

VANADIUM, NIOBIUM AND TANTALUM
 ANNUAL SURVEY COVERING THE YEAR 1978

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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.

CARBONYL AND DINITROGEN COMPLEXES

Magnetic circular dichroism studies on $V(CO)_6$ support a substantial Jahn-Teller distortion from O_h geometry (1), in agreement with previous spectroscopic studies. $V(CO)_6$ reacts with $S_2O_6F_2$ to give a CO-free product, $VO(SO_3F)_3$ (2). Photosubstitution of $V(CO)_6^-$ and $CpV(CO)_4$ with group V ligands ER_3 ($E = As, Sb, Bi$) gives $V(CO)_5(ER_3)^-$ and $CpV(CO)_3(ER_3)$ respectively; disubstituted $CpV(CO)_2(BiEt_3)_2$ was also obtained (3). With bidentate ligands LL, similar reactions afford $[V(CO)_5]_2(\mu-LL)]^{2-}$, $V(CO)_4(LL)$, $[V(CO)_4]_2(\mu-LL)_2]^{2-}$, and $CpV(CO)_2(LL)$, where LL variously = $Ph_2E(CH_2)_2E'Ph_2$ ($E, E' = P, As$) or $\underline{O-C_6H_4(AsMe_2)_2}$ (4). IR and ^{51}V NMR spectra for all complexes were reported. Chelate complexes $V(CO)_4(Ph_2P(CH_2)_n PPh_2)^-$ ($n = 1-4$) are converted to the corresponding hydrides $HV(CO)_4L_2$ when passed through a silica gel column; 1H NMR shows equal coupling to both P nuclei (5). Crystal structures have been determined for $CpV(CO)_2(Ph_2P(CH_2)_2 PPh_2)$ (6) and $(V(CO)_4)_2(\mu-PMe_2)_2$ (7). The latter has a V-V bond distances of 2.73 Å, considerably shorter than Cr and Mn analogs and consistent with a V=V double bond required to satisfy the 18 electron rule. The compound is blue, with the strong absorption at 596 nm assigned to a transition involving the metal-metal bond.

The chemistry of the hydridocarbonyl anion $CpV(CO)_3H^-$ is the subject of both a communication (8) and a subsequent full paper (9). The anion is prepared by reducing $CpV(CO)_4$ with sodium followed by

protonation by water; IR studies indicate cation-dependent ion pairing in solution. Reaction with alkyl or acyl halides results in hydrogenolysis to alkane or aldehyde, plus a mixture of organometallics: $\text{CpV}(\text{CO})_4$, $\text{CpV}(\text{CO})_3\text{X}^-$ and $[(\text{CpV}(\text{CO})_3)_2\text{H}]^-$; the latter two new compounds were prepared independently by irradiating $\text{CpV}(\text{CO})_4$ with X^- and $\text{CpV}(\text{CO})_3\text{H}^-$ respectively. Several lines of evidence indicate the alkyl halide reactions follow a radical chain path, analogous to the mechanism of alkyl halide reduction by R_3SnH ; a competing non-radical path may also be operative for cyclopropylcarbinyl halides. Also prepared were $\text{CpV}(\text{CO})_2\text{BH}_4^-$ (from $\text{CpV}(\text{CO})_4 + \text{BH}_4^-$ or $\text{CpV}(\text{CO})_3\text{H}^- + \text{BH}_3$) and $\text{CpV}(\text{CO})_3\text{Me}^-$.

