VANADIUM, NIOBIUM AND TANTALUM

ANNUAL SURVEY COVERING THE YEAR 1974

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Work in this area has expanded considerably, the number of papers increasing by 100% over last year.

Crystal Structures

Crystal and molecular structures of $TaH(CO)_2(Me_2PCH_2CH_2PMe_2)_2$ (1), $MeTaCl_2[N(C_6H_{11})C(Me)=N(C_6H_{11})_2]$ (2), $MeTaCl_2[ON(Me)NO]_2$ (3) and of the niobium complexes $\{[CpNb(O_2CH)(OH)]_3O\}H$[*] (4,5), $CpNb(PPh_3)_2(CO)H_2$ (6) and $Cp_2Nb(CO)SH$ (7) have been determined by X-ray diffraction. In the first compound the hydride ligand is capping a distorted capped octahedron; the second, containing acetamidinato ligands, is a highly distorted pentagonal bipyramid, as is the nitric oxide insertion product, in all cases the tantalum being seven-coordinate. Apart from the tetrahedral hydrosulphide the geometry of the niobium complexes was difficult to establish since the hydrides were not located.

Details of the structures will be found elsewhere in Annual Surveys in the review, "Organometallic Structures - Transition Metals".

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[*] Cp = π-cyclopentadienyl

Hydrido, Alkyl and Aryl derivatives (see also Cyclopentadienyl)

Hydrides:- Ultraviolet irradiation of the sodium diglyme salt of $V(CO)_6$ in the presence of PF_3, followed by treatment with phosphoric acid has given $HV(PF_3)_6$, in which the H-V bond is considerably stabilized thermally by the PF_3 ligand. The yellow crystalline hydride could be sublimed and did not decompose below 135° in sealed tubes. It reacted with oxygen- and nitrogen-containing donor solvents forming onium salts. The ^1H Fourier NMR spectrum in $Ni(PF_3)_4$ contained a five-line multiplet centred at 18.4 τ; the two remaining lines expected were not visible (8).

The formation of the tantalum aluminium hydride, $Ta(AlH_4)_4$, has been reported (9), the unstable red hydride eliminating AlH_3 and forming products of variable composition, $TaH_n(AlH_4)_{4-n}$. NbH_2 has been prepared by combination of the elements catalyzed by $LaNi_5$ (10).

Alkyls:- A useful discussion of stability and scission of transition metal-carbon σ-bonded compounds has been published (11). Considerable effort has gone into the preparation of alkyl derivatives of these metals and studies of their reactions and their complexes.

The π-allyl, $(\pi\text{-}C_3H_5)V(CO)_5$, was made from $NaV(CO)_6$ and allyl chloride, while substituted π-allyl derivatives were obtained by addition of $HV(CO)_6$ to the dienes, $CH_2=CR-CH=CH_2$ (R=H or Me). The mode of bonding was confirmed by infrared and ^1H-NMR spectroscopy (12).

The oxovanadium compound, $MeVO(O\text{-}iPr)_2$, has been prepared as a red-brown oil by the action of dimethylzinc on $VO(O\text{-}iPr)_3$ in pentane. The mass spectral decomposition routes were considered in some detail (13).

Methylniobium(V) and methyltantalum(V) oxohalide complexes of type, $MeMOX_2.2L$, have been synthesized by the action of MeMgI on $NbOCl_3$ in toluene-ether followed by addition of ligand, or by reaction of excess of an oxygen-containing ligand with $MeMCl_4$; e.g.

$$MeNbCl_4 \xrightarrow[-\ 35^\circ]{\text{excess ligand}} MeNbCl_4.L \xrightarrow[\text{temp.}]{\text{room}} MeNbOCl_2.2L$$

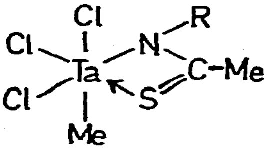
L= $ONMe_3$, ONC_5H_5, $OPMe_3$, $OPPh_3$, $OP(NMe_2)_3$, $OP(NMe_2)_2OMe$, $OP(NMe_2)(OMe)_2$, $OP(OMe)_3$, $O[OP(NMe_2)_2]_2$, $OAsPh_3$ and $OSMe_2$. The only tantalum oxocomplex was $MeTaOCl_2.2OPPh_3$. Throughout the oxygen-abstraction-halogen-exchange reaction the methyl-metal bonds appear to remain unaffected (14).

