*Journal of Organometallic Chemistry*, 218 (1981) 351—359
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

# σ–π-REARRANGEMENT OF THE ACETYLENE LIGAND ON PROTONATION OF $Cp(CO)_3W$—C≡CPh. THE CRYSTAL STRUCTURE OF [$\eta^2$-{($\eta^5$-CYCLOPENTADIENYL)(TRICARBONYL)($\eta^1$-PHENYLETHYNYL)-TUNGSTEN}-($\eta^5$-CYCLOPENTADIENYL)(CARBONYL)-($\eta^2$-PHENYLACETYLENE)TUNGSTEN] TETRAFLUOROBORATE

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(Received April 7th, 1981)

## Summary

The protonation of $\eta^5$-$Cp(CO)_3WC{\equiv}CPh$ by $HBF_4$ in $CH_2Cl_2$ gives the stable cationic binuclear complex of tungsten $[(\eta^5\text{-}Cp)(OC)_3W\{\mu\text{-}(\eta^1,\eta^2\text{-}C_2Ph)\}W(\eta^2\text{-}C_2PhH)(CO)(\eta^5\text{-}Cp)]^+BF_4^-$ (V). In the presence of $PPh_3$ this reaction leads to the formation of the phosphonium complex $[\eta^5\text{-}Cp(CO)_3W\{C(PPh_3){=}CPhH\}]^+BF_4^-$. The structure of complex V has been determined by X-ray diffraction methods.

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## Introduction

The protonation of σ-acetylides of Pt [1] and Fe [2—5] by strong protic acids results in the formation of cationic vinylidene (vinylcarbenium) complexes, in which an electrophilic centre is stabilized by a transition metal atom:

$$[M]{-}C{\equiv}CR \xrightarrow{H^+} [M]{-}C^+{=}CHR \rightleftharpoons [M]^+{=}C{=}CHR$$

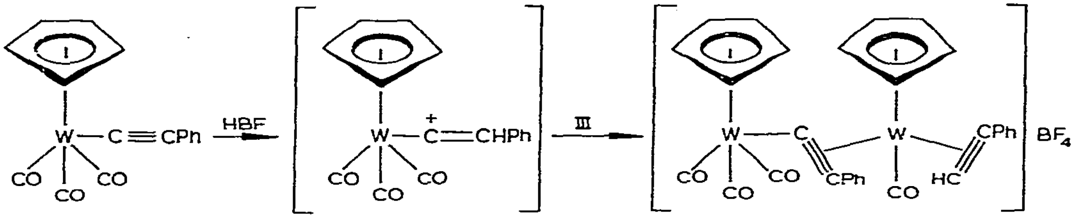
The reactivity of cationic vinylidene complexes depends on the nature of the metal and donating properties of the ligands coordinated to the metal atom. The protonation of $Cp(CO)_2FeC{\equiv}CPh$ (I) by HX (X = $ClO_4$ or $BF_4$) gives a reactive vinylidene complex $[Cp(CO)_2Fe^+{=}C{=}CHPh]\ X^-$ (II) which, in the absence of a competing nucleophile, reacts with a second molecule of I, to yield a binuclear complex of iron with a cyclobutenylidene ligand [2,4]. In the presence of $PPh_3$ the reaction results in a vinyl-metal complex containing a cationic phosphonium centre [3]. The protonation of acetylide complexes with increased electron density at the iron atom, viz. $Cp(CO)(PPh_3)FeC{\equiv}CPh$ and $Cp(Diphos)FeC{\equiv}CR$, where R = Me, H and Diphos = $Ph_2PCH_2CH_2PPh_2$, gives vinylidene compounds, more stable and less reactive than II [4—6].

0022-328X/81/0000—0000/$02.50

In an effort to determine the effect of the transition metal on the reactivity of cationic vinylidene complexes, we have studied the reaction of Cp(CO)$_3$W—C≡CPh (III) with HBF$_4$.