Reduction of $\text{TaCl}_2(\text{dmpe})_2$ ($\text{dmpe} = \text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$) with Vitride ($\text{NaH}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$) under CO gives previously reported $\text{TaCl}(\text{CO})_2^-(\text{dmpe})_2$; in the absence of CO, the H-bridged aluminate $[\text{Ta}(\text{H}_2\text{Al}(\text{OR})_2)(\text{dmpe})_2]_2$ was obtained and a crystal structure reported (10). Variable temperature NMR studies on a group of $\text{TaX}(\text{CO})_2(\text{LL})_2$ complexes support a mechanism for fluxional behavior involving polytopal rearrangement rather than reversible dissociation of one end of a chelating ligand (11). The analogous niobium complex, $\text{NbCl}(\text{CO})_2(\text{dmpe})_2$, was prepared by Mg reduction of $\text{NbCl}_4(\text{dmpe})_2$ under low CO pressure; also synthesized were $\text{CpNbCl}_2(\text{CO})\text{L}_2$ ($\text{L} = \text{PMe}_3, \text{PEt}_3$) (12).

A full paper on the crystal structure of $\text{Cp}_2\text{V}_2(\text{CO})_5$ has appeared; this molecule contains two highly asymmetric semibridging carbonyls ($\text{V}_1\text{-C} = 1.93$; $\text{V}_2\text{-C} = 2.42 \text{ \AA}$) and a V-V distance of 2.46 \AA . Based on IR considerations, the monosubstitution product $\text{Cp}_2\text{V}_2(\text{CO})_4(\text{PPh}_3)$ is believed to have the structure $\text{CpLV}_1(\text{CO})_2\text{V}_2(\text{CO})_2\text{Cp}$. The IR peaks assigned to the semibridging CO's in the parent ($1832, 1871 \text{ cm}^{-1}$) fall in between the ranges expected for terminal and normal bridging carbonyls (13).

In attempting to generate potential chiral vanadium centers, it was found that Cp_2VL ($\text{L} = \text{CO}, \text{RNC}$) both undergo reversible (by cyclic voltammetry) 1-electron reduction at -2.32 and -2.17 V respectively. However, bulk electrolysis gave decomposition to Cp^- and metallic vanadium; under CO, products characteristic of reduction of $\text{CpV}(\text{CO})_4$ (vide supra) could be trapped (14). A new route to $\text{Cp}_2\text{NbH}(\text{CO})$ involves treatment of $\text{Cp}_2\text{Nb}(\text{BH}_4)$ with Et_3N under CO; the hydride can be protonated to give $\text{Cp}_2\text{NbH}_2(\text{CO})^+$ (stable only below -30°) which goes on to $\text{Cp}_2\text{NbCl}(\text{CO})$ (from HCl) or $\text{Cp}_2\text{Nb}(\text{CO})(\text{THF})^+$ (from $\text{HBF}_4(\text{THF})$). The latter can be carbonylated to $\text{Cp}_2\text{Nb}(\text{CO})_2^+$ at $80^\circ/200 \text{ atm}$ (15). $\text{Cp}_2\text{NbCl}(\text{CO})$ was also prepared by reducing Cp_2NbCl_2 with sodium amalgam under CO; at higher pressures,

$\text{CpNb}(\text{CO})_4$ and a new product, $\text{Cp}_3\text{Nb}(\text{CO})$ are favored; the NMR of the latter suggests two $\eta^5\text{-Cp}$ rings and one η^1 ; thus it is analogous to $\text{Cp}_2\text{NbMe}(\text{CO})$, which was obtained from $\text{Cp}_2\text{NbCl}(\text{CO})$ plus MeLi (16).

The first example of CO reduction involving this group has been reported: heating $\text{Cp}_2\text{NbH}(\text{CO})$ under H_2 affords 5-10% (based on Nb) CH_4 , shown by ^{13}C labelling to come from reduction of coordinated CO (small amounts of higher alkanes do not incorporate label and hence presumably arise from Cp-ring degradation). Combinations of group V hydrides and later transition metal carbonyls are more reactive; Cp_2NbH_3 reacts with $\text{Fe}(\text{CO})_5$ at room temperature, via a formyl-type intermediate, to give the H-bridged, heterobimetallic complex $\text{Cp}_2(\text{CO})(\text{Nb})(\mu\text{-H})\text{Fe}(\text{CO})_4$ characterized by crystallographic means (17).

