VANADIUM, NIOBIUM AND TANTALUM
ANNUAL SURVEY COVERING THE YEAR 1979

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This survey is organized by ligand type, with complexes containing more than one class of ligand listed according to the feature of primary interest. The abbreviations Cp (for η^5-cyclopentadienyl) and Cp' (for any ring-substituted cyclopentadienyl group) are used throughout. Dates in parentheses indicate a reference to the survey for that year.

CARBONYL COMPLEXES

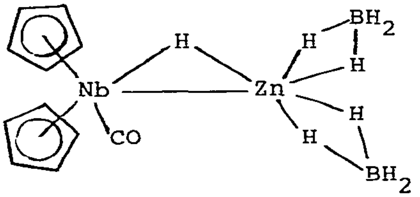
The first large-scale, high-yield synthesis of $CpNb(CO)_4$ has been reported. Cp_2NbCl_2 is heated with sodium sand, copper powder and aluminum dust in benzene, under 330 bar CO, at 135° for 125 hours. On a 20g scale, a 53% yield was obtained. The product is light-sensitive, especially in solution (vide infra) (1). The vibrational (IR and Raman) spectra of $CpNb(CO)_4$ show similar CO stretching frequencies to those of the V analog, but suggest stronger Cp-M bonding in the former (2).

An improved route to $Cp_2V_2(CO)_5$ involves photolysis of $CpV(CO)_4$ in THF solution, using a descending liquid film photoreactor; on a 5g scale, an 89% yield was obtained in two hours (3). Refluxing $Cp_2V_2(CO)_5$ in THF gives, in addition to $CpV(CO)_4$, new compounds $Cp_3V_3(CO)_9$ (1.7%) and $Cp_4V_4(CO)_4$ (32%), identified by analysis, MS and IR. According to the last, both compounds have terminal CO's only; this contrasts with $Cp_4Fe_4(CO)_4$ which has triple-bridging CO's (4). The tetrameric complex appears intriguing, in that the usual electron-counting rules for clusters lead to a count of <u>zero</u> electrons for framework bonding!

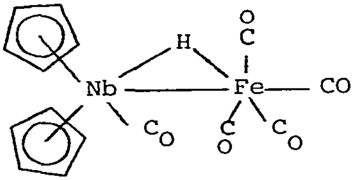
Additional work from Rehder's group on substitution products of $V(CO)_6^-$ and $CpV(CO)_4$ includes the photoreactions of both species with unsaturated bidentate phosphine ligands. With L–L = <u>cis</u>-$Ph_2PCH{=}CHPPh_2$ both monosubstituted, monodentate complexes ($V(CO)_5(L\text{-}L)^-$, $CpV(CO)_3(L\text{-}L)$) and chelated disubstituted complexes ($V(CO)_4(L\text{-}L)^-$, $CpV(CO)_2(L\text{-}L)$) were formed. The trans-bis(phosphino)ethylene gave $[(V(CO)_5)_2(\mu\text{-}L\text{-}L)]^{2-}$, $CpV(CO)_3(L\text{-}L)$, $(CpV(CO)_3)_2(\mu\text{-}L\text{-}L)$ and cis-$(CpV(CO)_2)_2(\mu\text{-}L\text{-}L)_2$. The acetylenic ligand $Ph_2PC{\equiv}CPPh_2$ led to analogs of the last group, as well as spectral evidence for a species with uncoordinated phosphine and coordinated acetylene. Not all the above products were isolated; some were characterized only by spectroscopic means(5).

Similar studies involving ligands E_2R_4, where E = P, As or Sb, led to monodentate complexes $V(CO)_5L^-$ (L = P_2Me_4, $P_2(cyclohexyl)_4$ As_2Ph_4 and Sb_2Ph_4) and $CpV(CO)_3L$ (L = P_2Me_4, P_2cyc_4, $P_2Me_2Ph_2$, P_2Ph_4, and As_2Ph_4); monobridged dimers $[(V(CO)_5)_2(\mu\text{-}L)]^{2-}$ (L = P_2Me_4, P_2cyc_4 and P_2Ph_4) and $(CpV(CO)_3)_2(\mu\text{-}L)$ (L = $P_2Me_2Ph_2$, Sb_2Ph_4); and dibridged dimers $[(V(CO)_4)_2(\mu\text{-}L)_2]^{2-}$ (L = P_2Ph_4, As_2Ph_4) and $(CpV(CO)_2)_2(\mu\text{-}L)_2$ (L = P_2Me_4, P_2cyc_4 and $P_2Me_2Ph_2$). IR and NMR (^{31}P, ^{51}V) spectra were reported and compared to the previously studied ER_3 derivatives (6).

A group of metal-metal bonded niobium carbonyl complexes with interesting structural features have been characterized crystallographically. Reaction of $NbCl_5$ with NaCp and Zn under CO, followed by reaction with $NaBH_4$, gives $Cp_2(CO)Nb(\mu\text{-}H)Zn(H_2BH_2)_2$, with structural parameters Nb-H = 1.75, Zn-H = 1.77, Nb-Zn = 2.829 Å;

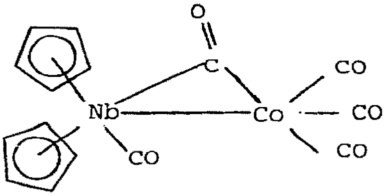


both a preliminary report (7) and full account (8) appeared. A full paper was published on the structurally related compound $Cp_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$, obtained from Cp_2NbH_3 plus $Fe(CO)_5$ (1978):

