$ in the presence of $Me_2PCH_2CH_2PMe_2$ (dmpe) to give the hydrides $MH_5(dmpe)_2$ (26).

(A paper on this reaction was surveyed in 1973.)

The crystal structure of the seven-coordinate methyltantalum complex, $TaCl_2(CH_3)(CH_3C(NPr^i)_2)_2$, has been reported; the molecule is basically a distorted pentagonal bipyramid with the bidentate nitrogen ligands occupying four equatorial positions; interestingly, the methyl group is disordered among the remaining three positions (27). Some chelate derivatives of the type $(CH_3)_3Ta(chel)_2$, where chel = β-diketonate, acetate, squarate, perchlorate, bis(pyrazolyl)borate, salen, or N,N-dialkyldithiocarbamate, have been prepared, as well as the non-chelate $(CH_3)_3Ta(N(CH_3)_2)_2$. Insertion reactions with CS_2 were also reported:

$$(CH_3)_3TaCl_2 + CS_2 \longrightarrow (CH_3CS_2)_3TaCl_2$$

$$(CH_3)_3Ta(N(CH_3)_2)_2 + CS_2 \longrightarrow (CH_3)_3Ta(S_2CN(CH_3)_2)_2$$

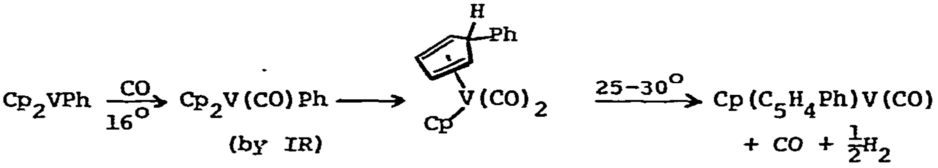
indicating insertion is substantially preferred for an M-N bond rather than an M-C bond (28).

A variety of cyclopentadienylvanadium alkyls, Cp_2VR, were prepared from Cp_2VCl and the corresponding Grignard reagent in pentane. The stability order, determined by decomposition temperature, was R = $CH_3 \sim CH_2SiMe_3 > CH_2CH_3 > CH_2CMe_3 >$ n-pentyl > n-butyl > n-propyl. R = t-butyl or i-propyl gave only reduction to Cp_2V. The surprising stability of the ethyl compound is not understood (29). An independent synthesis of Cp V(CH SiMe) was carried out in order to compare its stability

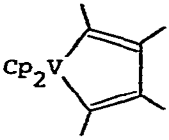
complexes showed very similar reactivity towards several protonic reagents (30).

A full paper gives details of the previously communicated CO-insertion reactions of Cp_2VR. For R = CH_3 or CH_2Ph,

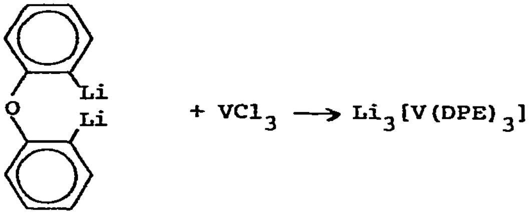
$Cp_2V(CO)(COR)$ was the only product observed; in contrast, for R = Ph a quite different course was followed (31);



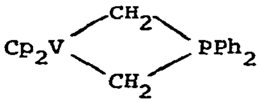
Several new vanadium-containing metallocycles were prepared. Reaction of Cp_2VCl_2 with 2,2'-dilithiobiphenyl, 2,2'-dilithioperfluorobiphenyl or 1,4-dilithiotetraphenylbutadiene gave the vanadium(IV) species:



characterized by magnetic properties and EPR. The stability of these metallocycles is comparable to the Ti analogs, although non-chelated Cp_2VR_2 compounds are usually much less stable (in fact non-existent) than the Ti analogs (32). An anionic complex was prepared from dilithiated diphenylether (DPE):



which has two unpaired electrons, as expected for octahedral V(III) (33). Cp_2VCl reacts with the anionic phosphorus ylide $Li[(CH_2)_2PPh_2]$ to give a metallocyclobutane:



which is capable of transferring a methylene group to cyclohexanone (34).