The vanadium(IV) complex $\text{V}(3,5\text{-di-}t\text{-butylcatecholate})_2$ forms a reversible CO adduct based on changes observed in its electronic spectrum (18). A brief review of $\text{MX}_n\text{-Mg}$ systems for N_2 reduction includes studies on VCl_4 (19).

ALKYL, ARYL AND ALKYLIDENE COMPLEXES

A series of benzylvanadium complexes have been prepared from VCl_3 (20) or $\text{V}(\text{acac})_3$ (21) and main-group organometallics RLi , RMgCl , R_2Mg and R_3Al ($\text{R} = \text{benzyl}$); in all cases the resulting R_2VCl or $\text{RV}(\text{acac})_2$ groups were obtained only complexed with the main group metal. Reaction of $(\text{Me}_3\text{Si})_2\text{CHLi}$ with $\text{VCl}_3(\text{NMe}_3)_2$ gives $\text{V}(\text{CH}(\text{SiMe}_3)_2)_3$; the Nb and Ta analogs could not be isolated in crystalline form (22). $\text{V}(1\text{-camphenyl})_4$ was found to act as a photocatalyst for olefin polymerization (23). The crystal structure of $\text{V}(\text{mesityl})_4$ shows a distorted tetrahedral geometry with an average V-C distance of 2.08 Å; the magnetic susceptibility and electronic spectrum are also reported (24). Reaction of NbCl_5 with $\text{C}_6\text{F}_5\text{Li}$ gives a compound of uncertain composition, $\text{Nb}(\text{C}_6\text{F}_5)_x\text{Cl}_{5-x}$, where x is between 2 and 3 (by analysis); ^{19}F NMR shows only one C_6F_5 environment, suggesting possible fast intermolecular exchange in a mixture. Adducts with P and As ligands were examined; the Ta analog was also studied (25). A "Reformatsky-like" alkyl compound was prepared by the reaction of $\text{Ph}_3\text{SnCH}_2\text{CONEt}_2$ with TaCl_5 ; IR and NMR studies on the resulting $\text{Ta}(\text{CH}_2\text{CONEt}_2)_3\text{Cl}_2$ suggest the presence of Ta-C bonding rather than bonding through oxygen (26).

The photoelectron spectrum of TaMe_5 has been examined, along with a number of other transition metal alkyls (27). A kinetic study on the decomposition of $\text{Ta}(\text{CH}_2\text{Ph})_5$ shows clean first-order behavior, with no evidence for any participation by free radicals.

A mechanism involving intramolecular α -hydrogen abstraction was proposed (28).

As noted last year, Cp_2VR_2 complexes are not stable except for $\text{R} = \text{Me}$; the ESR spectra (on *in situ* preparations) for $\text{R} = \text{Et}$ and Me_3SiCH_2 were determined for comparison to studies on Ziegler-type systems (29). Cp_2VMe_2 reacts with 1 mol HCl at -60° to give CH_4 and Cp_2VMeCl ; the latter decomposes at 90° to CH_4 and $(\text{Cp}, \text{Cp}')_2\text{VCl}$ (30). Reaction of Cp_2NbCl_2 with α -lithiothiophene gives $\text{Cp}_2\text{Nb}(\text{C}_4\text{H}_3\text{S})_2$ which shows the expected EPR signal; it forms complexes through the sulfur atoms with divalent metal ions (Cu, Mn, Fe) which, surprisingly, are all diamagnetic (31).

The following complexes of the highly substituted cyclopentadienyl $\text{C}_5\text{Me}_4\text{Et}$ were prepared: Cp_2^*V , Cp_2^*VBr , and $\text{Cp}_2^*\text{V-C}\equiv\text{C-M}$ ($\text{M} = \text{mesityl}$). The last is stable to $> 100^\circ$, in sharp contrast to unsubstituted Cp_2VR analogs. A crystal structure ($\text{V-C} = 2.03 \text{ \AA}$) and ^1H NMR spectrum were reported; the latter shows substantial delocalization of unpaired electrons onto the alkynyl ligand (32). Reaction of $\text{Cp}_2\text{VCH}_2\text{SiMe}_3$ with non-polar hydrogen compounds HX ($\text{X} = \text{SnEt}_3$, $\text{N}(\text{SiMe}_3)_2$, SR , SGeR_3) gives Cp_2VX plus SiMe_4 (33). Mesityllithium displaces Cp from vanadocene, giving first $\text{CpV}(\text{mesityl})_2(\text{THF})_2^-$ and, with a larger excess, known $\text{V}(\text{mesityl})_4(\text{THF})_4^-$ (34).