Pentamethylniobium and pentamethyltantalum have been prepared from methyllithium and the known compounds, Me_3MCl_2. The niobium derivative decomposed in ether above -50°, but the tantalum analogue was isolated as a yellow, volatile oil which decomposed apparently autocatalytically at 25° to give methane as the only detectable volatile product. Both pentamethyl derivatives were stabilized by $Me_2PCH_2CH_2PMe_2$ (dmpe) and could be isolated as mono-adducts, the ^1H-NMR spectra of which showed evidence of stereochemical non-rigidity (15).

The known trimethyl derivatives, Me_3NbCl_2 and Me_3TaCl_2, have been shown to form coordination compounds with a range of unidentate (L) and bidentate (B) ligands with stoichiometries, $Me_3MCl_2.L$, where L = $OPPh_3$ or Cl^-(Et_4N^+ as cation), $Me_3MCl_2.2L$, where L = pyridine or 3-methylpyridine, and $Me_3MCl_2.B$, where B = $MeOCH_2CH_2OMe$, $Me_2NCH_2CH_2NMe_2$, 2,2'-bipyridyl, 4,4'-bipyridyl, $Ph_2PCH_2CH_2PPh_2$, $MeSCH_2CH_2SMe$, $EtSCH_2CH_2SEt$ or $Ph_2PCH_2PPh_2$.

As with other complexes, the stability of the niobium compounds is lower than that of the corresponding tantalum derivatives. The six-coordinate complexes with unidentate ligands showed a single methyl resonance in their ^{1}H-NMR spectrum even at -80°. The remaining complexes showed splitting of the methyl resonance at low temperature and some evidence for two different types of seven-coordinate structures (16).

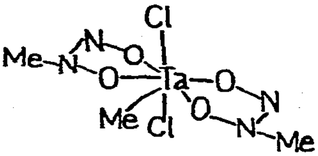
Several papers have described insertions of various molecules into the metal-methyl bonds of methylniobium (and-tantalum) chlorides. Insertion of isothiocyanates into $MeMCl_4$ and Me_2MCl_3 took place readily at room temperature giving thioacetamido derivatives, e.g.



The insertion rates followed the sequence, $MeMCl_4 > Me_2MCl_3 > Me_3MCl_2$ and MeNCS >PhNCS, suggesting that an important step in the insertion mechanism is formation of a donor-acceptor complex. With the thiocyanate, MeSCN, S- and N-bonded 1:1 complexes with $MeMCl_4$ and Me_2MCl_3 were detected (17).

Similarly the alkyls, Me_xMCl_{5-x}, where x=1,2 or 3 and M= Nb or Ta, were found to react rapidly with isocyanates, MeNCO and PhNCO, at room temperature in pentane to give bidentate N-methyl or N-phenylacetamido derivatives. The reactions and mode of insertion were similar to those of the isothiocyanates. Isonitriles, RNC, where R = C_6H_{11} or p-$CH_3C_6H_4$, reacted with the methylmetal chlorides giving, for example, $MeTaCl_2[C(Me)=NR]_2$, which decomposed around room temperature (18).

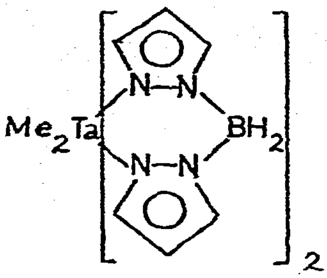
Insertion of nitric oxide into the methyl-metal bonds of Me_2MCl_3 and Me_3MCl_2, where M=Nb or Ta, gave N-methyl-N-nitrosohydroxylamino derivatives, $Me_xMCl_{3-x}[ON(Me)NO]_2$. In $MeTaCl_2[ON(Me)NO]_2$ X-ray crystal structure determination showed a distorted pentagonal bipyramid with two chlorine atoms in axial positions (3),



Insertion of carbodiimides, RNCNR, where R = isopropyl, cyclohexyl or p-tolyl, into Me_xMCl_{5-x}, where M=Nb or Ta; x = 1, 2 or 3, occurred at the metal-methyl groups leading to products containing one or two bidentate acetamidino groups, NR-C(Me)=NR (19).