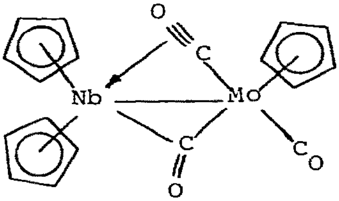


Here Nb-H = 1.91, Fe-H = 1.61, and Nb-Fe = 3.324 Å. Both of these species may be viewed in terms of the 18-electron group $Cp_2NbH(CO)$ acting as a 2-electron donor (through both Nb and H, as a 3-center bond) towards the Lewis acid moieties $Zn(BH_4)_2$ and $Fe(CO)_4$. The NMR of the latter complex shows no metal hydride signal at room temperature but does at lowered temperature; this may be an example of "thermal decoupling" of the quadrupolar Nb nucleus, since the Ta analog (prepared similarly but characterized only spectroscopically) shows the signal even at room temperature (9).

Reaction of Cp_2NbH_3 with $Co_2(CO)_8$ gives $Cp_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$, isoelectronic to the above Nb-Fe complex and containing a semibridging CO:

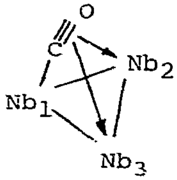


with Nb-Co = 2.992, Nb-$C_{(bridging)}$ = 2.531, Co-$C_{(b)}$ = 1.792 Å, and < Co-$C_{(b)}$-O = 154.1°. Comparison of the Nb-Fe and Nb-Co lengths in the last two complexes is in agreement with the general observation that singly H-bridged metal-metal bonds are longer than expected; this supports the above view of bonding here as a 3-center, 2-electron bond rather than a metal-metal bond supported by a hydrogen bridge (10). A more complex bridging arrangement is found in $Cp_2NbMo(CO)_3Cp$, obtained from Cp_2NbBH_4, $CpMo(CO)_3Me$ and Et_3N; crystallographic determination confirms the suggestion, based on IR (ν_{CO} = 1870, 1700, and 1560 cm^{-1}) (1978) that there is one terminal, one semibridging, and one 4-electron bridging CO:



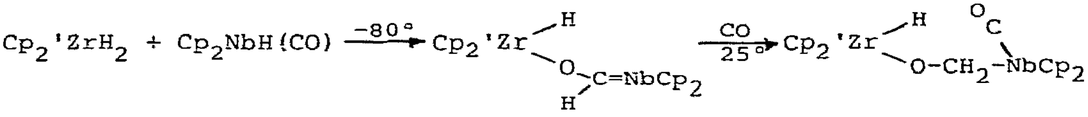
Here Nb-Mo = 3.073 Å; in the semibridging CO, Nb-C = 2.53, Mo-C = 2.02 Å, < Mo-C-O = 154.7°; in the 4-electron bridging CO, Mo-C = 1.94, Nb-C = 2.22, and Nb-O = 2.26 Å. This compound reacts with diphenylacetylene to cleave all the Nb-CO interactions, leaving $(CpMo(CO)_3)_2$ and an unidentified Nb-containing product (11). Escalating still further in complex M-CO interactions, exposure of $CpNb(CO)_4$ to sunlight in hexane solution gives $Cp_3Nb_3(CO)_7$, whose crystal structure shows a triangle of $CpNb(CO)_2$ units. The remaining CO is terminally bonded to one Nb and η^2-bonded to each of the other

Nb atoms, using the two orthogonal π orbitals in the same way that an acetylene bridges two metals:



Thus we have effectively a 6-electron bridging CO, one step beyond the 4-electron CO of the previous example. The angle Nb_1-C-O is 170°, nearly linear; $Nb_1-C = 1.97$; $Nb_{2,3}-C = 2.25$ and $Nb_{2,3}-O = 2.22$ Å (the last two are averaged values) (12).

Another bimetallic system is relevant to CO reduction chemistry: $(C_5Me_5)_2ZrH_2$ reacts with $Cp_2NbH(CO)$ at −80° to give a (zirconoxy)-alkylidene niobium complex, with NMR peaks at 5.70 (Zr–H) and −3.14 δ (Nb–H). Addition of H_2 at 25° gives Cp_2NbH_3 and $Cp_2'ZrH(OCH_3)$, while reaction with CO effects addition of the Nb–H group to the alkylidene moiety, resulting in a zirconoxymethyl complex (13):



$$Cp_2'ZrH_2 + Cp_2NbH(CO) \xrightarrow{-80°} Cp_2'Zr(H)(O\text{-}CH{=}NbCp_2) \xrightarrow[25°]{CO} Cp_2'Zr(H)(O\text{-}CH_2\text{-}Nb(CO)Cp_2)$$

Full details on electrochemical attempts to prepare $Cp_2V(CO)^-$ (1978) have appeared. $Cp_2V(CO)$ undergoes a reversible 1-electron reduction (−2.32 V vs. SCE), but preparative electrolysis consumes $2e^-$ per vanadium, giving metallic V and Cp^-. Under CO a $3e^-$ reduction is observed, generating $CpV(CO)_3^{2-}$ and $CpV(CO)_3H^-$. $Cp_2V(CO)$ also exhibits an irreversible oxidation peak at −0.3 V (14).