Full papers on (C,N)-chelating alkyl complexes of vanadium, communicated last year, have appeared; these include $\text{Cp}_2\text{V}(\text{CH}_2\text{C}_6\text{H}_4\text{-O-NMe}_2)$, $\text{Cp}_2\text{V}(\text{C}_6\text{H}_4\text{-O-CH}_2\text{NMe}_2)$ (35) and (dipivaloylmethanato) $\text{V}(\text{C}_6\text{H}_4\text{-O-CH}_2\text{NMe}_2)_2$ (36). Thermal decomposition of $\text{Ta}(\text{NEt}_2)_5$ gives the (ethylimino)ethyl complex $\text{Ta}(\text{EtNCHMe})(\text{NEt}_2)_3$ which loses C_2H_4 on further heating to form $\text{Ta}(\text{NEt})(\text{NEt}_2)_3$ and reacts with MeNCO to give the insertion product $(\text{Et}_2\text{N})_3\text{TaCH}(\text{Me})\text{N}(\text{Et})\text{CONMe}$ (37).

An impressive quantity of chemical and structural work on alkylidene complexes, primarily from the laboratories of Schrock and Churchill, has appeared during the past year. Full papers report details on two previously described systems. For $\text{M}(\text{neopentyl})_3\text{-}$ (neopentylidene), the Nb complex is considerably less stable than Ta but appears by NMR to be completely analogous. The nucleophilic character of the alkylidene ligand is manifested in reactions with acyl chlorides and nitriles. H-D exchange between the alkyl and alkylidene groups can be observed at 75° . The mechanism of formation from TaR_3Cl_2 and LiR is not completely clear but does not appear to go through a symmetric TaR_5 intermediate, loss of H by direct abstraction from R by some basic species was preferred over an α -elimination route (38). The methylene complex $\text{Cp}_2\text{Ta}(\text{CH}_2)\text{Me}$ was obtained by methyl abstraction from Cp_2TaMe_3 by Ph_3C^+ (labelling

studies indicate the central Me is removed selectively) followed by deprotonation (kinetic isotope effect ~ 3.4). The methylene group is also nucleophilic, forming an adduct with AlMe_3 and displacing halide from RX. The product of thermal decomposition is $\text{Cp}_2\text{TaMe}(\text{C}_2\text{H}_4)$, which appear to arise via a dimeric, doubly methylene-bridged intermediate; reaction with the phosphorus ylide Me_3PCH_2 gives the same product (39).

A group of substituted analogs of the methylene complex, Cp_2MX - (alkylidene), have been prepared, where X = halide or alkyl; alkylidene = PhCH , Me_3CCH or Me_3SiCH . In all cases (including also CH_2) NMR indicates that the alkylidene group is perpendicular to the CMX plane, with a barrier to rotation of 16 kcal/mol or higher (40). A related preparation of $\text{Cp}_2\text{M}(\text{CH}_2\text{SiMe}_3)(\text{CHSiMe}_3)$ was also reported by another group (41). Crystal structures for $\text{Cp}_2\text{Ta}(\text{CH}_2\text{Ph})(\text{CHPh})$ (40) and $\text{Cp}_2\text{TaCl}(\text{CHCMe}_3)$ (42) were reported. The latter is of particular interest: the Ta-C-C angle in the neopentylidene group is surprisingly obtuse (150.4°); it was suggested that this may signal relatively facile deformation in such groups which could be relevant to their role in olefin metathesis. Also, the alkylidene is not quite perpendicular to the CTaCl plane (dihedral angle 79.7°), probably for steric reasons; the barrier to rotation is lower than in the other complexes of this class.