With Me_xMCl_{5-x}, where N = Nb or Ta; x = 1 or 2, ketones, RR'CO, where R = R' = cyclohexyl; R = Me, R' = t--Bu; R = Me, R' = neopentyl, formed weak 1:1 complexes, yellow to red in colour. The frequency of the ketonic carbonyl group in the infrared dropped by 60 - 70 cm^{-1} on coordination. With less bulky ketones and with oxygen, addition of the methyl-metal groups to the ketones took place leading to complex products containing M-O-M species (20).

The chlorides of Me_3TaCl_2 were removed on treatment with potassium bis(pyrazolyl)borate, $K^+[pz_2BH_2]^-$, giving yellow, crystalline,



which did not sublime at temperatures below its decomposition point (120°). Extra thermal stability has been conferred by blocking with bulky groups sites required for decomposition. The non-rigid seven-coordinate complex showed broadening of the Ta-Me resonance in the ^{1}H-NMR spectrum on cooling, but no splitting even at -90°. At -75° one of the pyrazolyl resonances split, indicating non-equivalence of these two ligands (21). Also in this paper, preliminary ^{1}H-NMR data is given for the complexes, $Me_3Ta(CH_3COCHCOCH_3)_2$, $Me_3Ta(CF_3COCHCOCH_3)_2$, $Me_3Ta(O_2CCH_3)_2$ and $Me_3Ta(C_4H_2O_4)$ (squarate).

Full details of the preparation of the trimethylsilylmethyl derivatives, $(Me_3SiCH_2)_3NbCl_2$, $(Me_3SiCH_2)_3TaCl_2$ and $(Me_3SiCH_2)TaCl_3$ have now been published. In addition $(Me_3SiCH_2)_2TaCl_4$ was obtained from the redistribution reaction between $TaCl_5$ and either of the two trimethylsilylmethyltantalum compounds. As has been found for other alkyl derivatives, an increase in the number of trimethylsilylmethyl ligands shifts the methylene resonance in the ^{1}H-NMR spectrum to higher τ values (22). No reference to their preliminary communication (23) appears in this paper.

Addition of phenanthroline or bipyridyl to solutions of the trimethylsilylmethyls in hexane or ether caused precipitation of the pale yellow niobium or off-white tantalum complexes of enhanced thermal stability and supposedly seven-coordinate (22).

Use of the bulkier bis(trimethylsilyl)methyl ligand has allowed the isolation of $[(Me_3Si)_2CH]_3V$ as a green-blue solid (24).

A thermally stable neopentylidene complex of tantalum has been isolated in quantitative yield from the reaction between neopentyllithium and $Ta(CH_2CMe_3)_3Cl_2$ in pentane or ether, the penta(neopentyl) derivative being the probable intermediate,

$$\text{"}Ta(CH_2CMe_3)_5\text{"} \xrightarrow{-Me_4C} Ta(CH_2CMe_3)_3(CHCMe_3)$$

The reaction of five moles of neopentylmagnesium chloride with $TaCl_5$ in ether also produced the carbenoid complex in 50% yield. The orange crystalline compound reacted violently with oxygen and moisture but was stable in an inert atmosphere at room temperature. The neopentylidene α-carbon was found in the ^{13}C--NMR spectrum at 250.1 ppm downfield from TMS, while the proton resonances were at τ 8.09 (CH) and 8.57 (CH_3) as compared with 9.16 (CH_2) and 8.85 (CH_3) for the neopentyl ligands (25).

These findings were taken as demonstration of the stability of non-stabilized carbenoid complexes, and of the viability of α-hydrogen abstraction as a mode of decomposition of transition metal alkyls.

A benzylniobium compound, $(PhCH_2)_2NbCl_2$, has been reported (26).