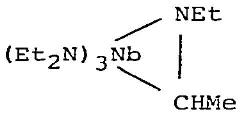
Irradiation of $CpV(CO)_4$ with MeSSMe gives $(CpV)_2(\mu\text{-}SMe)_4$, a previously reported type of compound (1977), plus a new species characterized by analysis and spectral data as $(CpV(CO)_2)_2(\mu\text{-}SMe)_2$. (15). Reaction of $CpV(CO)(NO)_2$ with $NOPF_6$ (or $CpV(CO)_4$ with $NOPF_6$ followed by NO) gives $CpV(NO)_3{}^+PF_6{}^-$ (16).

ALKYL AND ARYL COMPLEXES

Reaction of $TaCl_5$ with two equivalents of $NaN(SiMe_3)_2$, followed by LiMe, gives $Me_3Ta(N(SiMe_3)_2)_2$. With L = CH_2SiMe_3 an alkylidene complex, $(Me_3SiCH_2)(Me_3SiCH)Ta(N(SiMe_3)_2)_2$, is obtained instead. The latter gives ^1H and ^{13}C shifts of 6.3 and 231 δ, respectively, for the alkylidene proton and carbon (17). The phosphine adducts $MMe_5(PMe_3)_2$ have been prepared for M = Nb and Ta (18). New phenylvanadium(V) complexes include $PhVO(OR)_2$ from $VOCl(OR)_2$ plus LiPh, and $PhVOCl(OR)$, from $VOCl_2(OR)$ plus

$HgPh_2$ (R = i-Pr); both decompose to biphenyl and $VO(OR)_3$ (19). Attempts to prepare alkylvanadium acetylacetonates from $VCl_2(acac)_2$ and Grignard reagents gave no stable product, but vanadium(III) complexes $RV(acac)_2$ were obtained either from $V(acac)_3$ + RMgX or from VR_4 + 2 acacH (R = $PhCH_2$, Me_3SiCH_2, C_6F_5). The failure to observe any stable alkylvanadium(IV) complex recalls the unfavorability of Cp_2VR_2 species (20).

Cp_2NbCl_2 reacts with ferrocenyllithium to give $Cp_2Nb(ferrocenyl)_2$ which shows a typical Cp_2NbR_2 ESR signal and is more stable than the phenyl analog (21). Treatment of MCl_5 (M = Nb, Ta) with $Me_3SnCPh{=}CMe_2$ generates the alkenyl $(Me_2C{=}CPh)MCl_4$, characterized by NMR only (22). $NbCl_5$ plus $LiNEt_2$ yields an η^2-iminoalkyl complex (23):



Complexes Cp_2NbMeL, where L = CO, $P(OMe)_3$, PEt_3 and C_2H_4 were prepared; the carbonyl complex by the following route:

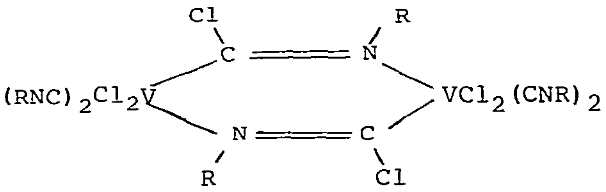
$$Cp_2NbMe_2 \xrightarrow{HCl} Cp_2NbMeCl \xrightarrow[CO]{Na/Hg} Cp_2NbMe(CO)$$

Exposure to air transforms it to Cp_2NbMeO. No insertion to give an acetyl complex could be observed, even at 50° and 200 atm CO. Similarly, addition of LiMe to $Cp_2Nb(CO)_2^+$ gave only $Cp_2NbMe(CO)$; the presumed intermediate acetyl was not detected. This contrasts with the related vanadium system: carbonylation of Cp_2VMe leads directly to the acyl with no intermediate $Cp_2VMe(CO)$ being detected (1976). An explanation on MO grounds was proposed: niobium lacks a sufficiently low-lying empty orbital for an η^2-interaction with the acyl, suggested to be essential for insertion to occur. Photolysis of $Cp_2NbMe(CO)$ at -78° generates Cp_2NbMe, which is stable to room temperature; at 40-50° it decomposes to several products including dimeric niobocene; carbonylation of the decomposition mixture leads to $Cp_2NbH(CO)$, suggesting α-elimination is involved (24).

In a related study, olefin complexes $Cp_2TaH(RCH{=}CH_2)$ react with CO at 75° to give alkyls, $Cp_2Ta(CH_2CH_2R)(CO)$; formation of acyls was never observed. With olefin complexes existing as an endo-exo mixture (1978), only the endo isomer (in which the R substituent on the olefin is oriented towards the Ta-H bond) gives insertion; exo isomers give $Cp_2TaH(CO)$ by simple displacement.

Cp_2TaH(cyclopentene) gives a mixture of insertion (90%) and displacement (10%). $Cp_2TaCl(CO)$ was obtained by reducing Cp_2TaCl_2 under CO with potassium sand or t-butyl Grignard; it was found to be inert to either $LiAlH_4$ or alkyllithium reagents (25).

CO insertion *was* observed on carbonylation of $(C_5Me_5)TaMe_4$; the initial product is $Cp'TaMe_2(\eta^2$-acetone); the bonding was so formulated on the grounds of an IR peak at 1200 cm^{-1} assigned to C-O stretching. This compound reacts with O_2 to give acetone; with H_2O to give isopropanol and methane; and with H_2 to give $Cp'TaHMe_2(OCHMe_2)$, which is unstable and evolves CH_4. Continued exposure of the acetone complex to CO gives a slower transformation to an oxo species, $Cp'Ta(O)Me(O\overset{*}{C}Me{=}\overset{*}{C}Me_2)$ wherein the two starred carbon atoms come from CO (by labelling) (26). VCl_3 plus excess (t-butyl)NC gives a compound of formula $VCl_3(RNC)_3$, for which molecular weight, IR and magnetic susceptibility measurements suggest the structure



With $NbCl_4(THF)_2$, $[NbCl_3(CClNR)(CNR)]_2$ is obtained; related Nb(V) species were previously reported (1977) (27).

