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Preliminary communication

PROTON-INDUCED DIMERISATION AND RELATED REACTIONS OF MONONUCLEAR TUNGSTEN CARBYNE COMPLEXES

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Summary

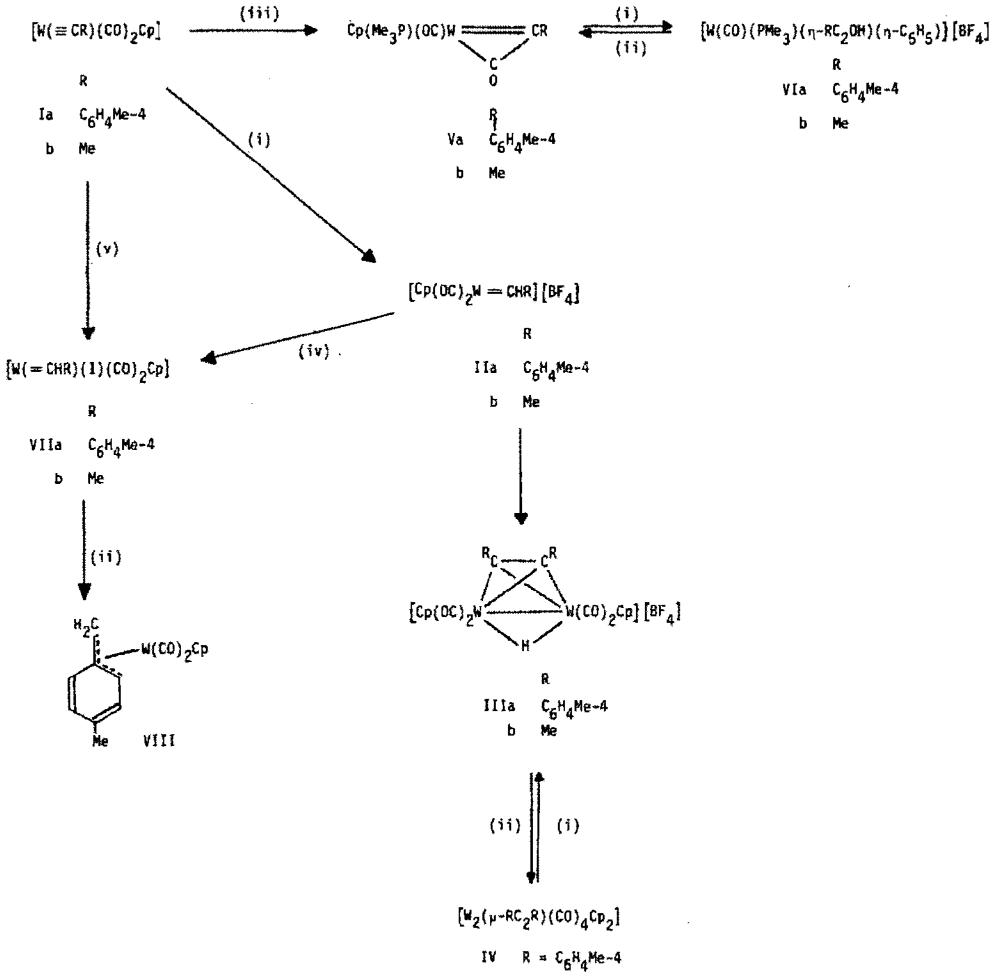
The products obtained by treating the compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me$-4 or Me) with $HBF_4 \cdot Et_2O$ or with HI are described and compared with species obtained by protonating or methylating the complexes $[W\{\eta^2\text{-}C(R)C(O)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$.

There is considerable interest in the chemistry of cationic carbene $[M(=CR^1R^2)L_3(\eta\text{-}C_5H_5)]^+$ and neutral carbyne $[M(\equiv CR)L_2(\eta\text{-}C_5H_5)]$ complexes, where M = Mo or W, and L is an electron-pair donor ligand [1]. Herein we report new chemistry of the species $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (I, $R = C_6H_4Me$-4 or Me), summarised in Scheme 1.