Aryl:- Trimesitylvanadium has been isolated as a tetrahydrofuranate, $V(C_9H_{11})_3 \cdot 1.25$ THF, from the reaction between VCl_3 and $C_9H_{11}MgBr$ in THF at -30°. The violet-blue crystalline complex had a magnetic moment of 2.74 B.M. and was stable under vacuum to about 120° (27).

Cyclopentadienyl derivatives

Vanadocene has been shown to react with carbon monoxide under mild conditions (atmos. press., 25°) in heptane or toluene giving the monocarbonyl, Cp_2VCO, as an air-sensitive deep brown solid with a single CO stretch in the infrared at 1881 cm^{-1}. The magnetic moment was 1.76 B.M. Under similar conditions Cp_2VI formed the spin-paired vanadium(III) carbonyl, $Cp_2VI(CO)$, which decarbonylated so readily that Cp_2VI was always present. The formation of the slightly soluble dicarbonyl, $[Cp_2V(CO)_2]I$, from Cp_2VI and CO at atmospheric pressure occurred only in the presence of a catalytic amount (10% by weight) of Cp_2V in toluene (28).

Vanadocene also split S-S bonds of disulphides giving green high-spin vanadium(III) compounds,

$$Cp_2V + 1/2\ RSSR \longrightarrow Cp_2VSR$$

$$R = Me,\ Et,\ Ph \text{ or } CH_2Ph$$

which could also be made by the redistribution reaction,

$$Cp_2V + Cp_2V(SR)_2 \longrightarrow Cp_2VSR$$

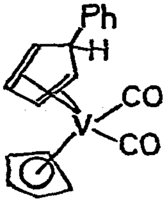
The monothio compounds added carbon monoxide reversibly in hydrocarbon solution at room temperature, in a similar manner to the iodide above, giving $Cp_2VSR(CO)$.

The black-green bis(phenylthio) derivative, $Cp_2V(SPh)_2$, was synthesized by further reaction of Cp_2VSPh with PhSSPh under forcing conditions (toluene under reflux) or by displacement of chloride from Cp_2VCl_2 using NaSPh (29).

In the case of the vanadium(III) alkyls, Cp_2VR, where R=Me or CH_2Ph, treatment with CO resulted in insertion as well as addition (30),

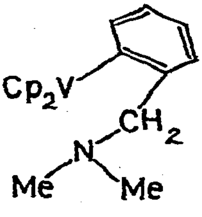
$$CP_2VR + 2CO \longrightarrow Cp_2V(CO)COR$$

In contrast, Cp_2VPh absorbed two moles of CO giving a red, crystalline thermally stable dicarbonyl (1861 and 1929 cm^{-1} in the infrared) in which migration of the phenyl group to one of the cyclopentadienyl ligands had occurred. The



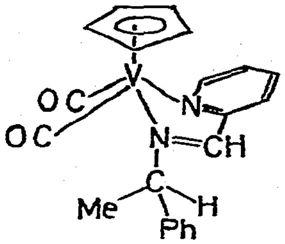
^{1}H-NMR spectrum showed resonances at $\tau(C_6D_6)$, 6.47 (2H,m), 5.80 (5H, s), 5.24 (2H,m), 4.90 (1H,m) and 2.65 (5H,m). Carbon monoxide was evolved rapidly from this complex at 25-30° giving a monocarbonyl, $Cp(\pi\text{-}C_5H_4Ph)VCO$, which could be oxidized by iodine under CO to the ionic dicarbonyl, $[Cp(\pi\text{-}C_5H_4Ph)V(CO)_2]^+\text{-}I_3^-$, (30).

A dimethylaminomethylphenyl derivative of vanadium(III),



was prepared for comparison with the corresponding titanium compound. In the vanadium analogue internal coordination of the nitrogen atom to vanadium is unlikely. Differential thermal analysis showed decomposition at 199° to benzyldimethylamine (63%), vanadocene (60%) and two unidentified vanadium-containing products (31).

An asymmetric square-pyramidal vanadium complex has been formed from $CpV(CO)_4$ and the Schiff base from pyridine carbaldehyde and S-(-)-α-methylbenzylamine. Two cis-CO groups were eliminated under the influence of irradiation.



The low yield (4%) and extreme sensitivity of this compound precluded any study of the expected diastereoisomeric forms (32).