ALKYLIDENE AND RELATED COMPLEXES (SCHROCK CHEMISTRY)

Both the fact that work in this area could variously be placed under several topics (alkyls, cyclopentadienyls, π-complexes) and the quantity of work that has appeared virtually necessitate a separate section for this material. Schrock has written a review on his group's work on alkylidene complexes for *Accounts of Chemical Research* (28).

Mechanistic aspects of the formation of alkylidenes by α-abstraction have been examined in detail. $TaCl_3Np_2$ (Np = neopentyl, Me_3CCH_2) rapidly reacts with TlCp at 0° to give $CpTaCl_2Np_2$, which is slowly transformed to the neopentylidene complex, $CpTaCl_2(CHCMe_3)$, plus NpH. The latter reaction is first-order, faster in more polar solvents, entirely intramolecular (at least in early stages) and shows an isotope effect of $k_H/k_D \simeq 6$. A number of studies varying the metal (Nb), halide (Br), cyclopentadienyl group (C_5Me_5) and alkyl group ($PhCH_2$) were also performed. The mixed compound $CpTaCl_2(Np)(PhCH_2)$ is less reactive than the -Np_2 analog and gives mostly loss of toluene to form the same product, suggesting steric crowding accelerates α-elimination; a cis arrangement of alkyls in the pyramidal $CpMX_2R_2$ species also may be essential.

Cp'$TaCl_3$Np plus LiNp gives Cp'$TaNp_2(CHCMe_3)$; with $LiCHDCMe_3$ a similar isotope effect was observed, suggesting NpH formation is intramolecular from a dialkyl species; this contrasts with the behavior of the $TaCl_2Np_3$ + LiNp system (1978). It is notable that all these coordinatively unsaturated alkyls and alkylidenes show exceptionally low values for $^1J_{CH}$ (75-100 Hz) and ν_{CH} (2500 cm^{-1} for $CpTaCl_2(CHCMe_3)$), suggesting substantial interaction between the α C-H bond and the metal. (Coordinatively saturated $Cp_2TaCl(CHCMe_3)$ shows no such low ν_{CH}). It was proposed that such interactions are crucial in promoting facile α-elimination, with factors enhancing the Lewis acidity of the metal (Br>Cl, Ta>Nb) increasing reactivity. The observed isotope effects may be due, at least in part, to an equilibrium effect: the H in a $TaCHDCMe_3$ grouping will prefer to be in the "bridging" position and thus will be preferentially eliminated (29).

Structural support for this view had previously been obtained from the large M-C-C angles observed in X-ray crystal structures. A full paper on the previously-communicated (1978) structure of $Ta(mesityl)(PMe_3)_2(CHCMe_3)_2$ shows a distorted trigonal bipyramid with PMe_3's axial, a C-Ta-C angle of 106° between the two alkylidene ligands, and alkylidene geometries Ta-C = 1.932, 1.955 Å; <TaCC = 169, 154° (30). Now a neutron diffraction study has permitted location of the crucial hydrogen. Reaction of $TaCl_3Np_2$ with PMe_3 gives $[TaCl_3(PMe_3)(CHCMe_3)]_2$ which shows the characteristic $^1J_{CH}$ (101 Hz), ν_{CH} (2605 cm^{-1}) and <TaCC (161.2°) values; the α-H is quite close to Ta (2.119 Å) and the C-H bond is unusually long (1.131 Å), consistent with a high degree of p character in the C-H bond (31). An alternative view suggests that large M-C-C angles in alkyls are due simply to non-bonded interactions: repulsion between M and the β-carbon impose a lower limit on <MCC for MCH_2R. Analysis of several known structures suggests that the non-bonded radii of Nb (2.07 Å) and Ta (2.01 Å) are especially large (32). This does not take into account the most recent structural work on such species, however. A full paper on the structure of the benzylidyne complex $(C_5Me_5)TaCl(CPh)(PMe_3)_2$ (1978) shows a tetragonal pyramidal ("four-legged piano-stool") geometry with Ta-C = 1.849 Å (cf. 2.25-2.3 in Ta alkyls; 2.03-2.07 in alkylidenes; 1.76

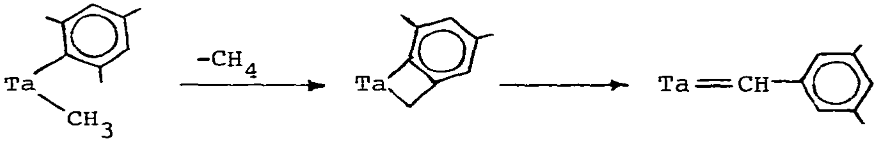
in $TaNp_3(CCMe_3)Li$). The phenyl group is somewhat distorted (e.g., <CCC = 115° at the ipso carbon), suggesting conjugative interactions in the Ta≡C–Ph group (33).