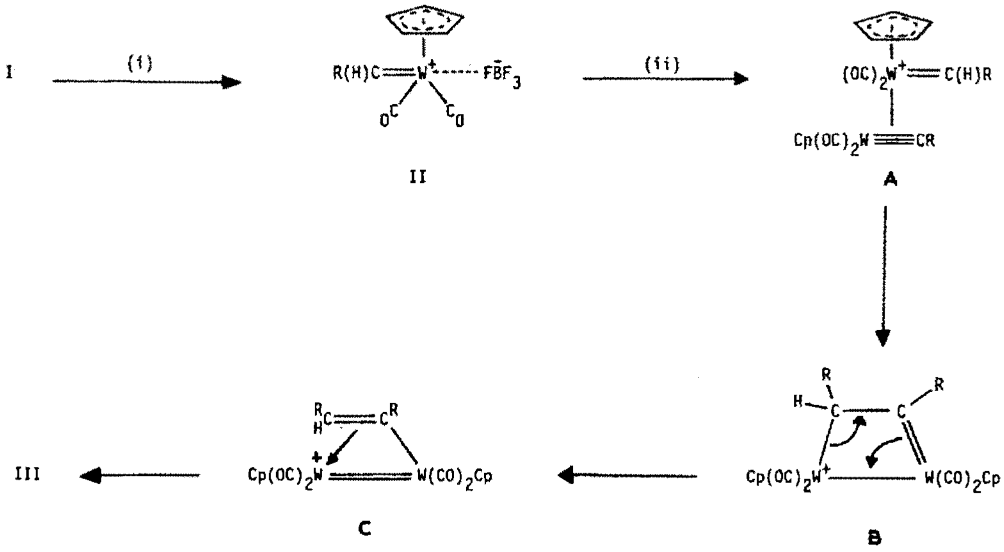
Protonation of I at −50°C with 0.5 equivalents of $HBF_4 \cdot Et_2O$ affords a yellow tinged-with-red solution which was allowed to warm to room temperature. Removal of solvent in vacuo, and crystallisation from dichloromethane/light petroleum (b.p. 40—60°C) gave yellow crystals of the hydrido- and alkyne-bridged ditungsten complexes III [2]. In view of the stoichiometry of the reaction it seems probable that the compounds III form via attack of $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ on the reactive and not isolated intermediates II (Scheme 2). The complexes II may be stabilised to some degree by ion-pairing between the cations and BF_4^- [3]. Intermediate A of Scheme 2 is similar to those invoked in alkyne or alkene dismutation, and is reasonable in the context of the isolobal relationship between I and RC_2R [4]. Moreover, C is modelled on the known dimolybdenum complex $[Mo_2(\mu\text{-}\eta^1,\eta^2\text{-}CH{:}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$ [5]. Perhaps in the ditungsten system, migration of hydrogen to the metal—metal bond is favoured. The salt IIIa is deprotonated on treatment with $K[BH(CHMeEt)_3]$ or PMe_3, giving the bridged alkyne complexes IV [6]. This reaction is reversed with $HBF_4 \cdot Et_2O$.

Protonation of V with $HBF_4 \cdot Et_2O$ gives the cationic hydroxy-alkyne compounds VI [7], thus providing an interesting contrast with the protonation of I. We have also prepared complexes $[W(CO)(PMe_3)(\eta\text{-}RC_2OMe)(\eta\text{-}C_5H_5)][SO_3CF_3]$ ($R = C_6H_4Me\text{-}4$ or Me) [8] by methylating V with CF_3SO_3Me. The compound $[W(CO)(PMe_3)(\eta\text{-}MeC_6H_4C_2OMe)(\eta\text{-}C_5H_5)][BF_4]$ has recently been reported by Kreissl and coworkers [9]. The $^{13}C\text{-}\{^1H\}$ chemical shifts of the ligated alkyne—carbon nuclei in VI, and in the compounds $[W(CO)(PMe_3)(\eta\text{-}RC_2OR')(\eta\text{-}C_5H_5)]^+$ ($R = C_6H_4Me\text{-}4$, $R' = Me$ or Et [9]; R = Me, R′ = Me [8]) are in the region expected for species in which the alkyne is donating 4 electrons to the metal centre [10].

In order to establish the molecular structures of VIa an X-ray diffraction study was carried out (see Fig. 1) [11]. The cation crystallises with a molecule of acetone which is hydrogen-bonded to the hydroxyl group of the η^2-coordinated alkyne (C(4)—C(5)).



SCHEME 1. Cp = $\eta\text{-}C_5H_5$. (i) $HBF_4 \cdot Et_2O$; (ii) $K[BH(CHMeEt)_3]$; (iii) PMe_3; (iv) Et_4NI; (v) HI.



SCHEME 2. (i) $HBF_4 \cdot Et_2O$; (ii) +[$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$].