A full paper reports preparative details and decomposition studies for the binary alkyls $M(CH_3)_5$ (M = Nb, Ta) and $Ta(CH_2Ph)_5$. The methyl compounds yield nearly exclusively methane on thermal decomposition, with all hydrogen coming from other methyl groups, excluding a pathway involving free methyl radicals. An isotope effect of $k_H/k_D \sim 2-3$ was estimated, although a substantial autocatalytic component in the decomposition of the methyl compounds made accurate kinetic determinations difficult. Increased steric bulk was found to retard decomposition; a mechanism involving α-hydrogen abstraction, probably intermolecular, was proposed (35). The heat of formation of $Ta(CH_3)_5$ was determined from calorimetry on the hydrolysis reaction, leading to an estimate of 62 kcal/mole for the average $Ta-CH_3$ bond dissociation energy (36). This quite high value may explain the relative unfavorability of homolysis relative to other mechanisms in the decomposition of such compounds.

The tantalum alkylidene complex $(Me_3CCH_2)_3Ta(CHCMe_3)$ is found to be a highly reactive alkylidene transfer reagent for carbonyl compounds:

$$(Me_3CCH_2)_3Ta{=}CHCMe_3 + R_2C{=}O \longrightarrow \underset{60-90\%}{R_2C{=}CHCMe_3} + [(Me_3CCH_2)_3TaO]_n$$

where the carbonyl compound may be an aldehyde, ketone, ester, amide or even CO_2; the last three are usually not reactive towards phosphorus ylides. With the less reactive substrates the reaction can be observed to proceed in two steps, suggested to be coordination of the carbonyl to the (formally 10-electron) tantalum complex followed by transfer. In agreement, the 18-electron complex $Cp_2Ta(CH_2)(CH_3)$ shows much lower reactivity towards carbonyl compounds (37).

CYCLOPENTADIENYL COMPLEXES

Several experimental and theoretical studies on vanadocene and ring-substituted vanadocenes have been reported. A measurement of the heat of formation for first-row metallocenes leads to the unexpected result that the mean M-Cp dissociation energy is greatest for M = V, following the order (38):

$$Cp_2V > Cp_2Fe > Cp_2TiCl_2 > Cp_2Cr > Cp_2Co > Cp_2Ni > Cp_2Mn$$

A CNDO study on first-row metallocenes and their cationic derivatives includes Cp_2V^{n+}, n = 0-2; the results suggest that Cp_2V^{2+}, if it existed, should have a bent sandwich structure (39). Second-order effects in magnetic properties of Cp_2V and other paramagnetic metallocenes were calculated using a pseudo-axial ligand field model (40). An extensive series of preparative and NMR (^1H and ^{13}C) studies on substituted vanadocenes (Cp'_2V; $Cp' = C_5H_4R$, 1,3-$C_5H_3Ph_2$, _inter alia_) have been described and related to bonding models for metallocenes (41-44).

Interpretation of the bonding in bent bis(cyclopentadienyl) complexes, Cp_2MX_n, continues to attract interest. A mostly qualitative MO study of such species includes a number of examples from group Va (45). Crystal structures have been determined for $Cp_2V(S_5)$ and $Cp_2V(SPh)_2$, as well as the titanium analogs (46,47). In both cases the S-M-S angle is about 5° larger for the Ti complex, in agreement with the conclusion based on EPR studies, reported last year, that the unpaired electron in the vanadium(IV) species resides primarily in an orbital lying outside the region between the X ligands, contradicting the older Ballhausen-Dahl model.

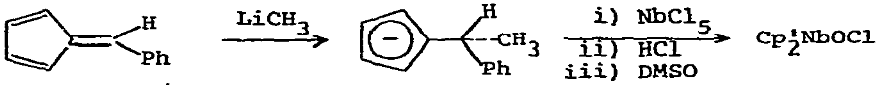
Several other interesting results appear in these studies. The V-S bond distances in both complexes are unexpectedly long compared to Ti; this was interpreted as resulting from either some V-S antibonding character for the extra electron, or increased crowding from the shorter V-Cp distances. It was suggested that this may be related to the instability of the alkyl compounds Cp_2VR_2 (*vide supra*) (46,47). The bis(phenylsulfide) complex was prepared from Cp_2V and PhSSPh; an alternate route, Cp_2VCl_2 + PhSH + Et_3N, was found to give only the sulfide-bridged dimer $Cp_2V_2(SPh)_4$ (46); the latter compound was also prepared, along with the selenium analog, by refluxing $CpV(CO)_4$ with PhMH (M = S, Se) (48). A patent reports somewhat different preparative results: $Cp_2V(SPh)_2$ *can* be obtained by treating Cp_2VCl_2 with NaSPh; Cp_2V reacts with RSSR under *mild* conditions to give the vanadium(III) species $Cp_2V(SR)$, R = CH_3, C_2H_5, Ph, CH_2Ph (49). (A full paper reporting the work covered by this patent was surveyed in 1974.)