Reaction of $Cp_2TaMe(PMe_3)$ with $Me_3P{=}CH_2$ gives slow formation of $Cp_2TaMe(CH_2)$ which reacts further (almost as fast as it is formed) to give $Cp_2TaMe(C_2H_4)$ (1978); since C_2H_4 is displaced by PMe_3 under irradiation this can serve as a photocatalyst for:

$$Me_3P{=}CH_2 \xrightarrow[Cp_2TaMe(CH_2)]{h\nu} Me_3P + 1/2\ C_2H_4$$

Use of $Me_3P{=}CHR$ gives $Cp_2TaMe(CHR)$, R = Ph, Me; the latter is the first stable ethylidene complex. Surprisingly, it shows no tendency to undergo a hydride shift, leading to $Cp_2TaMe(C_2H_4)$; instead, heating at 70° gives $Cp_2TaH(CH_2{=}CHMe)$, presumably <u>via</u> "insertion" of CHMe into Ta–Me, giving a propyl complex which would be expected to rearrange by β-hydride abstraction (cf. the reaction of Cp_2TaCl_2 with RMgX (1978)) (34).

Mesityl complexes $MX_{5-n}(mes)_n$ (M = Nb, Ta; X = Cl, Br; n = 1-3) are much more stable than the corresponding phenyls, probably because of the possibility of β-elimination in the latter (see below). Also prepared were $TaCl_{2,3}(mes)_{2,1}$ Np and $TaCl_3(mes)Me$. NMR suggests restricted rotation about M–C bonds. Addition of PMe_3 to $TaX_3(mes)Me$ gives unstable $TaX_3(mes)MeL_2$ which at 45° gives the substituted benzylidene, $TaX_3L_2(CH(3,5\text{-}C_6H_3Me_2))$, suggested to arise via γ-elimination, loss of CH_4 and hydrogen migration in a benzometallacyclobutane (35):

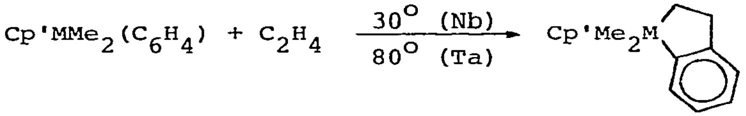


The first isolable mononuclear benzyne complexes were obtained by the following reactions:

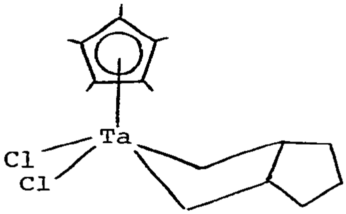
$$(C_5Me_5)TaCl_3Np + ZnPh_2 \longrightarrow Cp'TaCl_2(C_6H_4) + NpH$$

$$(C_5Me_5)TaClMe_3 + LiPh \longrightarrow Cp'TaMe_3Ph \xrightarrow{120^{\circ}} Cp'TaMe_2(C_6H_4)$$

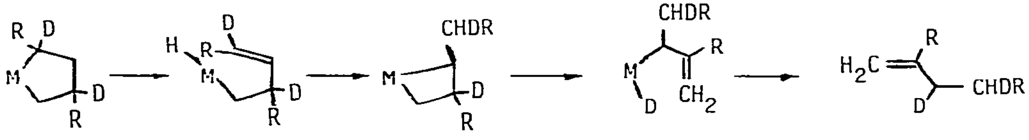
The crystal structure of the latter is <u>not</u> analogous to the piano stool arrangement in $CpTaL_4$ species; rather the C_6H_4 plane is virtually perpendicular to the $TaMe_2$ plane as well as to the Cp' plane (36). NMR shows that rotation of the C_6H_4 ligand is rapid even at -80°, suggesting (semantically at least) the ligand is better described as a π-benzyne than a di-σ-phenylene. The Nb analog of this compound was also prepared; both react with C_2H_4 to give benzometallacyclopentanes (37).



Several papers deal with olefin-metallacycle chemistry in these systems. A full paper has appeared on the reactions of olefins with $CpTaCl_2(CHCMe_3)$ (1977,1978). Reaction of $(C_5Me_5)TaCl_3Np$ with $ZnEt_2$ gives $Cp'TaCl_2(C_2H_4)$ which adds C_2H_4 at 35° to give the metallacycle $Cp'Cl_2Ta(CH_2)_4$. Mixed metallacycles can be generated, e.g. by adding propylene to the monoethylene complex, but rapid disproportionation to a mixture of symmetric metallacycles ensues even at 10° (38). The crystal structures of the above $Cp'Cl_2Ta(CH_2)_4$ as well as the bicyclic compound obtained from 1,6-heptadiene were determined.



In both structures the TaC_4 ring has the envelope conformation shown above, quite different from other structurally characterized metallacyclopentanes (39). $Cp'TaCl_2$(cyclooctene) catalyzes olefin dimerization at 50°: $CH_2{=}CHR$ gives both 2,3 (favored for small R) and 2,4 (favored for large R) disubstituted but-1-enes, although the (trans) 2,3 isomer is the only metallacycle detectable. With $CH_2{=}CDR$ the major and minor products are, respectively, $CH_2{=}CR\text{-}CDR\text{-}CH_2D$ and $CH_2{=}CR\text{-}CHD\text{-}CHDR$; these results plus the co-dimerization product of $CH_2{=}CHR$ plus $CH_2{=}CDR'$ appear to require a metallacyclobutane intermediate leading to loss of olefin. E.g., for the 2,4 product:

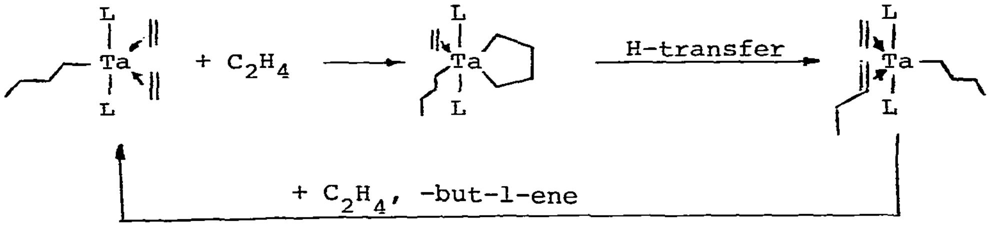


An analogous sequence leads to the major product. It may be noted this may provide a mechanism for generating the required catalytic intermediate for olefin metathesis from only a (reduced) metal center and olefins (40).