The ESR spectra of a series of bis(cyclopentadienyl)niobium and tantalum hydrides and alkyls have been examined (33). The compounds were prepared in solution, (a) from Cp_2MH_3 photolysis in the presence of the t-butyl peroxide,

$$Cp_2MH_3 + \text{t-BuO}\cdot \xrightarrow{-80^\circ} Cp_2MH_2 + \text{t-BuOH}$$

or (b) by addition of a hydride to isobutylene [giving Cp_2NbH-(t-Bu)] or (c) from the dichloride, Cp_2NbCl_2, and alkyl or aryllithium or magnesium halides (giving Cp_2NbR_2, where R=Me,CD_3 or

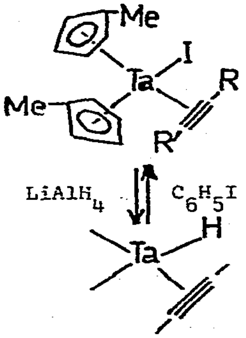
Ph). The niobium dihydride showed the expected triplet splitting (absent in the dideuteride), further split into ten lines by one niobium nucleus, while the methyl derivative showed hyperfine splitting due to one niobium and six equivalent protons of the methyl groups.

The niobium splitting in the diphenyl analogue was 88.8G but the couplings to the phenyl protons were unresolved. Line widths in the spectrum of Cp_2TaH_2 precluded the observation of smaller hyperfine splitting in the eight line spectrum. During this work the methyl derivatives, Cp_2NbMe_2 and $(\pi\text{-}MeC_5H_4)_2$-$TaMe_2$ were isolated as red crystalline solids and characterized by analytical and mass spectral data (33).

Bis(cyclopentadienyl)tantalum dichloride has been described for the first time as a brown paramagnetic solid and used, together with the analogous niobium compound, to prepare a range of π-allyl derivatives, Cp_2MR, where M=Nb or Ta; R=allyl, 1-methylallyl or 2-methylallyl, which were characterized by infrared, ^{1}H-NMR and mass spectra. They showed close similarities to the corresponding titanium compounds (34).

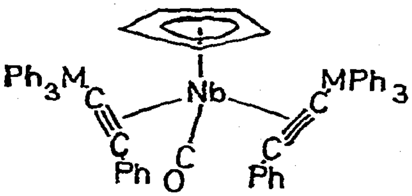
Complexes of tantalum with dialkylacetylenes resulted from the reaction,

$(\pi\text{-}MeC_5H_4)_2TaH_3 + C_6H_5I + RC \equiv CR' \xrightarrow[\text{dioxan}]{\text{reflux}}$



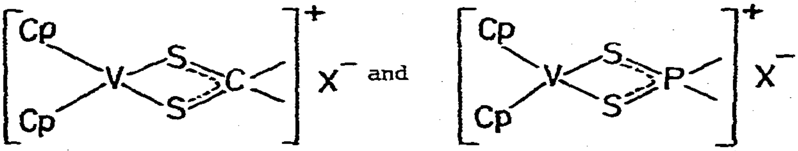
Replacement of iodide in the first product occurred on treatment with $LiAlH_4$ in boiling ether giving the corresponding hydrido complexes which were also made less conveniently from (π-$MeC_5H_4)_2TaH_3$ and RC≡CR'. The ^{1}H-NMR spectra of the complexes from unsymmetrical acetylenes showed the presence of the two expected isomers. With HBF_4 at room temperature or H_2 at 100°, the hydrido acetylene complex gave cis-oct-4-ene (35).

Silicon-, germanium- and tin-substituted acetylenes, $Ph_3MC{\equiv}CPh$, where M=Si, Ge or Sn, formed a bisacetylenic monocarbonyl on irradiation with $CpNb(CO)_4$ in pentane. The



yellow crystalline complexes were stable in air and showed two infrared bands due to coordinated acetylenes at 1660 and 1740 cm^{-1} (the silicon compound showed only one band at 1740 cm^{-1}) (36).