The niobium(V) complex Cp_2NbOCl (and substituted analogs), previously obtained as an unexplained side product from the reaction of $Cp_2Nb(S_2)Cl$ with CH_3I, has now been directly prepared by two different routes:

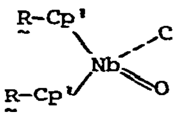
$$Cp_2NbCl_2 \xrightarrow[\text{ii) } O_2]{\text{i) Na, THF}} Cp_2NbOCl \qquad (50)$$

$$NbCl_5 \xrightarrow[\text{iii) DMSO}]{\substack{\text{i) xs LiCp'} \\ \text{ii) HCl}}} Cp'_2NbOCl \qquad (51)$$

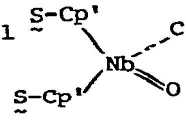
The first report also includes preparation of several alkyl derivatives, by reacting Cp_2NbCl_2 with LiR, followed by air-oxidation to give moderately air-stable $Cp_2Nb(O)R$ (50). A complex with chiral substituents was prepared by the following route:



This complex can exist in four isomers: an enantiomeric pair (1a and 1b) and a diastereomeric pair (2 and 3), the latter differing by configuration at Nb.



1a



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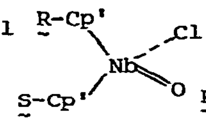

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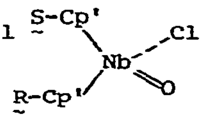

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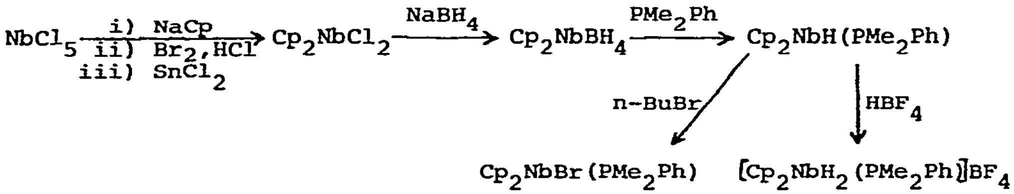
The isomers were separated by chromatography and identified by NMR; 2 and 3 were found to interconvert in a slow epimerization (52).

A full paper presents details of preparation of several adducts of $[Cp_2V]^+$, obtained by treating Cp_2VCl with $NaBPh_4$ in the presence of ligands. Complexes $[Cp_2VS]^+$ (S = acetone, pyridine) have two unpaired electrons, while $[Cp_2V(CO)_2]^+$, $[Cp_2VL(CO)]^+$ and $[Cp_2VL_2]^+$ (L = pyridine, RNC or R_3P) are diamagnetic (53). Reaction of Cp_2VX (X = Cl, SR) with CO in non-polar media gives neutral complexes $Cp_2VX(CO)$. Cp_2VCl does not react with $SnCl_2$ except in the presence of CO, when $Cp_2V(CO)(SnCl_3)$ is (reversibly) formed; longer reaction times give $[Cp_2V(CO)_2][SnCl_3]$. $Cp_2V(SR)$ inserts CS_2 to form $Cp_2V(S_2CSR)$; the temperature-dependent NMR and magnetic properties of this complex were interpreted in terms of an equilibrium between species where the trithiocarbonate ligand is mono- and bidentate, respectively. The related dithiocarbamate complex, $Cp_2V(S_2CNR_2)$, is strictly diamagnetic at all temperatures (31).

Preparative details for a series of bis(cyclopentadienyl)niobium complexes, according to the following scheme, have been provided (54):



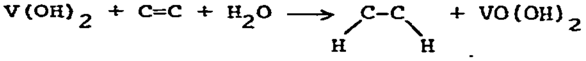
EPR evidence for an adduct between Cp_2VCl_2 and a trialkylphosphite has been observed, although no stable adduct was isolated (55).

