VANADIUM, NIOBIUM AND TANTALUM
ANNUAL SURVEY COVERING THE YEAR 1980 **

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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(s) of primary interest. The abbreviations Cp (η- C_5H_5), Cp* (η-C_5Me_5) and Cp' (any ring substituted cyclopentadienyl) have been used throughout. Dates in parentheses indicate a reference to the survey of that year.

CARBONYL COMPLEXES

Convenient preparations of $V(CO)_6$ and $[Et_4N][V(CO)_6]$ have been reported; the first monosubstituted derivative of the former, $V(CO)_5(PPh_3)$, can be obtained either by direct replacement or by oxidizing $[V(CO)_5(PPh_3)]^-$ with tropylium ion (1). Several other neutral $V(CO)_xL$ complexes, where L is a polyphosphine ($MeC(CH_2PPh_2)_3$ or $P(CH_2CH_2PPh_2)_3$) were also reported (2). Chromatography of substituted anions $[V(CO)_xL]^-$ (x = 2-4, L = tri- or tetra (tertiary phosphine ligand) on silica gel leads to the hydrides $HV(CO)_xL$, which were investigated by ^1H, ^{31}P and ^{51}V NMR; analysis of H-P coupling indicates facile mobility of hydride (3). Photolysis of $[V(CO)_6]^-$ in a methyltetrahydrofuran glass at 80K gives, successively, $[V(CO)_5(MTHF)]^-$ and cis-$[V(CO)_4(MTHF)_2]^-$ (4).

Although the neutral binary carbonyls of Nb and Ta are yet unknown, the completely substituted "derivatives" thereof, $M(dmpe)_3$ (M = V, Nb, Ta) were obtained by metal vapor synthesis. Crystallography indicates distorted octahedral structures (5). Electrochemical studies on $TaX(CO)_2(dmpe)_2$ (X = Cl, Br, I, Me, H) reveal a reversible (by cyclic voltammetry) one-electron oxidation (6).

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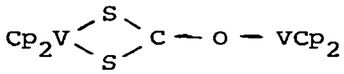
Reduction of $CpNbCl_4$ with Na, Cu and Al under CO at 135° gives the best yield yet reported for $CpNb(CO)_4$, 90% (7). For Ta, however, the same route fails; only a small amount of $CpTa(CO)_4$ is obtained, the major product being "$CpTa(CO)_xCl_y$" (8). The latter product is probably $CpTaCl_2(CO)_3$; this compound as well as the niobium analog are obtained by reducing $CpMCl_4$ under milder conditions: Al plus $HgCl_2$ under 1 atm CO (9). Reduction of $CpNbCl_3$(dmpe) under CO gives $CpNbCl_2$(CO)(dmpe); further reduction under CO gives $CpNb(CO)_2$(dmpe) (10). The dppe analog of the latter has also been reported (11); both compounds can be reversibly protonated by HPF_6.

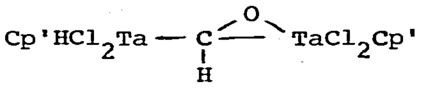
A detailed study on the photoreaction of $CpV(CO)_4$ with PPh_3 has been carried out; the maximum quantum yield for formation of $CpV(CO)_3(PPh_3)$ is 0.8. No disubstituted product formed, as photoexpulsion of PPh_3 appears to be more favorable (12). Photolysis of $CpNb(CO)_4$ in THF gives $CpNb(CO)_3$(THF), which was not isolable but could be used to make $CpNb(CO)_n(^*CO)_{4-n}$ or $CpNb(CO)_3(PPh_3)$ (7).