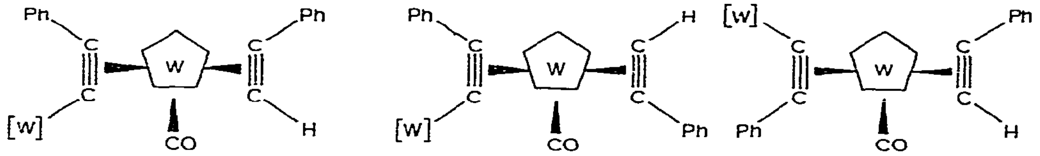
## Results and discussion

The protonation of III by HBF$_4$ in CH$_2$Cl$_2$ (1 h, at —20 to 20°C) gives complex V in 53% yield as orange-yellow crystals with m.p. 225—230°C (dec.):



(III) (IV) (V)

The IR spectrum of V contains absorption bands of terminal CO groups at 1950, 2040 and 2060 cm$^{-1}$. The PMR spectrum of V (δ in ppm, acetonitrile) shows proton singlets at 5.59. 5.76 and 5.64 ppm from the Cp ligands (Cp(CO)$_3$W fragment), singlets at 5.80, 6.02 and 6.05 ppm (Cp(CO)W fragment) and a multiplet centered at 7.44 ppm from the phenyl protons. Three signals from each of the two Cp ligands may be attributed to the presence in the solution of three rotamers, differing in orientation of the π-acetylene ligands with respect to the CO group:



(a) (b) (c)

[w] = Cp(CO)$_3$W

At room temperature the isomers are present, from the line intensities of Cp ligand protons, in the ratio 6:2.5:1.

The structure of complex V was determined unambiguously by X-ray analysis. Complex V has an ionic structure and is built up of tetrahedral anions BF$_4^-$ (av. B—F 1.34(4) Å, FBF 109(4)°) and binuclear cations [($\eta^5$-Cp)(CO)$_3$W{$\mu$-($\eta^1$,$\eta^2$-C$_2$Ph)}W($\eta^2$-C$_2$PhH)(CO)($\eta^5$-Cp)]$^+$. The cation geometry is presented in Fig. 1 and its main geometrical parameters are tabulated in Tables 1 and 2.

The binuclear cation in compound V includes as a ligand a molecule of the initial complex Cp(CO)$_3$W(1)(—C≡CPh), $\eta^2$-coordinated through its σ-acetylide ligand, as a bridge, to the W(2) atom of the fragment Cp(CO)W(2)($\eta^2$-C$_2$HPh). As the distance W(1)···W(2) = 4.216(I) Å in the cation significantly exceeds the doubled covalent radius of tungsten (3.18 Å [7]), direct W—W interaction is lacking and the metal atoms are bonded only through the σ,π-bridging phenylacetylide ligand.

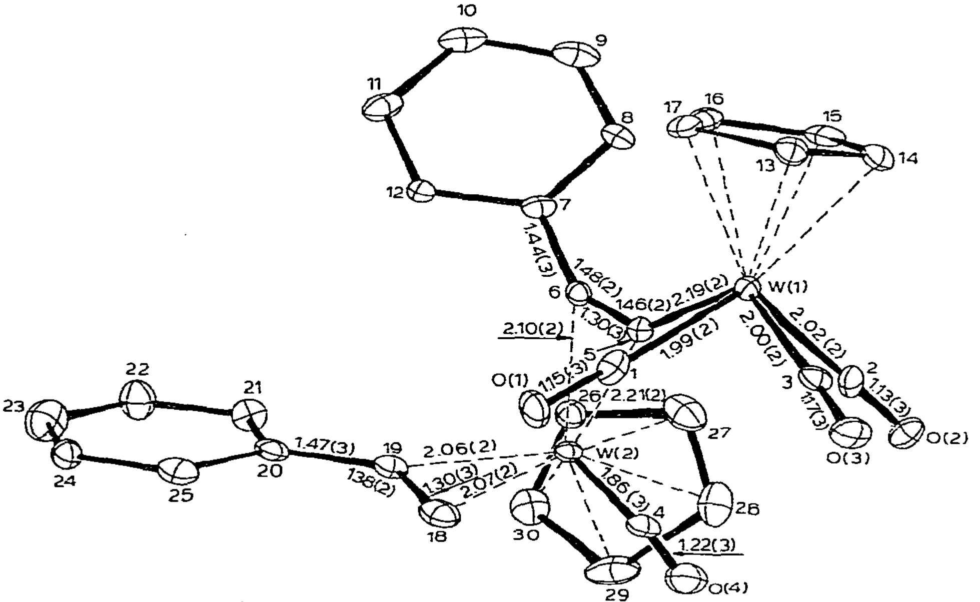


Fig. 1. The structure of cation V.