New developments include the synthesis of alkylidyne and bis(alkylidene) complexes. Reaction of $\text{CpTaCl}_2(\text{CHCMe}_3)$ with PMe_3 and Ph_3PCH_2 (or with $\text{LiCH}_2\text{CMe}_3$ followed by PMe_3) gives the neopentylidyne species $\text{CpTaCl}(\text{CCMe}_3)(\text{PMe}_3)_2$; analogs with C_5Me_5 and with benzylidyne were also prepared. The crystal structure of $(\text{C}_5\text{Me}_5)\text{TaCl}(\text{CPh})(\text{PMe}_3)_2$ shows a Ta \equiv C distance of 1.85 Å (about 0.2 Å shorter than alkylidene distances) and a TaCC angle of 172° . The α carbon of the alkylidyne group has a extreme downfield shift (~ 350 ppm) in the ^{13}C NMR spectrum (43). Treatment of $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CHCMe}_3)$ with PMe_3 gives loss of neopentane and the bis(neopentylidene) complex $\text{Ta}(\text{CH}_2\text{CMe}_3)_2(\text{CHCMe}_3)_2(\text{PMe}_3)_2$; also prepared were $\text{TaX}(\text{CHCMe}_3)_2(\text{PMe}_3)_2$, X = Cl or alkyl. Reaction of $\text{CpTaCl}(\text{CCMe}_3)(\text{PMe}_3)_2$ with $\text{Mg}(\text{CH}_2\text{CMe}_3)_2$ gives $\text{CpTa}(\text{CHCMe}_3)_2(\text{PMe}_3)_2$ rather than an alkyl-alkylidyne complex (44). A crystal structure for $\text{Ta}(\text{mesityl})(\text{CHCMe}_3)_2(\text{PMe}_3)_2$ shows trigonal bipyramidal geometry with axial PMe_3 's; interestingly, the alkylidene groups are quite different, one with Ta-C = 1.93 Å and $\angle \text{TaCC} = 169^\circ$; the other with Ta-C = 1.955 Å and $\angle \text{TaCC} = 154^\circ$ (45).

As noted last year, $\text{CpTaCl}_2(\text{CHCMe}_3)$ with olefins gives metallocycles; e.g., propylene gives $\text{CpCl}_2\text{Ta}(\text{CH}_2\text{CHMeCHMeCH}_2)$ (plus

$\text{Me}_3\text{CCH}_2\text{CMeCH}_2$). The metallocycle decomposes at 35° to 2,3-dimethylbut-1-ene; with excess propylene the latter is obtained catalytically. This is a potentially significant method for dimerization of olefins since metal hydride intermediates are apparently not involved; hence much less isomerization is observed than in other systems (46).

Reaction of TaCl_5 with $\text{Me}_3\text{SiCH}_2\text{Li}$ gives mostly Me_4Si ; it is presumed alkylidene complex formation is involved (47). In a study of aminoalkylidene complexes, $\text{CpV}(\text{CO})_3(\text{CHNMe}_2)$ was prepared from $\text{CpV}(\text{CO})_3^{2-}$ and $\text{Me}_2\text{NCHCl}^+\text{Cl}^-$ (48).

CYCLOPENTADIENYL COMPLEXES

Studies on metallocenes which included Cp_2V reported spectral and magnetic properties (49); determination of heat capacity over 4.5–300 K (50); and examination of the ^{13}C NMR isotope shift in paramagnetic $(\text{C}_5\text{D}_5)_2\text{M}$ complexes (51). The ^1H and ^{13}C NMR of paramagnetic Cp_2VCl (and $\text{Cp}_2'\text{VCl}$) have been examined; both ring and side-chain signals are reasonably sharp. The temperature dependence of chemical shifts follows the Curie law, indicating these 16 electron species do not have any tendency to dimerize (52).