The crystal structure of $[Cp_2V(CO)_2][BPh_4]$ has been determined; although there is substantial disorder, it appears to be a normal bent metallocene system, with a CVC angle of 92° (13). The carbonyls $Cp_2{}'TaX(CO)$, where $Cp' = C_5H_4Pr^i$ and X = H or Cl, have been prepared by routes similar to those previously found successful for the ordinary Cp analogs (14). Reaction of vanadocene with carbonyl sulfide gives $Cp_2V(CO)$ if the former is in excess; otherwise the compound



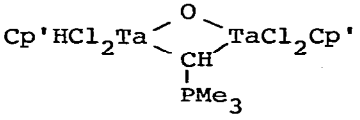
is obtained, as demonstrated crystallographically. The product has a magnetic moment of 2.72 B.M., corresponding to two unpaired electrons per V_2 unit (15).

The reactions of Cp_2NbH_3 with metal carbonyls have been examined as a possible route to CO reduction; organometallic products include $Cp_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$ (1978, 1979), $Cp_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$ (1979), and $Cp_2(CO)Nb(\mu\text{-}H)M(CO)_5$ (M = Mo,W). With $Cr(CO)_6$ ethane is produced; labelling shows this comes from CO reduction, probably initially to ethylene which is then hydrogenated (16). Reduced forms of CO were also obtained in reactions of $(Cp'TaHCl_2)_2$: addition of CO at 0° gives a product characterized as a formyl-bridged dimer (by NMR):



I

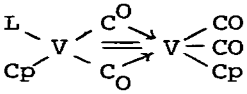
while reaction of the latter with PMe_3 gives complete C-O bond cleavage and the following structure (by X-ray):



II

The Ta-bonded hydride in II gives an NMR signal at 10.0 δ, while that for the (Me_3P-C<u>H</u>) proton is at 1.8 δ (17).

Further studies on $Cp_2V_2(CO)_5$ have been reported. Its synthesis by photolysis of $CpV(CO)_4$ apparently involves <u>two</u> photosteps, as thermal reaction of $CpV(CO)_3(THF)$ (the first photoproduct in THF at -42°) with $CpV(CO)_4$ gives only decomposition products. $Cp_2V_2(CO)_5$ undergoes thermal decomposition via a CO-dissociation path, and substitution by phosphines to make $Cp_2V_2(CO)_4L$ (L = PPh_3 or η^1-dppm) by an associative pathway. With PEt_2Ph, mononuclear products $CpV(CO)_3L$ and $CpV(CO)_2L_2$ form instead. Substitution can also be achieved photochemically (18). The crystal structure of $Cp_2V_2(CO)_5$ has been redetermined at -150°, along with the structure of $Cp_2V_2(CO)_4(PPh_3)$. A model was proposed which views the bridging CO's as "donor semibridges":



but the details of the structure do not offer any conclusive evidence. The metal-metal distance is 2.459 Å for L = CO and 2.466 Å for L = PPh_3 (19).

NMR studies on $Cp_3Nb_3(CO)_7$ (1979) reveal dynamic behavior: while the crystal structure shows all three Cp rings as non-equivalent, at room temperature only two different environments are seen; while at higher temperatures all three centers become equivalent. This indicates that the 6-electron bridging CO must become mobile in some fashion, although not necessarily interconverting with the terminal CO's; unfortunately ^{13}C NMR on the CO's gave no useful information, probably because of broadening due to coupling to ^{93}Nb (20).

ISONITRILE COMPLEXES

The product from VCl_3 plus Bu^tNC has been shown crystallographically to be octahedral mer-$VCl_3(CNBu^t)_3$, <u>not</u> the dimeric insertion product previously proposed (1979). With excess ligand $[V(CNBu^t)_6]^{2+}$ is obtained (21). Addition of several different isonitriles to the olefin complexes $Cp_2NbH(RCH=CH_2)$ (22) or $Cp_2TaH(RCH=CH_2)$ (23) gives $Cp_2M(CH_2CH_2R)(CNR')$; no further insertion to form iminoacyls was observed.

ALKYL AND ARYL COMPLEXES

A recent review on metal methyl complexes includes a brief discussion for $NbMe_5$ and $TaMe_5$ (24).

