Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 30.[1] Synthesis of the Vanadium–Tungsten Complexes $[VW(\mu\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3]$ (R = $C_6H_4Me\text{-}4$ or Me) and the Crystal Structure of the Tolylmethylidyne Compound *

Ulrich Behrens and F. Gordon A. Stone
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

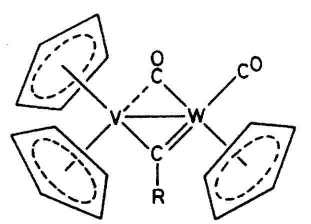
The compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = $C_6H_4Me\text{-}4$ or Me) and $[V(\eta\text{-}C_5H_5)_2]$ react slowly at 0 °C in light petroleum to give black crystalline dimetal compounds $[VW(\mu\text{-}CR)(CO)_2(\eta\text{-}C_5H_5)_3]$ in good yield. Whereas in the solid state the compounds are reasonably stable, in solution they partially dissociate into the precursors. Spectroscopic data are reported and discussed, including e.s.r. studies which confirm the expected paramagnetism of the complexes. The molecular structure of the complex $[VW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)_3]$ has been established by single-crystal *X*-ray diffraction. As expected, the vanadium–tungsten bond [2.994(5) Å] is bridged by the $CC_6H_4Me\text{-}4$ ligand [V–C 2.21(2) and W–C 1.86(1) Å]. One of the two CO ligands on tungsten semi-bridges the V–W bond [W–C–O 167(3)°, V–C(O) 2.63(3) and W–C(O) 1.97(3) Å]. The vanadium and tungsten atoms are also η^5-bonded to two and one cyclopentadienyl groups, respectively. Crystals of $[VW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)_3]$ are monoclinic, space group $P2_1/c$ (no. 14) and the structure has been refined to *R* 0.097 (*R′* 0.093) for 1 699 reflections measured to 2θ = 50° at room temperature.

Because the complex $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4-Me-4) readily combines with low-valent metal–ligand fragments it has become a versatile reagent for preparing compounds with bonds between tungsten and other transition elements.[2,3] In the products the metal–metal bonds are spanned by the tolylmethylidyne ligand, and two or more metal atoms may be present. For dimetal species, complexes are known with bonds between W and Ti, Zr, Cr, Mn, Re, Fe, Co, Rh, Ir, or Pt.[4] With the object of extending still further the range of heteronuclear dimetal compounds, we have studied the reaction between $[V(\eta\text{-}C_5H_5)_2]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$.

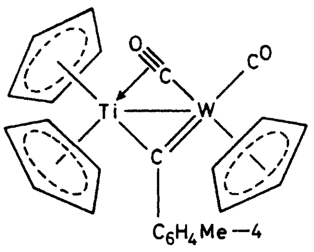
The vanadium compound $[V(\eta\text{-}C_5H_5)_2]$ is known to react with alkynes affording the 17-electron complexes $[V(\eta\text{-}RC_2R)(\eta\text{-}C_5H_5)_2]$ (R = CO_2Me, Ph, CF_3, C_6F_5, *etc.*).[5-8] Since $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and alkynes have similar reactivity patterns, it was anticipated that we would be able to obtain the first example of a compound with a vanadium–tungsten bond *via* the tolylmethylidynetungsten species.

Results and Discussion

The compounds $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[V(\eta\text{-}C_5H_5)_2]$ react very slowly in light petroleum at 0 °C to afford black crystals of compound (1) in *ca.* 70% yield. If the reaction is terminated after 3 or 4 d, rather than weeks, the yields fall to *ca.* 30—40%. By using $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$, the related compound (2) was similarly prepared. In the solid state the complexes are air stable at room temperature over a period of several minutes. In solution, complexes (1) and (2) dissociate into the precursors $[V(\eta\text{-}C_5H_5)_2]$ and $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = $C_6H_4Me\text{-}4$ or Me). At room temperature in toluene, the degree of dissociation is *ca.* 4%, as judged by i.r. measurements. The equilibrium point is reached for complex (1) in about 1 d, and for (2) in about 2 h.