This indicates that the positive charge of the cation is probably localized at the W(2) atom. The metal atoms in cation V have different electron shells (18-electron in W(1) and 16-electron in W(2); the coordination numbers are 7 and 6, respectively), This difference probably explains the significantly shorter length, 1.86(3) Å, of the W(2)—CO bond in comparison with the W(1)—CO bonds, 1.99, 2.00 and 2.02(2) Å, although W—C(Cp) distances for both tungsten atoms to similar to within $\sigma$. In both alkyne ligands $\eta^2$-coordinated to the W(2) atom the C≡C bonds have equal lengths (1.30(3) Å), increased compared with that of an uncoordinated triple bond (1.205 Å) [8]. The phenylacetylene ligand C(18)—C(19) is symmetrically coordinated to W(2) (W(2)—C(18) 2.07, W(2)—C(19) 2.06(2) Å), while the $\sigma,\pi$-bridging phenylacetylide ligand C(5)—C(6) is bonded asymmetrically (the W(2)—C(5) distance 2.21(2) Å is significantly greater than W(2)—C(6), 2.10(2) Å). The elongation of the W(2)—C(5) distance may be attributed to participation of C(5) in a $\sigma$-bond with W(1), the length of which, 2.19(2) Å, is somewhat shorter than that of the $\sigma$-bond W—C($sp^3$) 2.28(1) Å in $Cp_2W(\sigma\text{-}CH_2C_6H_3Me_2)_2$ [9], and to steric hindrance caused by short intramolecular contacts involving the C(5) atom: C(5)···C(4) 2.59, C(5)···C(I) 2.58 and C(5)··· C(2) 2.60 Å. The $\eta^2$-coordinated alkyne ligands acquire a *cis*-stilbene configuration (the W(1)C(5)C(6), C(5)C(6)C(7) and C(18)C(19)C(20) angles are equal to 146(2), 148(2) and 138(2), respectively) and exhibit distortion of planarity (the torsion angle around the C(5)—C(6) bond is 6.8°). The dihedral angles between the Ph rings C(7)—C(12) and C(20)—C(25) and the planes of the corresponding C≡C—C(Ph) fragments are equal to 55.4 and 13.5°, respectively.

Complex V is obtained through the conversion of a vinylcarbenium ligand of the intermediate complex IV into a $\eta^2$-phenylacetylene one, loss of two CO groups and $\eta^2$-coordination of the triple bond of a $\sigma$-phenylacetylide ligand of III to a

TABLE 1

BOND LENGTHS $d$(Å) IN CATION V

| Bond | $d$ | Bond | $d$ | Bond | $d$ | Bond | $d$ |
|---|---|---|---|---|---|---|---|
| W(1)—C(1) | 1.99(2) | W(2)—C(4) | 1.86(3) | C(1)—O(1) | 1.15(3) | C(15)—C(16) | 1.42(4) |
| W(1)—C(2) | 2.02(2) | W(2)—C(5) | 2.21(2) | C(2)—O(2) | 1.13(3) | C(16)—C(17) | 1.40(3) |
| W(1)—C(3) | 2.00(3) | W(2)—C(6) | 2.10(2) | C(3)—O(3) | 1.17(3) | C(13)—C(17) | 1.44(3) |
| W(1)—C(5) | 2.19(2) | W(2)—C(18) | 2.07(2) | C(4)—O(4) | 1.22(3) | C(26)—C(27) | 1.32(3) |
| W(1)—C(13) | 2.34(2) | W(2)—C(19) | 2.06(2) | C(5)—C(6) | 1.20(3) | C(29)—C(30) | 1.37(4) |
| W(1)—C(14) | 2.31(2) | W(2)—C(26) | 2.37(2) | C(6)—C(7) | 1.44(3) | C(27)—C(28) | 1.38(4) |
| W(1)—C(15) | 2.35(2) | W(2)—C(27) | 2.35(2) | C(18)—C(19) | 1.30(3) | C(28)—C(29) | 1.45(4) |
| W(1)—C(16) | 2.36(2) | W(2)—C(28) | 2.34(2) | C(19)—C(20) | 1.47(3) | C(26)—C(30) | 1.35(4) |
| W(1)—C(17) | 2.37(2) | W(2)—C(29) | 2.36(2) | C(13)—C(14) | 1.41(4) | Av. C—C(Ph) | 1.38(4) |
|  |  | W(2)—C(30) | 2.42(2) | C(14)—C(15) | 1.48(4) |  |  |