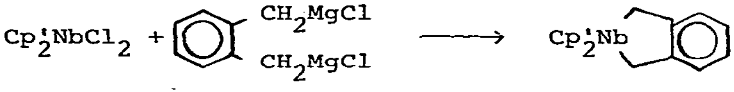
The EPR spectrum of $V(mesityl)_4$ has been examined in both solution and single crystal; only ^{51}V coupling was detected (25). The analogous (2,6-dimethoxyphenyl) complex does not form; instead complexes $Li[V(2,6-(MeO)_2C_6H_3)_4]$ and $Li_2[V(2,6-(MeO)_2C_6H_3)_4]$ were obtained; some metal-oxygen interaction appears to be present (26). $V(1\text{-camphenyl})_4$ is a polymerization catalyst (27). The mixed compounds $[Li(THF)_4][VR(mesityl)_3]$ were prepared for R = phenyl, o-tolyl, methyl and others; with potentially bridging alkyl groups dimers are obtained, e.g.

$$V(mesityl)_3 + p\text{-}Li_2C_6H_4 \longrightarrow [Li(THF)_4]_2\ [V_2(mesityl)_6(\mu\text{-}C_6H_4)]$$

Decomposition of these compounds gives some R-mesityl (28). The EPR of Li_4VPh_6 in a frozen solution is the same as in the fluid; parameters suggest a regular octahedral V(II) complex (29).

Mixed alkyltantalum complexes $TaMe_3(CH_2SiMe_3)_2$ and $TaMe_3(CH_2PPh_2)_2$ were obtained starting with $TaCl_2Me_3$ (30). The reaction of $VCl(NEt_2)_3$ with LiR(R = Pr^n, Bu^n) gives $VR(NEt_3)_2$ – rare examples of stable, electron-deficient complexes of alkyls with β-hydrogens (31). Complexes of the 1-adamantylmethyl group $VR_2(OBu^t)_2$, $NbR_2(OBu^t)_3$ and $TaCl_2R_3$ were all prepared; the last is air-stable (32). The chelating alkyl complex $V(o\text{-}C_6H_4CH_2PPh_2)_3$ was obtained from VCl_3 and the lithium reagent; its electrochemistry was briefly examined (33). Reduction of VCl_4 with magnesium in THF gives some hydrocarbons, especially after hydrolysis, suggesting formation of a metal alkyl (perhaps a vanadacyclopentane) from THF and the reduced metal species (34).

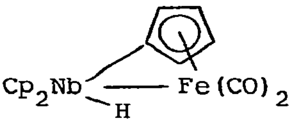
Oxidation of Cp_2VR (R = Me, CH_2SiMe_3) by AgCl, CuCl or $CuCl_2$ gave Cp_2VClR (isolable for Me); redistribution reactions subsequently lead to Cp_2VR_2 and $Cp_2VMe(CH_2SiMe_3)$ (35). Reaction of Cp_2V with R_3SiCH_2Cl (R = Me, Et) affords $Cp_2V(CH_2SiR_3)$, along with Cp_2VCl (36). A new synthesis of Cp_2VMe_2 was reported; it decomposes photochemically to give methane and ethane in about 2:1 ratio. This contrasts with the thermal decomposition which gives all methane (1976). Both Cp_2VMe and Cp_2NbMe_2 give mostly methane, plus traces of ethane and ethylene, either thermally or photochemically (37). A chelating dialkyl was prepared as follows:



III

The X-ray structure (Cp' = $C_5H_4SiMe_3$) and EPR of III were reported (38). An EPR study was also carried out for $Cp_2Ta(\eta^1\text{-}Cp)_2$ (39). The Nb(IV) alkyl Cp_2Nb(2-thienyl)$_2$ can be oxidized to pentavalent alkyls Cp_2NbIR_2 or $Cp_2NbClIR$ (from Cp_2NbClR); photolysis with sulfur gives $Cp_2NbR_2(S_2)$ (40).