R
(1) C_6H_4Me-4
(2) Me



(3)

Spectroscopic studies (e.s.r. and i.r.) on the two compounds (1) and (2) were informative. The e.s.r. spectra consisted of an eight-line signal, as expected for the presence of one unpaired electron coupled to the quadrupolar ^{51}V nucleus (99.8%, $I = \frac{7}{2}$). The A_{iso} (^{51}V) values [(1), 42.4; (2), 41.8 G] are very similar to those found for the vanadocene–alkyne adducts $[V\{\eta\text{-}C_2(C_6F_5)_2\}(\eta\text{-}C_5H_5)_2]$ (44.6 G)[6] and $[V\{\eta\text{-}C_2(CO_2Me)_2\}(\eta\text{-}C_5H_5)_2]$ (43.4 G).[8] These values are appreciably lower than those obtained from the spectra of vanadocene d^1 complexes, such as $[VMe_2(\eta\text{-}C_5H_5)_2]$ (64 G), and it has been concluded[6,8] that in the former complexes the unpaired electron is delocalised on to the alkyne ligand. Similar reasoning would imply that in complexes (1) and (2) the unpaired electron is appreciably associated with the alkylidyne tungsten group. The *g* values for (1) and (2) are essentially the same (2.025 and 2.024) and are larger than those for the $C_2(C_6F_5)_2$ (1.998) and $C_2(CO_2Me)_2$ (1.997) adducts of vanadocene.

---

* *Supplementary data available* (No. SUP 23905, 16 pp.): thermal parameters, complete list of internuclear separations and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: G = 10^{-4} T.

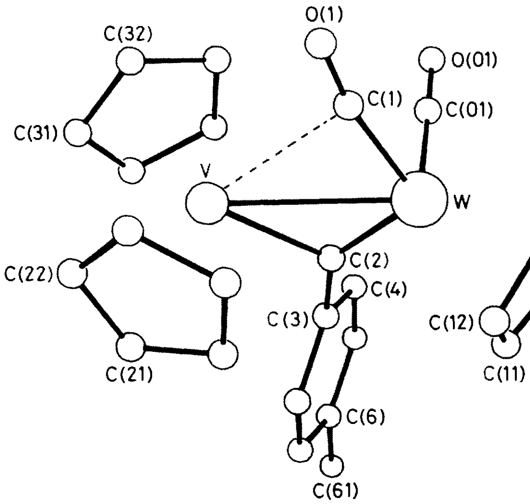


Figure. Molecular structure of [VW(μ-CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)$_3$] (1) showing the atom numbering scheme

The i.r. spectra of complexes (1) and (2) in the carbonyl-stretching region, both in solution and in Nujol, show two bands, one of which is at a frequency [(1), 1 766; (2), 1 758 cm^{-1} (CH_2Cl_2)] suggesting the presence of a bridging CO ligand. In order to establish the origin of this band, and fully to determine the structures of the complexes, a single-crystal *X*-ray diffraction study was carried out on (1). Selected data obtained are listed in Table 1, and the molecule is shown in the Figure with the crystallographic numbering scheme.