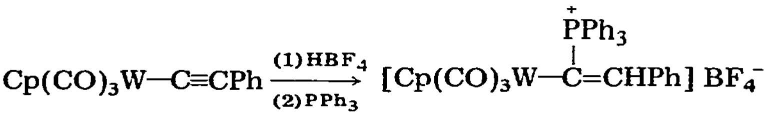
TABLE 2

BOND ANGLES ω(deg) [a]

| Angle | ω | Angle | ω | Angle | ω |
|---|---|---|---|---|---|
| C(1)W(1)C(2) | 111.9(9) | C(4)W(2)Ac(1) | 95.5 | W(1)C(5)C(6) | 146(2) |
| C(1)W(1)C(3) | 75.3(9) | C(4)W(2)Ac(2) | 91.8 | C(5)C(6)C(7) | 148(2) |
| C(1)W(1)C(5) | 76.0(8) | C(4)W(2)Cp(2) | 114.7 | C(6)C(7)C(8) | 120(2) |
| C(1)W(1)Cp(1) | 125.3 | Ac(1)W(2)Ac(2) | 106.5 | C(6)C(7)C(12) | 121(2) |
| C(2)W(1)C(3) | 79.3(9) | Ac(1)W(2)Cp(2) | 116.0 | C(8)C(7)C(12) | 118(2) |
| C(2)W(1)C(5) | 75.9(8) | Ac(2)W(2)Cp(2) | 125.9 | C(18)C(19)C(20) | 138(2) |
| C(2)W(1)Cp(1) | 122.8 | W(1)C(1)O(1) | 178(2) | C(19)C(20)C(21) | 123(2) |
| C(3)W(1)C(5) | 131.1(8) | W(1)C(2)O(2) | 179(2) | C(19)C(20)C(25) | 118(2) |
| C(3)W(1)Cp(1) | 115.4 | W(1)C(3)O(3) | 177(2) | C(21)C(20)C(25) | 118(2) |
| C(5)W(1)Cp(1) | 113.5 | W(2)C(4)O(4) | 176(2) | | |

[a] Cp(1) and Cp(2) denote the centroids of the cyclopentadienyl ligands C(13)—C(17) and C(26)—C(30). Ac(1) and Ac(2) are the midpoints of the $\eta^2$-coordinated bonds C(5)≡C(6) and C(18)≡C(19).

tungsten atom of IV. The participation of the vinylcarbenium complex IV is confirmed by the formation of the phosphonium cation VI by the reaction:



$$Cp(CO)_3W{-}C{\equiv}CPh \xrightarrow[(2)PPh_3]{(1)HBF_4} [Cp(CO)_3W{-}\overset{\overset{+}{PPh_3}}{\underset{}{C}}{=}CHPh]\ BF_4^-$$

(III) (VI)

Complex VI is a yellow crystalline substance with a melting point of 121—122°C (dec.). The IR spectrum of VI taken in $CH_2Cl_2$ exhibits $\nu$(C≡O) bands at 1860, 1965 and 2040 $cm^{-1}$. The PMR spectrum of VI ($\delta$ in ppm, acetonitrile) shows a singlet at 5.16 ppm (Cp) and a multiplet at 7.60 ppm (Ph). The $^{31}P$ NMR spectrum in $CH_2Cl_2$ reveals a singlet at 36.72 ppm characteristic of phosphonium salts [10].