Niobium alkyls $Cp_2Nb(CH_2CH_2R)(CO)$ were obtained from CO-induced insertions of olefin hydride complexes; as with the Ta analogs (1979), of the two possible olefin orientations only the endo leads to insertion (22). Analogous isonitrile complexes for both metals were also reported (22, 23). Reaction of $Cp_2'TaCl(PMe_3)$ with LiMe gives $Cp_2TaMe(PMe_3)$ (Cp' = $C_5H_4Pr^i$) (14); $Cp_2TaCl(CO)$ could not be thus alkylated (1979). The reactions of $Cp_2Nb(BH_4)$ with $CpFeMe(CO)_2$ and Et_3N gives a compound with an Nb-C bond (41):



IV

A study on NO insertions focusses on the differing behavior of diamagnetic and paramagnetic alkyl complexes. The pentamethyls of niobium and tantalum give $NbMe_2(ON(Me)NO)_3$ and $\{TaMe_3(ON(Me)NO)_2\}_2$ respectively, while $V(CH_2SiMe_3)_4$ affords $VO(CH_2SiMe_3)_3$. With Cp_2NbMe_2 the final product is $Cp_2NbO(ON(Me)NO)$, but evidence for several intermediates, possibly including $Cp_2NbMe_2(NO)$, was obtained during low-temperature reactions (42).

ALKYLIDENE AND RELATED COMPLEXES (SCHROCK CHEMISTRY).

A highly interesting paper on theoretical treatment of alkylidene complexes, as well as the α-elimination reactions leading thereto, has appeared (43); while not limited to these metals, it is clearly of greatest relevance here. Examples of "authentic" α-elimination have been reported: that is, cases where $M(CH_2R)$ goes to MH(CHR), or M(CHR) to MH(CR), in the following reactions:

$$TaCl_4(CH_2CMe_3) + PMe_3 + Na/Hg \longrightarrow TaHCl_2L_3(CHCMe_3)$$

V

$$Cp'TaCl_3(CH_2CMe_3) + PMe_3 + Na/Hg \longrightarrow Cp'TaHClL(CHCMe_3)$$

VI

$$\mathrm{Cp'TaBr_2(CHCMe_3) + PMe_3 + Na/Hg \longrightarrow \underset{VII}{Cp'TaHL_2(CCMe_3)}}$$

$$\mathrm{TaCl_3L_2(CHCMe_3) + PMe_3 + Na/Hg \longrightarrow \underset{VIII}{TaClL_4(CHCMe_3)}}$$

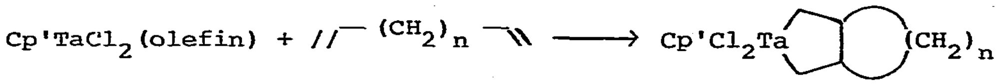
The ^{1}H NMR of V is striking; the tantalum-bonded hydride appears at low field (10 δ) and the alkylidene hydrogen at high field (0.24 δ), contrary to what is commonly expected. The last reaction gives, not α-elimination, but the low-valent alkylidene complex VIII, which shows evidence (1979) for a remarkably strong interaction between metal and α-hydrogen: shift = 7.4 δ, $^1J_{CH}$ = 69 Hz, ν_{CH} = 2200 cm^{-1} (44).

Several benzylidene complexes were obtained from the reactions of benzyl complexes (the complete set, $TaCl_n(CH_2Ph)_{5-n}$ where n = 0-4, is now known) with LiC_5Me_5 or LiC_5Me_4Et; products include $Cp'TaCl(CH_2Ph)(CHPh)$ and $Cp'Ta(CH_2Ph)_2(CHPh)$. The crystal structure of the latter was determined and shows a "piano stool" geometry; the Ta-C distance for the benzylidene carbon is 1.88 Å (vs. 2.21 for the benzyl groups) (45). An extensive group of octahedral alkylidene complexes was generated by the following route:

$$\mathrm{MX_3(CH_2R)_2 + 2L \longrightarrow MX_3L_2(CHR) + RCH_3}$$

where (not all combinations) M = Nb or Ta; X = Cl or Br; R = CMe_3, $SiMe_3$, Ph; L = PMe_3, PMe_3Ph, $PMePh_2$, THF, py, or L_2 = dmpe, dppe, diars, tmeda, bipy. NMR was used to determine geometry as well as the course of these elimination reactions (46). The complexes, and more importantly, analogs wherein one or more X is an alkoxide such as $OCMe_3$, show metathesis-like reactions with olefins (47).