An ethylene dimerization catalyst can be prepared by the following sequence.

$$TaNp_3(CHCMe_3) + PMe_3 \longrightarrow TaNpL_2(CHCMe_3)_2 \xrightarrow{C_2H_4} \text{Catalyst} + 3\ NpCH{=}CH_2$$

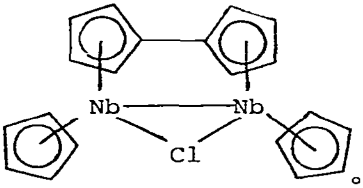
The Nb analog leads to $Nb(C_2H_5)(C_2H_4)_2L_2$ which is not active. $Ta(C_2H_5)L_2(C_2H_4)_2$ could be prepared from $TaCl_3L_2(C_2H_4)$ and C_2H_5MgBr; addition of C_2H_4 gives the same (by NMR) catalyst, which appears to contain two components, the major one being $Ta(C_4H_9)L_2(C_2H_4)_2$. The following mechanism was proposed:



Metallacycle formation may be the rate-determining step; this would be slower for Nb (41). $Cp_2TaCl_2(CHMe_3)$ reacts with PhCCPh to form a new alkylidene complex, $CpCl_2Ta{=}C(Ph){-}C(Ph){=}CHCMe_3$, probably via a metallacyclobutene intermediate. The product reacts with C_2H_4 to give $CpTaCl_2(CH_2)_4$ and $CH_2{=}CH{-}CHPh{-}CPh{=}CHCMe_3$ (29).

CYCLOPENTADIENYL COMPLEXES

Further details support the proposed (1977) existence of monomeric niobocene as a moderately stable species. Reduction of Cp_2NbCl_2 with sodium naphthalenide at -78° gives a 10-line ESR signal, assigned to Cp_2Nb, with a yield (by integration of the ESR signal) of 54%. At -20° the signal disappears, following second-order kinetics, to give the familiar dimeric form $[CpNbH(\mu\text{-}C_5H_4)]_2$. Both the monomer and the dimer react with oxidizing agents Br_2 and RSSR to form monomeric Cp_2NbX_2 (X = Br, RS); thus reaction products alone cannot be used as indication of the presence of monomeric species (42). Reduction of Cp_2NbCl_2 with sodium naphthalenide at high temperature, or treatment of dimeric niobocene with $HgCl_2$ gives a mixed-valence, fulvalenide complex:



The crystal structure shows Nb-Nb = 3.27 Å; the magnetic moment of 1.5 B.M. indicates one unpaired electron per dimer (formal oxidation state = 2.5) (43). A fulvalenide vanadium complex, $(C_{10}H_8)_2V_2$, was prepared from $C_{10}H_8{}^{2-}$ and $VCl_2 \cdot 2THF$;, it is purple like vanadocene but diamagnetic. Oxidation with $Cp_2Fe^+PF_6{}^-$ in MeCN gives $(C_{10}H_8)_2V_2(MeCN)_2{}^{2+}(PF_6{}^-)_2$, whose crystal structure was determined; the fulvalenide ligands are folded somewhat (dihedral angle between 5-membered rings = 14°) to give two reasonably normal Cp_2MX bent-sandwich structures. The V-V bond which joins them is 3.329 Å, considered to be a (weak) single bond, although each V center has formally 16 electrons (exclusive of V-V bonding). In agreement, the magnetic moment (2.9 B.M.) indicates two unpaired electrons per dimeric unit (44).

Another improved preparation of vanadocene involves reducing VCl_3 with $LiAlH_4$ (instead of Zn (1977)) to give $VCl_2 \cdot 2THF$; treatment with NaCp gives Cp_2V in 78% yield (45). Cp_2Pb plus VCl_3O gives Cp_2VClO; with $TaMe_3Cl_2$, $CpTaMe_3Cl$ is obtained (46).

A study on thermochemistry of metallocenes included calorimetry on decomposition of Cp_2V; in agreement with a prior study (1976) the M-Cp bond energy is highest for M = V and Fe. Also the favorability of oxidation to Cp_2M^+ is lowest for V and Fe, somewhat surprising in view of the susceptibility of Cp_2V to oxidation. However, this is due to the relative magnitude of the term for $M^{2+} \longrightarrow M^{3+}$ in the cycle used to calculate enthalpies (47). This point was also made in a review on structural aspects of the 3d metallocenes; if M-Cp bond energy is taken from the reaction $Cp_2M \longrightarrow M^{2+} + 2Cp^-$, the value for Cp_2V is lower. M-C bond distances increase in the order Fe<Co<Cr<V<Mn, while M-C stretching constants follow the opposite order, as expected (48).