$\text{TaCl}_2(\text{dmpe})_2$ reacts with NaCp to give, at room temperature, $\text{CpTaCl}(\text{dmpe})_2^+\text{Cl}^-$; at higher temperatures, $\text{Cp}_2\text{Ta}(\text{dmpe})^+\text{Cl}^-$ is obtained. Yields are only ~ 50%, suggesting a disproportionation in going from Ta(II) to Ta(III); the crystal structure of the latter shows a normal Cp_2MX_2 geometry (53). Cp_2TaX_2 can be prepared in 85% yield from TaX_5 and Bu_3SnCp ; reaction with Vitride gives Cp_2TaH_3 . This in turn reacts with BuLi to give an uncharacterized, orange crystalline product thought to contain Ta-Li bonding; it reacts with PhCH_2Cl to form $\text{Cp}_2\text{TaCl}(\text{CH}_2\text{Ph})$ (54).

A variety of substituted Cp complexes $\text{Cp}_2'\text{NbCl}_2$ have been prepared and examined by EPR (55). They can be converted to $\text{Cp}_2'\text{NbOCl}$ by treatment with DMSO, boiling glyme, or concentrated HCl followed by NaHCO_3 . Mixed species $\text{Cp}'\text{Cp}''\text{NbOCl}$ can be prepared and separated chromatographically, for continued studies (see 1975 survey) on these chiral systems (56).

Several intermetallic complexes have been reported: in addition to the Nb-Fe complex surveyed above, Cp_2NbBH_4 reacts with $\text{CpMo}(\text{CO})_3\text{Me}$ to give $\text{Cp}_2\text{NbMo}(\text{CO})_3\text{Cp}$; based on spectroscopic evidence a structure with one terminal CO (on Mo), one normal bridging CO and one 4-electron bridging CO was suggested (57). Cp_2VCl_2 plus $\text{NaCo}(\text{CO})_4$ gives $\text{CpVCo}_3(\text{CO})_9$, characterized by IR and MS, apparently a "vanadylidyne" - $\text{Co}_3(\text{CO})_9$ cluster (58). Reaction of Cp_2NbCl_2 with RSH followed by MCl_2 gives an already-known type of complex, $\text{Cp}_2\text{Nb}(\mu\text{-SR})_2\text{MCl}_2$ (M = Ni, Cu, Mn) (59).

Cp_2NbMe_2 reacts with S_8 to form $\text{Cp}_2\text{NbMe}(\text{S}_2)$ and with CS_2 (photochemically) to give $\text{Cp}_2\text{NbMe}(\text{CS}_2)$ (60). Addition of PhSH to vanadocene gives Cp_2VSPH (61). Preparative details for previously communicated $\text{Cp}_2\text{V}(\text{NN}(\text{SiMe}_3)_2)$ have been reported (62). Treatment of Cp_2NbBH_4 with $\text{Me}_3\text{CCO}_2\text{H}$ gives, successively, diamagnetic $\text{Cp}_2\text{Nb}(\text{O}_2\text{CCMe}_3)$, paramagnetic blue $\text{Cp}_2\text{Nb}(\text{O}_2\text{CCMe}_3)_2$, $\text{Nb}(\text{O}_2\text{CCMe}_3)_4$ and $\text{Nb}(\text{O}_2\text{CCMe}_3)_5$; no bridged $\text{M}_2(\text{O}_2\text{CR})_4$ species of the type known for vanadium were detected (63). Reaction of NaCp (or indenylsodium) with $\text{NbCl}_3(\text{SR})_2$ and $\text{NbCl}_2(\text{OR})_3$ gives, respectively, $\text{Cp}_3\text{Nb}(\text{SR})_2$ (64) and $\text{Cp}_2\text{Nb}(\text{OR})_3$ (65). Cp_2NbX_2 where X is a pseudohalide (CN, NCS, NCO, N_3) have been prepared (66). Cp_2VCl_2 plus $\text{Cd}(\text{GeEt}_3)_2$ gives a product of formula $\text{Cp}_2\text{VCl}_2 \cdot \text{Cd}(\text{GeEt}_3)_2$ and unknown structure (67).