The formation of metallacycles in reactions of olefins with alkylidene or olefin complexes has received additional study: a full paper on the dimerization of olefins involving $Cp'TaX_2$(olefin) species (1978, 1979) has appeared (48), as well as an account of a talk on the same subject (49). Metallabicycles are obtained from α,ω-dienes:



IX

where n = 3, 4, or 5 (50). A full paper on the crystal structures of IX (n = 3) as well as the simple metallacyclopentane has appeared (51); features were previously summarized (1979).

Several unusual complexes with nitrogen ligands have been prepared:

$$\mathrm{TaCl_2(THF)_2(CHCMe_3)} + \mathrm{RN{=}CHPh} \longrightarrow \underset{\mathrm{X}}{\mathrm{TaCl_3(THF)_2(NR)}}$$

$$\mathrm{TaClL_4(CHCMe_3)} + \mathrm{Me_3SiN_3} \longrightarrow \underset{\mathrm{XI}}{\mathrm{TaClL_2(NSiMe_3)(CHCMe_3)}}$$

$$\mathrm{TaCl_3L_2(CHCMe_3)} + \mathrm{Na/Hg} \xrightarrow{N_2} \underset{\mathrm{XII}}{\{\mathrm{TaClL_2(CHCMe_3)}\}_2\ (\mu\text{-}\mathrm{N_2})}$$

$$\mathrm{XII} \xrightarrow{\mathrm{LiR}} \underset{\mathrm{XIII}}{\{\mathrm{TaRL_2(CHCMe_3)}\}_2(\mu\text{-}\mathrm{N_2})} \quad (\mathrm{R} = \mathrm{Me},\ \mathrm{CH_2CMe_3})$$

$$\mathrm{TaCl_3L_2(C_2H_4)} + \mathrm{L} + \mathrm{Na/Hg} \xrightarrow{N_2} \underset{\mathrm{XIV}}{\{\mathrm{TaClL_3(C_2H_4)}\}_2(\mu\text{-}\mathrm{N_2})}$$

$$\mathrm{X} + \mathrm{Na/Hg} + \mathrm{L} + \mathrm{C_2H_4} \longrightarrow \underset{\mathrm{XV}}{\mathrm{TaClL_3(NR)(C_2H_4)}}$$

In all these reactions L = $\mathrm{PMe_3}$. The crystal structure of XIII ($\mathrm{R} = \mathrm{CH_2CMe_3}$) has been determined and shows an exceptionally long N-N distance (1.298 Å), suggesting a diimide description, Ta=N-N=Ta (i.e., XI and XII are close analogs) (52, 53). Hydrogenolysis of $\mathrm{Cp'TaCl_2}$(propylene) gives a hydride complex $\mathrm{(Cp'TaHCl_2)_2}$ (see above for its reactions with CO) (17).

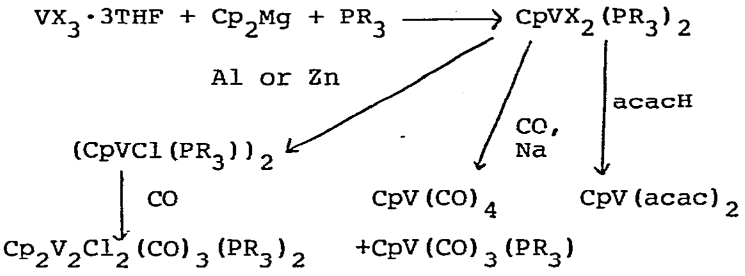
CYCLOPENTADIENYL COMPLEXES

Work continues on synthetic avenues for mono-Cp complexes. Both $\mathrm{CpNbCl_4}$ and $\mathrm{CpTaCl_4}$ are obtained from $\mathrm{CpSiMe_3}$ and the corresponding metal pentachloride (54). $\mathrm{CpNbCl_4}$, prepared from the analogous tin reagent, undergoes the following transformations (10, 11):