The structure of (1) is similar to that of the titanium-tungsten compound (3),[4b] except that the latter contains a σ,μ-CO ligand [$\nu_{max.}$(CO) 1 638 cm^{-1}], whereas the former has a semi-bridging CO group [W–C(1)–O(1) 167(3)°]. In the former, the atoms V, W, C(1), and C(2) are not coplanar, with C(2) being displaced by 0.25 Å from the plane of the other three. Attention is directed at the dimensions of the V–W–C(2) ring [V–W 2.994(5), V–C(2) 2.21(2), and W–C(2) 1.86(1) Å]. In the compound [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)] the W≡C distance is 1.82(2) Å, while the W–μ-C distances within the dimetallacyclopropene rings of the complexes [PtW(μ-CR)$(CO)_2$$(PMe_2Ph)_2$(η-$C_5H_5$)],[4a] [CoW(μ-CR)$(CO)_3$(η-$C_5H_5$)(η-$C_5Me_5$)],[4c] [CrW(μ-CR)$(CO)_4$(η-$C_6Me_6$)(η-$C_5H_5$)] (R = C_6H_4Me-4),[4c] and (3)[4b] are 1.967(6), 1.913(7), 2.025(6), and 1.91(2) Å, respectively. It is apparent that in complex (1) the W–μ-C(2) distance is little changed from that in [W(≡CR)$(CO)_2$(η-C_5H_5)]. This implies a weak attachment between the latter and the V(η-C_5H_5)$_2$ group in (1), thus explaining the ready dissociation in solution.

Since no other complex containing a V–W bond appears to have been reported, the metal–metal distance in (1) [2.994(5) Å] can only be compared with the Ti–W separation in (3) [2.977(4) Å].[4b] The M–μ-C (M = V or Ti) separations in complexes (1) [2.21(2) Å] and (3) [2.19(3) Å] are essentially the same. However, since the covalent radius of vanadium is less than that of titanium, as seen in the shorter V–C(η-C_5H_5) distances [2.33(3) Å] in (1) compared with the Ti–C(η-C_5H_5) separations [2.40(3) Å] in (3), the M–W and M–μ-C bond lengths in the two complexes imply weaker bonding in the vanadium compound. Moreover, in the alkyne adducts [V(η-RC_2R)(η-C_5H_5)$_2$] (R = C_6F_5 or CO_2Me) the V–η²-C distances of 2.077(5) Å (R = C_6F_5)[6] and 2.090(3) Å (R = CO_2Me)[7,8] are appreciably shorter than the V–μ-C(2) separation in (1), reflecting stronger bonding in the alkyne complexes.

Table 1. Selected bond lengths (Å) and angles (°) for the compound [VW(μ-CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)$_3$] (1)

V–W	2.994(5)	W–C(1)	1.97(3)
V–C(1)	2.63(3)	W–C(2)	1.86(1)
V–C(2)	2.21(2)	W–C(01)	1.97(3)
mean V–C(cp) *	2.33(3)	mean W–C(cp)	2.38(2)
V–W–C(2)	47.4(4)	W–V–C(2)	38.3(2)
V–W–C(1)	59.9(9)	W–V–C(1)	40.4(7)
V–W–C(01)	96.5(9)	V–C(2)–W	94.3(4)
V–C(2)–C(3)	124.2(10)	W–C(2)–C(3)	141.5(11)
W–C(1)–O(1)	167(3)	W–C(1)–V	79.7(10)
W–C(01)–O(01)	176(3)		

* cp = η-C_5H_5.

The presence of the unpaired electron in (1) and (2) suggested that these compounds might be oxidised to stable cations isoelectronic with (3), and possibly having a σ,η²-CO ligand to give vanadium an 18-electron shell. However, attempts to prepare a cation were not successful, and cyclo-voltammetric measurements showed that (1) undergoes an irreversible easy oxidation at 0 V.

Experimental

The techniques used and instrumentation employed have been described previously.[4] Light petroleum refers to that fraction of b.p. 40—60 °C. The compounds [W(≡CR)$(CO)_2$(η-C_5H_5)][9] and [V(η-C_5H_5)$_2$][10] were prepared by literature methods.