Simple adducts of vanadocene with CS_2, bipyridyl, dimethyl maleate and dimethylfumarate have been prepared; all have a single unpaired electron. Reduction of vanadocene with Na in the presence of CO gave $CpV(CO)_4$ in 75% yield, rather than the hoped-for $[Cp_2V(CO)]^-$ (53). Addition of bis(trimethylsilyl)-diazene to vanadocene at -78° gives black-green $Cp_2V(Me_3SiN{=}NSiMe_3)$, tentatively assigned a π-bonded structure like the known azobenzene adduct. On warming to -20° this rearranges to a red-brown isomer (56) which was shown by a crystal structure to be an isodiazene complex, $Cp_2V{-}N{-}N(SiMe_3)_2$. Bond lengths suggest a multiple V-N bond and a virtually single N-N bond. The Cp rings show distortion from planarity, suggested to result from a tendency towards an η^3-mode of bonding (57).

Carboxylate-bridged dimers $CpV(O_2CR)_4VCp$ have been prepared from either $CpV(CO)_4$ or a solution containing VCl_3 and NaCp, and the corresponding carboxylic acid (58,59). $CpVCl_3$ was obtained by chlorination of Cp_2VCl_2 or $CpV(CO)_4$ with $SOCl_2$ under mild conditions; further reaction gave VCl_4. $CpVCl_3$ could not be alkylated; lithium, magnesium and zinc alkyls all gave only reduction products (60).

OTHER π-BONDED COMPLEXES

A gel obtained by coprecipitating $V(OH)_2$ with $Mg(OH)_2$ was found to reduce ethylene and acetylenes according to the stoichiometry:



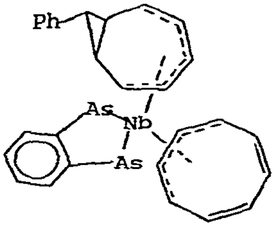
$$V(OH)_2 + C{=}C + H_2O \longrightarrow \underset{H\qquad H}{C{-}C} + VO(OH)_2$$

Since 2-butyne yields only <u>cis</u>-2-butene, these reductions are thought to proceed <u>via</u> π-complexes. This system also shows activity for nitrogen reduction (61).

A crystal structure of $(\eta^3\text{-allyl})V(CO)_4(PPh_3)$ shows normal η^3-allyl bonding to V, with the PPh_3 ligand <u>trans</u> to the allyl group (62). A crystallographic study of $V(1,4\text{-}C_6H_4F_2)_2$, prepared by metal vapor methods, shows the expected sandwich structure; the arene rings are parallel but slightly bent out of planarity, with the carbon atoms bearing the fluorines displaced away from the metal (63). An INDO calculation on $V(C_6H_6)_2$ gives good agreement with experimentally observed geometry and ESR spectral data (64).

The first neutral arenevanadium carbonyl has been obtained by treating $V(CO)_6$ with diphenylacetylene, giving $(C_6Ph_6)V(CO)_3$ in 2% yield; the major product is free hexaphenylbenzene. Direct reaction of the latter with $V(CO)_6$ gives only the previously known type of arene complex, $[(C_6Ph_6)V(CO)_4][V(CO)_6]$ (65). Co-condensation of vanadium vapor with cycloheptatriene gives a complex of formula $VC_{14}H_{16}$, but it was not readily possible to distinguish between the isomeric possibilities $V(\eta^7-C_7H_7)-(\eta^5-C_7H_9)$ and $V(\eta^6-C_7H_8)_2$. The titanium analog has the first structure (66).

Further details of the cyclooctatetraene (COT) complexes of Nb and Ta, reported last year, are contained in a full paper (67) as well as a patent (68). Depending upon reagents and conditions, complexes of formula $[M(COT)_3]^-$, $M(COT)_2R$ ($R = CH_3$, Ph) and $Ta(COT)(CH_3)_3$ were obtained. The $M(COT)_2R$ species appear to have one η^8- and one η^4-ring, which interconvert on the NMR time scale. Most of the compounds formed reversible adducts with phosphine and arsine ligands, but structures were uncertain. Refluxing $Nb(COT)_2Ph$ with $o-C_6H_4(AsMe_2)_2$ (diars) causes the phenyl group to migrate to the ring, giving



for which a crystal structure determination was reported. Similar complexes of the (η^5-bicyclo[5.1.0]octadienyl) ring structure were also obtained by treating $[M(COT)_3]^-$ with electrophiles such as H^+ or Ph_3C^+ in the presence of dmpe (67).

Nb(COT)$_2$Ph was found to be a catalyst for ethylene dimerization (68).

A full paper gives details on the metallocarborane complexes [V(C$_2$B$_{10}$H$_{10}$R$_2$)]$^{2-}$ (R = H, CH$_3$), first reported last year (69).

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