$$\begin{tikzcd}
\mathrm{CpNbCl_4} \arrow[r, "\mathrm{Et{+}AlCl2}", "\mathrm{dppe}"'] \arrow[d, "\mathrm{EtAlCl_2}"', "\mathrm{dmpe}"] & \underset{\mathrm{XVI}}{\mathrm{CpNbCl_3(dppe)}} \arrow[r, "\mathrm{Na/Hg}", "\mathrm{CO}"'] & \mathrm{CpNb(CO)_2(dppe)} \arrow[d, "\mathrm{HPF_6}"] \\
\mathrm{CpNbCl_3(dmpe)} \arrow[r, "\mathrm{Mg/Hg}", "\mathrm{CO}"'] & \mathrm{CpNbCl_2(CO)(dmpe)} \arrow[r, "\mathrm{Vitride}", "\mathrm{CO}"'] & \mathrm{CpNb(CO)_2(dmpe)} \quad [\mathrm{CpNbH(CO)_2(dppe)}]^+
\end{tikzcd}$$

$$\mathrm{(MeCp)NbCl_4} + \mathrm{RCN} \longrightarrow \mathrm{(MeCp)NbCl_4(NCR)} \xrightarrow{\mathrm{H_2O}} \underset{\mathrm{XVII}}{\{\mathrm{(MeCp)NbCl_3(H_2O)}\}_2\mathrm{O}}$$

The crystal structures of XVI and XVII were determined (11); the latter had previously been incorrectly formulated (1977). Related studies have been carried out for vanadium (55):

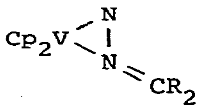


XVIII

Only the formula is known for XVIII.

Among bis(cyclopentadienyl) complexes the largest amount of work in the past year has been on vanadocene and its derivatives. The temperature dependence of the magnetic moment (56), X-ray powder pattern and heat capacity (57) of Cp_2V have been studied to characterize the order-disorder phase transition in the solid state. The crystal structure of Cp_2V shows staggered rings (58), contrasting with the prior electron diffraction study (1975). ^1H and ^{13}C NMR studies were reported for a variety of ring-substituted paramagnetic metallocenes, including $(EtCp)_2V$ (59). ZDO-type calculations for first row metallocenes, including Cp_2V, were performed (60). The effect of Cp_2V intercalation on the Mössbauer spectrum of FeOCl was examined (61).

Chiral vanadocene derivatives were prepared from CpCp'V, where Cp' = $C_5H_4CMe_2Ph$ or $C_5H_4CHMePh$; adducts with CS_2 or $PhC{\equiv}CCO_2R$ are chiral at V. In the latter case, with R also chiral, diastereomers were separated by chromatography and show no epimerization at V (62). Addition of diazo compounds $N_2CH(CO_2Et)$, N_2CPh_2 or N_2(fluorenylidene) to Cp_2V gives products which (spectroscopically) appear to be (63):



Reaction of Cp_2V with silyl azides R_3SiN_3 (R = Me, Ph) and related species gives a variety of products; $Cp_2V(NSiR_3)$ (crystal structure determined for R = Me), $(Cp_2V)_2(NSiMe_3)$, $Cp_2VNN(SiMe_3)_2$ (previously known), and others (64).