A full paper on metallocene electrochemistry, including Cp_2V, has appeared; as previously noted (1977), Cp_2V undergoes a reversible one-electron reduction (-2.74 V) and successive one-electron oxidations (-0.55 V, reversible; +0.59 V, irreversible). Cp_2VCl_2 exhibits three successive one-electron reductions at -0.29, -1.54

and -2.74 V; the second is irreversible, suggesting the sequence is (49):

$$Cp_2VCl_2 \xrightarrow{e^-} Cp_2VCl_2 \xrightarrow{e^-} Cp_2V + 2Cl^- \xrightarrow{e^-} Cp_2V^-$$

Cp_2V is oxidized by AgCl to Cp_2VCl and, more slowly, on to Cp_2VCl_2. A reactive alkyl bromide oxidized Cp_2VCl to Cp_2VClBr which is in equilibirum with the two symmetric dihalides (by ESR) (50).

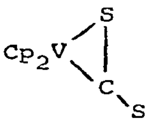
Pyrolysis of vanadocene at 500-550° gives first-order decomposition, giving mostly H_2 and CpH in the gas phase, and hydrocarbons (mostly CpH oligomers) in the solid (51). Decomposition of group IV metal alkyls, Cp_2MR_2, in the presence of $(C_5D_5)_2V$, gave $C_{10}H_xD_{10-x}V$ where x = 0-10, showing intermolecular exchange between Cp_2V rings and intermediates of the Cp_2MR_2 decomposition (52).

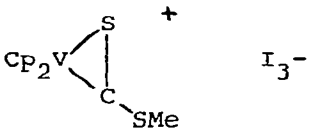
The mechanism of formation of Cp_2NbH_3 from reduction of Cp_2NbCl_2 has been examined. Reaction of the latter with $LiAlH_4$ leads to $Cp_2NbH_2AlH_2$; immediately after reaction, however, an equimolar mixture of Cp_2NbH_3 and $Cp_2NbH_2AlH_2$ is present (by NMR). Red-al ($NaAlH_2(OCH_2CH_2OCH_3)_2$) gives analogous results, except that higher yields of Cp_2NbH_3 can be observed. Reduction in the presence of ligands (L = CO, C_2H_4 $PMePh_2$) gives <u>up to</u> 50% Cp_2NbHL, suggesting the following:

$$\begin{tikzcd}
2\ Cp_2NbCl_2 + 4\ MH_2AlR_2 \arrow[r] & 2\ Cp_2NbH_2 \arrow[d] & + 4\ AlR_2H + 4\ MCl \arrow[d, dash] & \\
& Cp_2NbH_3 + Cp_2NbH \arrow[d, "L"] \arrow[r, dash] & {} \arrow[r] & Cp_2NbH_2AlR_2 \\
& Cp_2NbHL & &
\end{tikzcd}$$

Hydrolysis of $Cp_2NbH_2AlH_2$ leads quantitatively to Cp_2NbH_3; labelling shows that the Nb-H bonds remain intact (53).

The crystal structure of Cp_2VCS_2 has been determined; it reacts with MeI to give $Cp_2V(CS_2Me)I$ which adds I_2 to give $Cp_2V(CS_2Me)I_3$ which was also crystallographically characterized; the structures are (54);



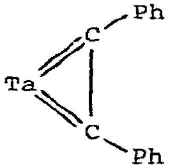


Cp_2V reacts with $(SeCN)_2$ to give $Cp_2V(NCSe)_2$, and with $X(CN)_2$

to give $Cp_2V(CN)(NCX)$ (X = S, Se) (55). Cp_2NbCl_2 reacts with $Cd(GeEt_3)_2$ to give $Cp_2NbCl(GeEt_3)$ (56), and with ferrocenoylacetone to give $CpNb(FcCOCHCOCH_3)_2Cl$ (57). The reactions of Cp_2V with $Hg(OAc)_2$, $Hg(O_2CPh)_2$ and $Hg(C_6F_5)_2$ have been examined (58). ESR studies on polymer-supported niobium compounds, Ⓟ-$CpNbCl_3$ (monomeric analog unknown) and Ⓟ-Cp_2NbCl_2 were reported; the latter is very similar to monomeric Cp_2NbCl_2 (59). Cp_2VCl_2 is found to have antitumor properties (60).

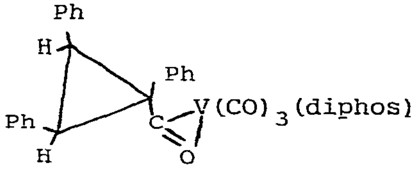
OTHER π-BONDED COMPLEXES

Crystal structures have been reported for vanadocene adducts of dimethyl acetylenedicarboxylate and diethyl fumarate; interestingly, the latter product can be obtained by reacting Cp_2V with either fumarate or maleate. Both have fairly normal geometries, with the unsaturated ligand nearly perpendicular to the plane defined by V and the two ring centers; C-C distances are 1.29 and 1.47 Å for the acetylene and olefin, respectively (61). $Cp_2Nb(O_2CCMe_3)$ forms an adduct with diphenylacetylene; the crystal structures of both starting compound and adduct were determined. That of the latter is similar to previously-studied Cp_2NbX(olefin or acetylene) complexes; the carboxylate ligand is monodentate (bidentate in starting compound) (62). Diphenylacetylene also reacts with the nonorganometallic Ta(III) complex $Ta_2Cl_6(THT)_3$ (THT = tetrahydrothiophene) to give $TaCl_3(THT)_2(PhCCPh)$ which with wet pyridine forms $pyrH^+\ TaCl_4(pyr)(PhCCPh)^-$ whose crystal structure was determined. The acetylene coordination shows notably short Ta-C (2.07 Å) and long C-C (1.325 Å) distances, suggested to indicate some contribution of a bis(alkylidene) bonding mode:



i.e., the acetylene acts as a four-electron donor, as has been proposed for a number of early transition metal complexes (63). Irradiation of Cp_2NbH_3 with hexafluorobut-2-yne gives a mixture of four products: Cp_2NbF_2 (30%; characterized by ESR); metallacycle $Cp_2Nb(C(CF_3))_4$ (20%; X-ray crystal structure); alkenyl complex $Cp_2NbF(C(CF_3){=}CHCF_3)$ (10%); and alkyne complex $Cp_2NbH(CF_3CCCF_3)$ (trace). No details of characterization for the last two products were given (64).