A number of bis(cyclopentadienyl)vanadium(IV) dithio chelates of type,



have been prepared and studied by ESR and electrochemical techniques. Dithiocarbamates, $[Cp_2VS_2CNRR']X$, where R=R'=Me, Et, iPr, Bu; R=H, R'=Me, were made in water, and dithiophosphates, $[Cp_2VS_2P(OR)_2]X$, where R=Me, Et, C_2H_4Cl, Pr, in the appropriate alcohol. Large anions were used to precipitate the complexes which were characterized by magnetic susceptibility measurements, infrared, electronic and ESR spectra. The ESR solution spectra of the dithiocarbamates showed eight lines ($I = 7/2$ for ^{51}V) which were split into sixteen in the dithiophosphates by interaction with the phosphorus atom (37).

Ligand superhyperfine splittings in the ESR spectra of the dicyclohexylphosphinate, $[Cp_2VS_2P(C_6H_{11})_2]Cl$, and of the diethyldithiocarbamate, $[Cp_2VS_2CNEt_2]BF_4$, enriched with ^{13}C, have been attributed to a direct *trans*-annular interaction (38).

The dithiocarbamates, dithiophosphates and xanthates of this type all showed two one-electron polarographic reduction waves, the first of which corresponded with the formation of an oxygen-sensitive vanadium(III) complex which then underwent additional reduction and/or chemical decomposition (39, 40).

Vanadocene has been reported to react with carboxylic acids giving the carboxylato compounds, $CpV(O_2CR)_2$, where R=H, Me or Ph, and $Cp_2VO_2CCCl_3$ (41).

Measurement of the ESR spectrum of the mixture, Cp_2VCl_2+ $EtAlCl_2$, showed initially the presence of three species, but over a period of two weeks the eight-line spectrum assigned to the chloride-bridged complex, $Cp_2VCl_2AlCl_2$, developed (42).

$CpV(CO)_4$ has been found to be an efficient catalyst for the stereoselective oxidation of cyclohexene to cis-1,2--epoxycyclohexan-3-ol (43).

Other π-bonded complexes

π-Bonded cycloolefinic derivatives of these metals have been synthesized by the now well-established technique of treating a cyclopentadienylmetal halide with excess isopropylmagnesium halide in the presence of the cycloolefin. In this way the cycloheptatrienyl derivatives, $CpV(C_7H_7)$ (44) and $CpNb(C_7H_7)$ (45) were made. In the presence of 1,3-cyclohexadiene a non-separable mixture containing Cp_2V, $(C_6H_6)_2V$ and $CpV(C_6H_6)$ was formed. 1,3,5-Cyclooctatriene gave a mixture of $CpV(C_8H_{10})$ and $CpV(C_8H_9)$ which was catalytically dehydrogenated over platinum in hexane at 20° giving only olive-brown crystalline $CpV(C_8H_9)$. The mass spectral decomposition routes of these compounds were considered in some detail (44). The paramagnetic niobium compound was thermally stable but more sensitive to air than the titanium or vanadium analogues (45).

Metallation of $CpV(C_7H_7)$ with butyllithium was found to be more difficult than with the corresponding titanium compound. Metallation took place preferentially in the seven-membered ring for titanium. Qualitative molecular orbital consideration of the charge distribution in these compounds led to the conclusion that the enhanced negative charge on the C_7H_7 ligand of $CpTi(C_7H_7)$ led to preferential metallation in this ring, whereas the two rings of $CpV(C_7H_7)$ carry about equal negative charge (46,47) which was estimated at about 0.3 - 0.4 electrons per ring by X-ray photoelectron spectroscopy. Estimates for $CpTi(C_7H_7)$ gave 0.3 - 0.4 electrons for the Cp ring and 0.7 - 0.8 for the C_7H_7 ring (48).

The products of the Friedel-Crafts synthesis of bis(ethylbenzene)vanadium have been shown by mass spectrometric and gas chromatographic analyses to consist of $(C_6H_5)V(EtC_6H_5)$, $(Et_2C_6H_4)V(EtC_6H_5)$, $(EtC_6H_5)_2V$, $(Et_2C_6H_4)_2V$ and $(Et_2C_6H_4)V(Et_3C_6H_3)$ (49).