Addition of $SiHCl_3$ to Cp_2V at 80° affords $Cp_2V(SiCl_3)_2$ (65), while $SnHEt_3$ adds at 20° to give $Cp_2V(SNEt_3)$; the Ge analog can also be obtained starting with Cp_2VMe_2 (66). A variety of halides, including ethylene bromide, $SbBrEt_2$, EXR_3 (E = Si,Ge,Sn; X = Cl, Br; R = Me, Et) and Ph_3CCl yield Cp_2VX (36).

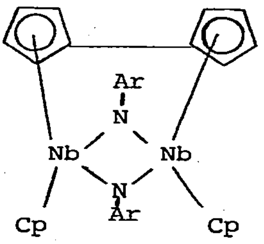
As for the heavier metals, a series of transformations of Cp_2TaCl_2 has been reported (11):

$$\begin{tikzcd}
CpTaCl_4 \arrow[r, "EtAlCl_2"] & Cp_2TaCl_2 \arrow[r, "\mathrm{Vitride}"] \arrow[d, "\mathrm{NaSMe}"] & Cp_2TaH_3 \arrow[r, "\mathrm{BuLi}"] & {} \arrow[r, "PhCH_2Br"] & Cp_2TaBr(CH_2Ph) \\
 & Cp_2Ta(SMe)_2 \arrow[r, "PtCl_2"] & {[\{Cp_2Ta(SMe)_2\}_2Pt]^{2+}} & &
\end{tikzcd}$$

Related substituted products ($Cp' = C_5H_4Pr^i$) include Cp'_2TaCl_2, Cp'_2TaH_3, Cp'_2TaClL ($L = CO, PMe_3, MeC{\equiv}CMe$) and $Cp'_2TaH(CO)$ (14).

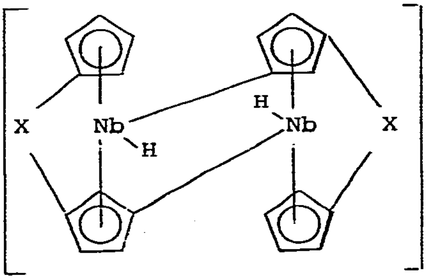
Reaction of Cp_2NbCl_2 with H_2O_2 gives the O_2 complex $Cp_2NbCl(O_2)$; it resembles peroxide-like O_2 adducts of the later metals, having $\nu_{OO} = 870\ cm^{-1}$, and oxidizing PPh_3 and SO_2 (the latter reaction gives $Cp_2NbCl(SO_4)$ (67). The crystal structure of the O_2 complex shows the expected side-bonded geometry, with an O-O distance of 1.47 Å (68). Cp_2NbCl_2 reacts with P_4S_{10} in alcohols to give $[Cp_2Nb(S_2P(OR)_2)]^+$ and $Cp_2Nb(S_2P(OR)_2)(S_2)$; spectroscopy of the latter suggests a monodentate dithiophosphate and side-bonded S_2 (69). Reduction of $(MeCp)_2TaBr_2$ in the presence of dmpe gives $[(MeCp)_2Ta(dmpe)]^+$, which is oxidized to the dication by trityl ion; the EPR indicates substantial delocalization of spin onto phosphorus (6). Variable-temperature EPR studies on Cp_2MCl_2 (M = V, Nb, Ta) have been used to estimate hyperfine coupling to Cl (70). Thermal decomposition of $Cp_2NbCl(GeEt_3)$ gives a niobium carbide phase (71). Cp_2NbCl_2 has some antitumor activity (72).

Full papers have appeared on the fulvalenide complexes $(C_{10}H_8)_2V_2$ (and oxidation products thereof) (73) and $(C_{10}H_8)Cp_2Nb_2Cl$ (74), both of which were communicated last year. Dimeric niobocene reacts with azobenzene and other aryl compounds to give fulvalenide product XIX; the crystal structure was determined for Ar = P-anisyl, and shows a strongly bent $C_{10}H_8$ group and Nb-Nb = 2.834 Å (75).