Allyl (and methallyl) complexes $(\eta^3\text{-allyl})V(CO)_3(L\text{-}L)$ were prepared from $V(CO)_4(L\text{-}L)^-$ and allyl chloride ($L\text{-}L = Ph_2P(CH_2)_nPPh_2$, where n = 1 or 3). For the case n = 4 only $(\text{allyl})V(CO)_4(L\text{-}L)$, with the bis(phosphine) ligand monodentate, was obtained (65). The crystal structure of $(\eta^3\text{-1-methallyl})V(CO)_3(\text{diars})$ shows rather asymmetric bonding of the allyl group, with the methyl substituent (in a syn conformation) bent well out of the C_3 plane (66). In attempting to make a substituted derivative of the cyclopropenyl complex $(C_3Ph_3)V(CO)_5$ (1977), $V(CO)_4(\text{diphos})^-$ was irradiated with $C_3Ph_3{}^+Br^-$; however, the product is a η^2-acyl complex (x-ray structure):



The source of the hydrogens is uncertain (67).

A full paper has appeared on $TaCl(\text{dmpe})_2(\eta^4\text{-naphthalene})$ (1977); as previously described (x-ray structure), it has pentagonal bipyramidal structure with the naphthalene, two P's and the Cl equatorial; the naphthalene is bent well out of planarity (as expected for η^4-coordination). The $\eta^4\text{-}C_6H_8$ analog was also prepared but not obtained completely pure. A hydride complex, $TaH(\text{dmpe}_2)(\eta^4\text{-}C_{10}H_8)$, was found to be a (poor) catalyst for olefin hydrogenation; the methyl analog of the latter was also synthesized. Fluxional behavior is described (68).

APPLICATION IN SYNTHESIS AND CATALYSIS

The reduction of C_2H_2 and N_2 by $V(OH)_2\text{-}Mg(OH)_2$ gels (1976, 1978) has been re-examined; stoichiometry of the acetylene reduction suggests that V undergoes only a one-electron change:

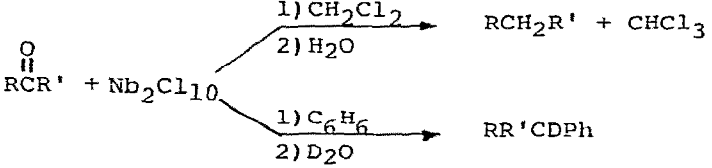
$$2V(OH)_2 + C_2H_2 + 2H_2O \longrightarrow 2V(OH)_3 + C_2H_4 \xrightarrow{?} C_2H_6$$

in contrast to the previous proposal of $V^{2+} \rightarrow V^{4+}$. Formation of clusters of V^{2+} centers by diffusion was proposed; the dependence of the C_2H_4/C_2H_6 ratio on $[V^{2+}]$ could be modelled by assuming they are produced by reactions at dimeric and tetrameric sites, respectively (69). The reduction of N_2 by the system $Li/\text{naphthalene}/VCl_3$ has also been re-examined (70).

The ESR of the system $Cp_2VCl_2 + Et_2AlCl$ has been examined as a model for Ziegler-Natta polymerization. A doublet splitting (detected only in the 5th derivative spectrum!) superimposed upon ^{51}V coupling was interpreted in terms of the compound

$Cp_2HV(Cl_2AlX_2)$ (X = Cl or Et). Pyridine or THF generates a new species, suggested to be Cp_2VHCl, which reacts with HCl to reform Cp_2VCl_2 (71). Reaction of the olefin complex $VCl_3(C_6H_{10})$ (1978) with aluminum alkyls gives polymerization catalysts, having different properties from those obtained from VCl_3 (72). The polymerization of propene by VCl_4/Et_2AlX has been studied (73). Reaction of $VO(OBu)_3$ or $V(NEt_2)_4$ with hydrido-aluminum species generates olefin hydrogenation catalysts (74).

Nb_2Cl_{10} effects ketone deoxygenation:



$$R\overset{O}{\overset{\|}{C}}R' + Nb_2Cl_{10} \xrightarrow[2)\,H_2O]{1)\,CH_2Cl_2} RCH_2R' + CHCl_3$$

$$R\overset{O}{\overset{\|}{C}}R' + Nb_2Cl_{10} \xrightarrow[2)\,D_2O]{1)\,C_6H_6} RR'CDPh$$

Spectroscopic studies suggest the ketone initially coordinates, and that a species like RR'PhC-O-Nb (in benzene) is present before hydrolysis (75). Several vanadium compounds alter the $PdCl_2$-catalyzed carbonylation of nitrobenzene (76). Cocondensation of vanadium atoms with quadricyclane causes substantial isomerization to norbornadiene (77).

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