## Experimental

A 40% aqueous solution of $HBF_4$ was used in the study. The IR spectra were recorded on a Zeiss UR-20 spectrophotometer. The PMR spectra were recorded on Hitachi-60 and RYa-2309 spectrometers. The $^{31}P\ \{^1H\}$ NMR-spectra were run on a Bruker-90 instrument at 36.43 MHz, using 85% $H_3PO_4$ as an internal standard. Melting points were determined in sealed capillaries. Crystal data were determined on a Syntex $P2_1$ four-circle diffractometer (temperature 20°C, $\lambda$ Mo, graphite monochromator, $2^\circ \leqslant 2\theta \leqslant 50^\circ$, $\theta/2\theta$ scan, 3924 reflections with $F^2 \geqslant 2\sigma$). Absorption correction was carried out with the OPABS-II program [11] *. The structure was determined by the heavy atom method and refined by the full-matrix anisotropic least-squares method. Hydrogen atoms were included in the refinement with fixed calculated positional parameters and assigned isotropic thermal parameters ($B_{iso}$ = 5 Å$^2$). Finally, $R$ = 0.0390, $R_W$ = 0.070. Crystals of V are triclinic, at 20°C $a$ = 9.385(3), $b$ = 11.938(4),

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* Details of the method of absorption correction used in this study are given in ref. 12.

TABLE 3

ATOMIC POSITIONAL (X$10^3$, FOR W X $10^5$) AND THERMAL PARAMETERS
$T = \exp[-1/4(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*)]$

| Atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| W(1) | 12801(8) | 77647(7) | 101036(6) | 2.95(4) | 2.75(4) | 2.62(4) | 0.92(3) | 0.77(3) | 0.84(3) |
| W(2) | 30663(8) | 58449(7) | 75215(6) | 2.45(4) | 3.18(4) | 2.60(4) | 0.85(3) | 0.63(3) | 0.59(3) |
| O(1) | 326(2) | 634(1) | 1068(1) | 6.3(9) | 5.0(8) | 7(1) | 2.8(7) | −0.7(8) | 2.6(8) |
| O(2) | 296(2) | 949(1) | 894(1) | 5.6(9) | 4.9(8) | 7(1) | 0.7(7) | 1.8(8) | 3.7(8) |
| O(3) | 378(2) | 988(1) | 1187(1) | 4.4(8) | 5.2(8) | 5.5(9) | 0.9(7) | −0.1(7) | 0.0(8) |
| O(4) | 529(2) | 805(2) | 927(1) | 4.1(8) | 5.6(9) | 5.8(9) | 1.4(7) | 0.6(7) | 0.7(8) |
| C(1) | 257(2) | 688(2) | 1047(2) | 5(1) | 3.4(9) | 3(1) | 0.6(8) | 0.3(9) | 1.1(8) |
| C(2) | 236(2) | 888(2) | 936(2) | 5(1) | 2.9(9) | 5(1) | 1.4(8) | 1(1) | 1.3(9) |
| C(3) | 283(2) | 912(2) | 1123(2) | 3.0(9) | 4.0(9) | 3(1) | 1.7(8) | 0.6(8) | 0.1(8) |
| C(4) | 439(2) | 720(2) | 858(2) | 3.5(9) | 6(1) | 6(2) | 2.4(9) | 2(1) | 3(1) |
| C(5) | 151(2) | 642(2) | 862(1) | 2.7(8) | 3.1(8) | 2.5(9) | 0.9(7) | 0.3(7) | 1.2(7) |
| C(6) | 82(2) | 543(2) | 782(1) | 2.8(9) | 3.0(8) | 2.9(9) | 1.3(7) | 0.4(7) | 1.5(7) |
| C(7) | −58(2) | 452(2) | 726(1) | 2.6(8) | 3.5(8) | 2.0(8) | 0.8(7) | 1.0(7) | 0.9(7) |
| C(8) | −172(2) | 492(2) | 697(2) | 3.3(9) | 5(1) | 4(1) | 1.9(9) | 0.7(9) | 1.7(9) |
| C(9) | −304(2) | 402(3) | 643(2) | 2.7(9) | 8(2) | 5(1) | 2(1) | −0.1(9) | 2(1) |
| C(10) | −329(2) | 277(3) | 618(2) | 3(1) | 8(2) | 4(1) | 0(1) | 0.6(9) | 1(1) |
| C(11) | −218(3) | 235(2) | 644(2) | 4(1) | 3(1) | 4(1) | −0.3(9) | 1(1) | 0(1) |