OTHER π -BONDED COMPLEXES

Reduction of Cp_2NbCl_2 with sodium amalgam in the presence of unsaturated compounds $\text{CF}_3\text{C}\equiv\text{CF}_3$, $\text{CH}_3\text{C}\equiv\text{CH}$ and cyclopropene gives $\text{Cp}_2\text{NbCl}(\text{olefin or acetylene})$; protonolysis of the last affords cyclopropane (16). Reaction of Cp_2TaCl_2 with RMgCl (where R has a β -hydrogen) gives $\text{Cp}_2\text{TaH}(\text{olefin})$, for propene, butene, pentene and cyclopentene; mixtures of isomers are obtained in some cases (68). VCl_4 forms poorly characterized adducts with olefins which appear to contain V(III); some oligomerization, isomerization, chlorination and metathesis products were detected (69). Further studies on the reduction of acetylene by $\text{V}(\text{OH})_2\text{-Mg}(\text{OH})_2$ gel were reported (70). An ethylene-propylene copolymerization catalyst was obtained from $\text{VOCl}_3\text{-R}_3\text{Al}$ (71). TaS_2 and intercalates thereof convert cyclohexene to benzene, methylcyclopentane and methylcyclopentene (72).

Reaction of $\text{V}(\text{CO})_4(\text{LL})^-$ with substituted allyl halides gave a number of (allyl) $\text{V}(\text{CO})_3(\text{LL})$ complexes, which were studied by ^1H , ^{13}C and ^{31}P NMR (73). $\text{HV}(\text{CO})_4(\text{LL})$ plus isoprene gives mostly ($\eta^3\text{-3,3-dimethylallyl})\text{V}(\text{CO})_3(\text{LL})$ in addition to other isomers and $\text{V}(\text{CO})_4(\text{LL})$ (74). Successive treatment of NbCl_5 with $\text{C}_8\text{H}_8^{2-}$ and NaCp (or of Cp_2NbCl_2 with C_8H_8 and $i\text{PrMgCl}$) gives $\text{Cp}_2\text{Nb}(\text{C}_8\text{H}_8)$, thought to have an η^2 -cyclooctatetraene; NaBH_4 converts it to $\text{Cp}_2\text{Nb}(\eta^3\text{-C}_8\text{H}_9)$, reported last year (75). $\text{Cp}_2\text{Nb}(\text{C}_9\text{H}_9)$ (from Cp_2NbCl_2 and $\text{C}_9\text{H}_9\text{Li}$) is also believed to have an allylic, $\eta^3\text{-C}_9\text{H}_9$ ligand (76).

Photolysis of $\text{CpV}(\text{CO})_4$ plus photo- α -pyrone yields $\text{CpV}(\text{CO})_2(\text{C}_4\text{H}_4)$, the first unsubstituted cyclobutadiene complex in this group (77). Metal vapor synthesis methods have been used to prepare $\text{V}(\text{arene})_2$ (toluene, 1-methylnaphthalene) (78) and $\text{Nb}(\text{arene})_2$ (benzene,

toluene, mesitylene) (79). For the latter, ESR, IR and photoelectron spectroscopy all indicate a low spin, Nb(O) sandwich structure. The organic byproducts in the Friedel-Crafts preparation of bis(ethylbenzene)vanadium do not appear to form via any organovanadium intermediate (80). Cyclic voltammetric studies on bis(methylborinato)vanadium, $(\text{MeBC}_5\text{H}_5)_2\text{V}$, show an irreversible oxidation at +0.76 V and a reversible reduction at -1.34 V (vs. SCE); the analogous processes in Cp_2V occur at potentials more negative by ~ 1.5 V (81).

An SCF-type calculation on $\text{CpM}(\text{C}_7\text{H}_7)$ complexes has been reported for V, among others (82).

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