Preparation of the Complexes [VW(μ-CR)$(CO)_2$(η-C_5H_5)$_3$] (R = C_6H_4Me-4 *or* Me).—(*a*) A light petroleum (40 cm^3) solution of [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)] (0.36 g, 0.88 mmol) was treated with a solution of [V(η-C_5H_5)$_2$] (0.16 g, 0.88 mmol) in the same solvent (20 cm^3). The mixture was maintained at *ca.* 0 °C for 4 weeks, thereby affording large black *crystals* of [VW(μ-CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)$_3$] (1) (0.36 g, 70%) (Found: C, 51.1; H, 3.7. $C_{25}H_{22}O_2VW$ requires C, 51.0; H, 3.8%), m.p. 105—115 °C (decomp.); $\nu_{max.}$(CO) at 1 896s and 1 766s cm^{-1} (CH_2Cl_2), and at 1 873s and 1 761s cm^{-1} (Nujol). E.s.r. (in toluene): *g* 2 025; A_{iso}(^{51}V) 42.4 G.

(*b*) In a similar manner to that described above, black *crystals* of [VW(μ-CMe)$(CO)_2$(η-C_5H_5)$_3$] (2) (0.21 g, 55%) were obtained in 3 d after mixing light petroleum (10 cm^3) solutions of [W(≡CMe)$(CO)_2$(η-C_5H_5)] (0.25 g, 0.75 mmol) and [V(η-C_5H_5)$_2$] (0.135 g, 0.75 mmol). For compound (2) (Found: C, 44.7; H, 3.6. $C_{19}H_{18}O_2VW$ requires C, 44.5; H, 3.5%), m.p. 138—140 °C (decomp.); $\nu_{max.}$(CO) at 1 896s and 1 758s cm^{-1} (CH_2Cl_2), and 1 866s and 1 730s cm^{-1} (Nujol). E.s.r. (in toluene): *g* 2.024; A_{iso}(^{51}V) 41.8 G.

Crystal Structure Determination of [VW(μ-CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)$_3$] (1).—Crystals of complex (1) grow as black distorted octahedra from dilute equimolar light petroleum solutions of [V(η-C_5H_5)$_2$] and [W(≡CC_6H_4Me-4)$(CO)_2$(η-C_5H_5)] maintained at 0 °C for a few days. Although the crystals were well shaped they diffracted weakly. Diffracted intensities were recorded at room temperature from a crystal of dimensions 0.45 × 0.40 × 0.16 mm, sealed in a Lindemann tube under nitrogen. Of the 4 227 reflections measured for $3 \leqslant 2\theta \leqslant 50°$ on a Nicolet *P*2$_1$*m* four-circle diffractometer, 1 699 had $I \geqslant 2\sigma(I)$, and only these were used in the refinement of the structure. Corrections were applied for Lorentz, polarisation, and anomalous dispersion, and for *X*-ray absorption effects; the maximum and minimum transmission

Table 2. Atomic co-ordinates ($\times 10^4$) for [$VW(\mu-CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)_3$] (1)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	1 474(2)	1 390(1)	4 122(1)	C(12)	4 156	735	4 017
V	221(7)	2 173(4)	2 713(3)	C(13)	3 181	84	4 410
O(01)	−1 495(32)	2 037(25)	5 045(13)	C(14)	2 746	514	5 076
O(1)	−772(32)	58(18)	3 221(12)	C(15)	3 452	1 430	5 095
C(01)	−374(36)	1 828(30)	4 716(15)	C(21)	2 164(40)	2 656(17)	1 881(15)
C(1)	−18(40)	632(22)	3 503(17)	C(22)	894	2 166	1 502
C(2)	1 557(16)	2 590(6)	3 713(7)	C(23)	917	1 212	1 736
C(3)	2 192(23)	3 553(12)	3 856(10)	C(24)	2 200	1 112	2 260
C(4)	1 560	4 081	4 426	C(25)	2 970	2 005	2 350
C(5)	2 248	4 955	4 600	C(31)	−1 998(38)	2 818(31)	2 097(12)
C(6)	3 569	5 302	4 204	C(32)	−2 553	1 995	2 458
C(7)	4 202	4 773	3 633	C(33)	−2 394	2 151	3 216
C(8)	3 513	3 899	3 459	C(34)	−1 741	3 071	3 323
C(61)	4 356(52)	6 310(27)	4 420(22)	C(35)	−1 496	3 483	2 631
C(11)	4 324(29)	1 567(22)	4 441(14)				

coefficients were 0.494 and 0.228. Two check reflections ($\bar{1}$ 0 2 and $\bar{1}$ 0 4) were measured every 100 reflections, and showed no significant decay over 150 h of data collection. Computations were carried out in the laboratory on an Eclipse (Data General) computer with the SHELXTL system of programs.[11]