|  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
| C(12) | −83(2) | 323(2) | 696(2) | 3.1(9) | 3.6(9) | 4(1) | 1.2(8) | 0.7(9) | 1.1(9) |
| C(13) | −43(2) | 804(2) | 1130(2) | 4(1) | 5(1) | 5(1) | 2.1(9) | 2.6(9) | 1.7(9) |
| C(14) | −56(2) | 868(2) | 1066(2) | 4(1) | 5(1) | 6(1) | 3.0(9) | 2(1) | 2(1) |
| C(15) | −111(2) | 776(2) | 960(2) | 3(1) | 8(1) | 5(1) | 2(1) | 1.3(9) | 3(1) |
| C(16) | −129(2) | 655(2) | 963(2) | 3.4(9) | 5(1) | 4(1) | 0.5(8) | 1.2(9) | 1.4(9) |
| C(17) | −92(2) | 671(2) | 1065(2) | 2.6(9) | 4.2(9) | 5(1) | 0.4(7) | 1.4(9) | 2.0(9) |
| C(18) | 421(2) | 509(2) | 826(2) | 4(1) | 5(1) | 4(1) | 1.9(9) | 1.5(9) | 1.9(9) |
| C(19) | 335(2) | 418(2) | 746(2) | 2.3(8) | 4.4(9) | 2.8(9) | 1.4(7) | 0.9(7) | 1.1(8) |
| C(20) | 302(2) | 280(2) | 695(2) | 2.4(8) | 4.2(9) | 4(1) | 1.8(7) | 1.3(8) | 1.9(9) |
| C(21) | 225(2) | 213(2) | 600(2) | 5(1) | 4(1) | 3(1) | 2.8(9) | 0.3(9) | 1.1(9) |
| C(22) | 198(3) | 86(2) | 556(2) | 7(2) | 5(1) | 5(1) | 2(1) | 0(1) | 1(1) |
| C(23) | 245(3) | 22(2) | 606(2) | 8(2) | 4(1) | 4(1) | 1(1) | 1(1) | 0(1) |
| C(24) | 320(3) | 85(2) | 700(2) | 6(1) | 5(1) | 7(2) | 3(1) | 2(1) | 4(1) |
| C(25) | 352(2) | 215(2) | 746(2) | 4(1) | 6(1) | 4(1) | 1.9(9) | 0.8(9) | 1.8(9) |
| C(26) | 201(2) | 518(2) | 580(2) | 3.2(9) | 4.1(9) | 4(1) | 1.3(8) | 1.1(8) | 1.3(9) |
| C(27) | 341(3) | 514(2) | 578(2) | 5(1) | 5(1) | 3(1) | 2.0(9) | 1.4(9) | 1.6(9) |
| C(28) | 442(2) | 634(3) | 626(2) | 4(1) | 9(2) | 4(1) | 1(1) | 2(1) | 4(1) |
| C(29) | 351(4) | 717(2) | 658(2) | 10(2) | 4(1) | 4(1) | 3(1) | 2(1) | 1.9(9) |
| C(30) | 205(3) | 640(3) | 624(2) | 6(1) | 9(2) | 5(1) | 5(1) | 3(1) | 4(1) |
| B | 113(3) | 175(3) | 316(3) | 5(1) | 5(1) | 8(2) | 1(1) | −1(1) | 3(1) |
| F(1) | 115(2) | 62(1) | 318(1) | 11(1) | 6.0(8) | 7(1) | 4.1(8) | 1.8(9) | 2.9(7) |
| F(2) | −11(2) | 156(2) | 254(1) | 6.8(9) | 9(1) | 8(1) | 2.8(8) | 0.2(9) | 3.3(9) |
| F(3) | 224(2) | 208(2) | 256(2) | 7(1) | 13(1) | 16(2) | 3(1) | 1(1) | 9(1) |
| F(4) | 136(3) | 263(1) | 397(1) | 32(2) | 7.3(8) | 3.7(6) | 9(1) | −5(1) | −2.5(6) |