Oligomerization of butadiene occurred when atoms of vanadium (prepared by electrical discharge) were condensed in toluene (or benzene) in the presence of Et_2AlCl giving cyclododeca-1,5,9-triene, cyclooctadiene and linear trimers (50).

Several papers describe physical measurements carried out on known compounds. Wideline NMR spectra of $(C_6H_6)_2V$ and $(Me_3C_6H_3)_2V$ have been examined in the temperature range 178-381 K. Line shapes and second moment calculations indicated essentially free rotation of both rings (51). He(1) photoelectron spectra of $(Me_3C_6H_3)_2V$ and $CpV(C_7H_7)$ have been assigned using a simple molecular orbital model and the electronic structure of the compounds discussed with reference to the ionization energies of the electrons in each ring (52).

The fundamental bands in the infrared spectrum of bis-(cyclooctatetraene)vanadium have been assigned using group theory and the ionicity of the bonds considered (53). Also reported is a study of the ESR spectrum of $(C_5H_5)_4Nb$ at various temperatures (54) and a ligand field treatment of metal sandwich compounds including Cp_2V (55).

References

1. P. Meakin, L. J. Guggenberger, F. N. Tebbe and J. P. Jesson, *Inorg. Chem.*, 13 (1974) 1025.
2. M. G. B. Drew and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, (1974) 1973.
3. J. D. Wilkins and M. G. B. Drew, *J. Organometal. Chem.*, 69 (1974) 111.
4. N. I. Kirillova, A. I. Gusev, A. A. Pasynskii and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 14 (1973) 1075.

5. V. T. Kalinnikov, A. A. Pasynskii, G. M. Larin, V. M. Novotortsev, Yu. T. Struchkov, A. I. Gusev and N. I. Kirillova, *J. Organometal. Chem.*, 74 (1974) 91.