Crystal data. $C_{25}H_{22}O_2VW$, $M = 588.9$, monoclinic, $a = 8.118(7)$, $b = 14.172(26)$, $c = 18.457(9)$ Å, $\beta = 90.71(6)°$, $U = 2\,123(4)$ Å^3, $Z = 4$, $D_c = 1.84$ g cm^{-3}, $F(000) = 1\,140$, space group $P2_1/c$ (no. 14), Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 59.8 cm^{-1}.

The structure was solved by heavy-atom methods, and was refined by blocked-cascade least squares with anisotropic thermal parameters for all atoms. Hydrogen atoms were not incorporated. The carbon atoms of the cyclopentadienyl ligands and of the tolyl ligand were constrained to ideal geometry, and both CO distances were fixed to 1.14 Å. Individual weights were ascribed according to the scheme $w = [\sigma^2(F_o) + 0.0025|F_o|^2]^{-1}$. Scattering factors and corrections for anomalous dispersion were from ref. 12. Convergence was reached at R 0.097 (R' 0.093). A final electron-density difference synthesis showed a maximum of 4.8 and a minimum of −3.9 e Å^{-3} in the region of the tungsten atom but much lower values elsewhere. The final atom co-ordinates are listed in Table 2.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for a grant (to U. B.).

References

1 Part 29, G. A. Carriedo, J. C. Jeffery, and F. G. A. Stone, preceding paper.

2 F. G. A. Stone, in 'Inorganic Chemistry: Toward the 21st Century,' ed. M. H. Chisholm, *ACS Symp. Ser.*, 1983, **211**, 383.

3 G. A. Carriedo, J. A. K. Howard, and F. G. A. Stone, *J. Organomet. Chem.*, 1983, **250**, C28; *J. Chem. Soc., Dalton Trans.*, 1984, 1555; G. A. Carriedo, J. A. K. Howard, K. Marsden, F. G. A. Stone, and P. Woodward, *ibid.*, p. 1589; M. R. Awang, G. A. Carriedo, J. A. K. Howard, K. A. Mead, I. Moore, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1983, 964.

4 (*a*) T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1609; (*b*) G. M. Dawkins, M. Green, K. A. Mead, J-Y. Salaün, F. G. A. Stone, and P. Woodward, *ibid.*, 1983, 527; (*c*) J. A. Abad, L. W. Bateman, J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, and P. Woodward, *ibid.*, 1983, 2075 and refs. therein.

5 R. Tsumara and N. Haghira, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 861.

6 D. F. Foust, M. D. Rausch, W. E. Hunter, J. L. Atwood, and E. Samuel, *J. Organomet. Chem.*, 1980, **197**, 217.

7 G. Fashinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1979, **18**, 2282.

8 J. L. Petersen and L. Griffith, *Inorg. Chem.*, 1980, **19**, 1852.

9 E. O. Fischer, T. L. Lindner, G. Huttner, P. Friedrich, F. R. Kreissl, and J. O. Besenhard, *Chem. Ber.*, 1977, **110**, 3397.

10 R. B. King, 'Organometallic Syntheses,' Academic Press, New York, 1965, vol. 1, p. 64.

11 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *P*3*m* *X*-ray system, University of Cambridge, 1976; updated at Göttingen, 1981.

12 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

Received 10*th October* 1983; *Paper* 3/1790