$c = 14.113(4)$ Å, $\alpha = 110.76(3)$, $\beta = 90.40(3)$, $\gamma = 107.18(2)°$, $V = 1401.6(8)$ Å$^3$. $M = 904.6$, $D_{calcd.} = 2.15$ g cm$^{-3}$, $Z = 2$, space group $P\bar{1}$. Atomic positional and thermal parameters are listed in Table 3.

*($\eta^5$-cyclopentadienyl)(tricarbonyl)($\eta^1$-phenylethynyl)tungsten (III)*

A solution of 28 g (61 mmol) $Cp(CO)_3WI$ in 125 ml THF was added at —15°C with stirring to a suspension of 15 g (120 mmol) $PhC{\equiv}CNa$ in 75 ml THF. The temperature of the reaction mixture was allowed to rise to ca. 20°C and the solution was stirred for 2 h. The solution was filtered and the filtrate concentrated in vacuo. Chromatography on a $SiO_2$ column (eluent benzene) yielded 13.2 g (50%) of III, m.p. 139—142°C (hexane/benzene, 4/1) (lit. 142—143°C [13]). (Found: C, 44.36; H, 2.23; W, 42.24. $C_{16}H_{10}O_3W$ calcd.: C, 44.20; H, 2.30; W, 42.30%.) IR spectrum ($\nu$, cm$^{-1}$, in cyclohexane): 1950, 1975, 2050 ($C{\equiv}O$).

*[{$\eta^2$-($\eta^5$-cyclopentadienyl)(tricarbonyl)($\eta^1$-phenylethynyl)tungsten} {($\eta^5$cyclopentadienyl)(carbonyl)($\eta^2$-phenylacetylene)tungsten}] tetrafluoroborate (V)*

0.24 g (1.1 mmol) $HBF_4$ was added dropwise with stirring to a solution of 0.2 g (0.46 mmol) III in 5 ml $CH_2Cl_2$ cooled to —20°C. The reaction mixture temperature was allowed to rise to ca. 20°C and the mixture was left to stand for 1 h; the solvent was then removed in vacuo. Chromatography on a $SiO_2$ column (eluent MeOH) gave 0.11 g (53%) of orange-yellow crystals; m.p. 225—230°C (dec., MeOH/ether, 5/1). (Found: C, 39.79; H, 2.30; F, 10.05. $C_{30}H_{21}W_2O_4BF_4$ calcd.: C, 40.0; H, 2.33; F, 8.45%.)

*[(1-triphenylphosphonium)(2-phenylvinyl)($\eta^5$-cyclopentadienyl)(tricarbonyl)-tungsten] tetrafluoroborate (VI)*

A solution of 0.2 g (0.46 mmol) III in 5 ml $CH_2Cl_2$ was added with stirring to the mixture of 0.24 g (0.92 mmol) $PPh_3$ in 20 ml $CH_2Cl_2$ and 0.24 g (I mmol) $HBF_4$ in 1 ml ether, cooled to —70°C. The reaction mixture temperature was raised to ca. 20°C and the mixture left to stand for 1.5 h. The solvent was removed in vacuo and the solid residue washed with ether (4 × 10 ml). 0.12 g (33%) of yellow crystals was isolated; m.p. 121—122°C (dec., $CHCl_3$/ether, 9/1). (Found: C, 46.33; H, 3.27; P, 3.83. $C_{34}H_{26}O_3BF_4$ calcd.: C, 52.00; H, 3.32; P, 3.95%.)

## Acknowledgements

The authors express their sincere thanks to P.V. Petrovsky and V.A. Antonovich for recording PMR and $^{31}$P NMR spectra.

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