6. N. I. Kirillova, A. I. Gusev, A. A. Pasynskii and Yu. T. Struchkov, *Zh. Strukt, Khim.*, 15 (1974) 288.

7. N. I. Kirillova, A. I. Gusev, A. A. Pasynskii and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 14 (1973) 868.

8. T. Kruck and H.-U. Hempel, *Angew. Chem.* internat. Edition, 13 (1974) 201.

9. A. I. Golovanova, M. E. Kost and V. I. Mikheeva, *Izvest. Akad. Nauk SSSR*, Ser. Khim., (1973) 1448.

10. D. H. W. Carstens and J. D. Farr, *J. Inorg. Nuclear Chem.*, 36 (1974) 462.

11. M. C. Baird, *J. Organometal. Chem.*, 64 (1974) 289.

12. M. Schneider and E. Weiss, *J. Organometal. Chem.*, 73 (1974) C7.

13. K.-H. Thiele, B. Adler, H. Grahlert and A. Lachowicz, *Z. anorg. allg. Chem.*, 403 (1974) 279.

14. C. Santini-Scampucci and J. G. Riess, *J. Chem. Soc.*, *Dalton Trans.*, (1974) 1433.

15. R. R. Schrock and P. Meakin, *J. Amer. Chem. Soc.*, 96 (1974) 5288.

16. G. W. A. Fowles, D. A. Rice and J. D. Wilkins, *J. Chem. Soc.*, *Dalton Trans.*, (1974) 1080.

17. J. D. Wilkins, *J. Organometal. Chem.*, 65 (1974) 383.

18. J. D. Wilkins, *J. Organometal. Chem.*, 67 (1974) 269.

19. J. D. Wilkins, *J. Organometal. Chem.*, 80 (1974) 349.

20. J. D. Wilkins, *J. Organometal. Chem.*,80 (1974) 357.

21. D. H. Williamson, C. Santini-Scampucci and G. Wilkinson, *J. Organometal. Chem.*, 77 (1974) C25.

22. S. Moorhouse and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, (1974) 2187.

23. S. Moorhouse and G. Wilkinson, *J. Organometal. Chem.*, 52 (1973) C5.

24. G. K. Barker and M. F. Lappert, *J. Organometal. Chem.*, 76 (1974) C45.

25. R. R. Schrock, *J. Amer. Chem. Soc.*, 96 (1974) 6796.

26. K. Jacob, *Z. Chem.*, 14 (1974) 364.

27. W. Seidel and G. Kreisel, *Z. Chem.*, 14 (1974) 25.

28. F. Calderazzo, G. Fachinetti and C. Floriani, *J. Amer. Chem. Soc.*, 96 (1974) 3695.

29. G. Fachinetti and C. Floriani, *J. Chem. Soc.,Dalton Trans.*, (1974) 2433.

30. G. Fachinetti and C. Floriani, *J. Chem. Soc., Chem. Commun.*, (1974) 516.

31. D. Ytsma, J. G. Hartsuiker and J. H. Teuben, *J. Organometal. Chem.*, 74 (1974) 239.

32. H. Brunner and W. A. Herrmann, *Z Naturforsch.*, 28b (1973) 606.

33. I. H. Elson, J. K. Kochi, U. Klabunde, L. E. Manzer, G. W. Parshall and F. N. Tebbe, *J. Amer. Chem. Soc.*, 96 (1974) 7374.

34. A. van Bealen, G. J. Groenenboom and H. J. de Liefde Meijer, *J. Organometal. Chem.*, 74 (1974) 245.

35. J. A. Labinger, J. Schwartz and J. M. Townsend, *J. Amer. Chem. Soc.*, 96 (1974) 4009.

36. A. N. Nesmeyanov, N. E. Kolobova, A. B. Antonova, K. N. Anisimov and O. M. Khitrova, *Izv. Akad. Nauk* SSSR, *Ser. Khim.*, (1974) 859.

37. A. T. Casey and J. R. Thackeray, *Aust. J. Chem.*, 27 (1974) 757.

38. H. J. Stoklosa and J. R. Wasson, *Inorg. Nucl. Chem. Lett.*, 10 (1974) 401.

39. A. M. Bond, A. T. Casey and J. R. Thackeray, *J. Chem. Soc., Dalton Trans.*,(1974) 773.

40. A. M. Bond, A. T. Casey and J. R. Thackeray, *Inorg. Chem.*, 13 (1974) 84.

41. V. N. Razuvaev, V. N. Latyaeva, A. N. Lineva and S. V. Zelenev, *Dokl. Akad. Nauk* SSSR, 216 (1974) 573.

42. A. G. Evans, J. C. Evans and E. H. Moon, *J. Chem. Soc., Dalton Trans.*, (1974) 2390.

43. J. E. Lyons, *Tetrahedron Lett.*, (1974) 2737.

44. J. Müller and W. Goll, *J. Organometal. Chem.*, 71 (1974) 257.

45. H. O. van Oven, C. J. Groenenboom and H. J. de Leifde Meijer, *J. Organometal. Chem.*, 81 (1974) 379.

46. C. J. Groenenboom, H. J. de Liefde Meijer and F. Jellinek, *Rec. Trav. Chim. Pays-Bas*, 93 (1974) 6.

47. C. J. Groenenboom, H. J. de Liefde Meijer and F. Jellinek, *J. Organometal. Chem.*, 69 (1974) 235.

48. C. J. Groenenboom, G. Sawatsky, H. J. de Liefde Meijer and F. Jellinek, *J. Organometal. Chem.*, 76 (1974) C4.

49. G. G. Devyatykh, P. E. Gaivoronskii, N. V. Larin, V. A. Umilin and V. K. Vanchagova, *Zh. Obshch. Khim.*, 44 (1974) 590.

50. V. M. Akhmedov, M. T. Anthony, M. L. H. Green and D. Young, *J. Chem. Soc., Chem. Commun.*, (1974) 777.

51. S. E. Anderson, *J. Organometal. Chem.*, 71 (1974) 263.

52. S. Evans, J. C. Green, S. E. Jackson and B. Higginson, *J. Chem. Soc., Dalton Trans.*, (1974) 304.

53. L. Hocks, J. Goffart, G. Duyckaerts and P. Teyssié, *Spectrochim. Acta*, 30A (1974) 907.

54. Yu. A. Bobrov, A. D. Krivospitskii and G. K. Chirkin, *Zh. Strukt. Khim.*, 14 (1973) 813.

55. K. D. Warren, *Inorg. Chem.*, 13 (1974) 1243.