XIX

The "niobocenophanes" $(X(C_5H_4)_2)NbCl_2$ ($X = SiMe_2OSiMe_2$ or $-CMe_2CMe_2-$) were prepared (76); the former can be reduced by Na to the ring-linked dimeric niobocene form and <u>further</u> reduced (as can ordinary dimeric niobocene) to the dianion XX, whose crystal structure shows an expected non-bonding Nb-Nb distance, 3.932 Å (77).



XX

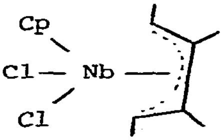
Addition of NaCp to $NbCl_3((O_2C)_2X)$ (where $X = (CH_2)_n$, n = 0, 1, 2 or 4, or $X = o-C_6H_4$) gives products formulated as $Cp_3Nb((O_2C)_2X)$; the nature of bonding is not clear (78).

OTHER π-BONDED COMPLEXES

The olefin complexes $Cp_2NbH(RCH{=}CH_2)$ are obtained from Cp_2NbCl_2 and Grignard reagents and exist as two isomers (22), as do the tantalum analogs (1978). Previously known $TaCl_3(PMe_3)_2(C_2H_4)$ (1979) was obtained by a new route: addition of C_2H_4 to $Ta_2Cl_6(PMe_3)_4$ (79). The crystal structure and EPR of $Cp_2V(C_6F_5C{\equiv}CC_6F_5)$ have been reported (80); the structure is similar to that of the $MeO_2CC{\equiv}CCO_2Me$ adduct (1979). Other acetylene adducts prepared include $Cp_2TaCl(MeC{\equiv}CMe)$ ($Cp' = C_5H_4Pr^i$) (14) and $Cp_2Nb(SMe)(RC{\equiv}CR)$ ($R = CF_3$, CO_2Me) (81). The full paper on the structure of $[TaCl_4(py)(PhC{\equiv}CPh]^-$ (1979) has appeared (82); an analogous reaction using $Bu^tC{\equiv}CBu^t$ gives instead $Ta_2Cl_6(THF)_2Bu^tC{\equiv}CBu^t)$, whose crystal structure shows a bridging alkyne and the shortest Ta-Ta distance (2.677 Å) yet found (83).

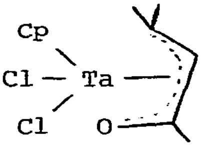
Endocyclic allyl complexes were obtained from $[V(CO)_6]^-$ and 3-halocycloalkenes: products $V(CO)_5(\eta^3-C_nH_{2n-3})$ (as well as some phosphine-substituted derivatives) were made where n = 5-8 (84). Reaction of Cp_2TaH_3 with butadiene gives the mixed complexes $M(C_4H_7)(C_4H_6)_2$; NMR shows <u>seventeen</u> different hydrogen environments (85)!

Reduction of $CpNbCl_3(dmpe)$ in the presence of 2-butyne, followed by protonolysis, gives the tetramethylbutadiene complex XXI, whose crystal structure was determined (10).



XXI

Addition of mesityl oxide to $Cp_2TaCl_2(CO)_3$ gives XXII, which was described as an "oxallyl-alkyl" complex, but is probably better considered as an η^4-oxabutadiene complex; note its close relation to XXI (8).



XXII

The electrochemistry of $TaCl(dmpe)_2(\eta^4-C_{10}H_8)$ was examined (6).

Reaction of $V(CO)_6$ in benzene at room temperature gives $V_2(CO)_4(C_6H_6)_2$; the crystals are twinned so accurate structural characterization was not possible, but the IR suggests a structure like that of $Cp_2Mo_2(CO)_4$; V-V = 2.26(6) Å (86). Evaporation of vanadium (or vanadium plus chromium) into poly(methylphenylsiloxane) gives apparent arene-like complexes (87). Mass spectral studies on $V(C_6H_6)_2$, $V(C_6H_5Et)_2$ and $V(C_6H_4Et_2)_2$ were reported (88), as well as purification methods for the middle compound (89).

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