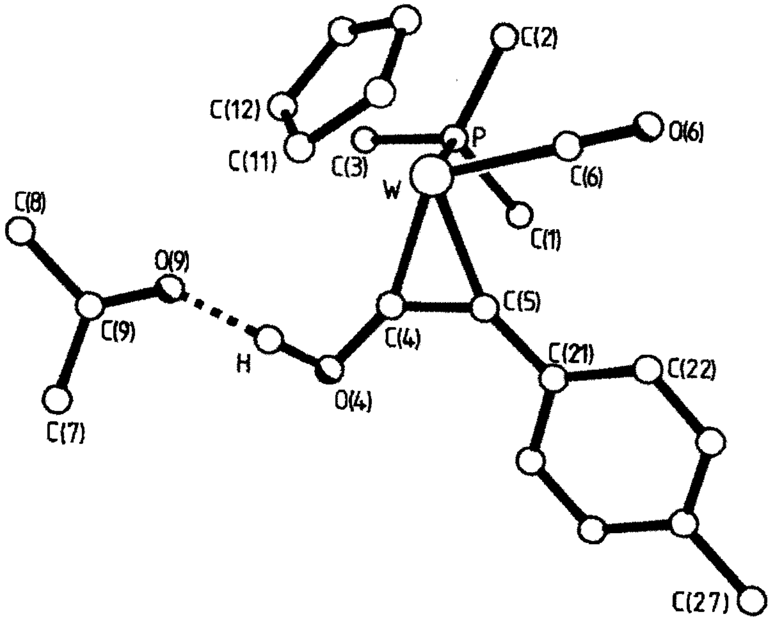


Fig. 1. Molecular structure of the cation [$W(CO)(PMe_3)(\eta\text{-}HO \cdot C_2 \cdot C_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)$]·($OCMe_2$) of VIa showing the hydrogen bonded acetone molecule. W—P 2.449(2), W—C(4) 2.000(7), W—C(5) 2.059(6), W—C(6) 1.992(7), C(4)—C(5) 1.365(7), C(4)—O(4) 1.325(9), C(5)—C(21) 1.440(7), O(4)—H 1.00, O(9)—H 1.63 Å (hydroxyl hydrogen not refined); W—C(6)—O(6) 177.9(6), O(4)—C(4)—C(5) 133.0(5), C(4)—C(5)—C(21) 135.1(7), C(4)—W—C(5) 39.3(2)°.

The instability of II, which is not surprising in view of the probable electron deficiency at the tungsten centre, contrasts with the stability of the salts [$W(=CHR)(CO)_2(PR'_3)(\eta\text{-}C_5H_5)$][$PF_6$] [1] wherein tungsten has an 18 electron closed shell. Treatment of Ia in CH_2Cl_2 at −60°C with 1 equivalent of $HBF_4 \cdot Et_2O$ followed (5 min) by addition of Et_4NI affords a mixture which after chromatography on alumina (CH_2Cl_2-light petroleum) gives the neutral iodo(carbene)tungsten complex VIIa [12]. This complex, and its less stable methyl analogue VIIb, can be prepared by adding HI (aqueous ca. 50%) to I in CH_2Cl_2 and chromatographing the products on alumina. Treatment of VIIa in CH_2Cl_2 with $K[BH(CHMeEt)_3]$ affords the known 1,2,7-trihaptobenzyl compound VIII [13] in a novel reaction which perhaps involves an intermediate hydrido tungsten species which transfers hydride to the carbene carbon in the reverse of an α-hydrogen elimination step.

Acknowledgement

We thank the S.E.R.C. for research studentships (J.C.V.L. and I.M).

References and notes

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2 For compound IIIa, ν_{max}(CO) at 2024s, and 1976s cm^{-1} (CH_2Cl_2). NMR: ^1H (CD_2Cl_2), δ 7.2 (s, 8 H, C_6H_4), 5.5 (s, 10 H, C_5H_5), 2.4 (s, 6 H, Me-4), and −17.0 ppm (s, 1 H, μ-H, *J*(WH) 33 Hz); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2 - CH_2Cl_2), δ 209.1 (CO, *J*(WC) 153 Hz), 203.3 (CO, *J*(WC) 154 Hz), 139.3—129.1 (C_6H_4), 91.8 (C_5H_5), 60.7 (C_2R_2), and 21.3 ppm (Me-4). For compound IIIb, ν_{max}(CO) at 2060(sh), 2023s, and 1973s cm^{-1} (CH_2Cl_2). NMR: ^1H ($(CD_3)_2CO$), δ 5.9 (s, 10 H, C_5H_5), 3.0 (s, 6 H, Me), and −18.5 ppm (s, 1 H, μ-H, *J*(WH) 32 Hz); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2-CH_2Cl_2), δ 209.8 (CO, *J*(WC) 150 Hz), 202.5 (CO, *J*(WC) 159 Hz), 90.1 (C_5H_5), 64.9 (C_2Me_2), and 22.9 ppm (Me).

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7 For compound VIa, ν_{max}(CO) at 1975s(br) cm^{-1}. NMR: $^{31}P\text{-}\{^1H\}$ (in $(CD_3)_2CO$ and rel. to 85% H_3PO_4 (external)), δ −17.2 ppm (*J*(WP) 398 Hz); $^{13}C\text{-}\{^1H\}$ ($(CD_3)_2CO$ - Me_2CO), δ 226.7 (d, RC≡*C*OH, *J*(PC) 7, *J*(WC) 80 Hz), 224.6 (d, CO, *J*(PC) 5, *J*(WC) 130 Hz), 191.7 (R*C*≡COH, *J*(WC) 75 Hz), 142.1—130.8 (C_6H_4), 95.3 (C_5H_5), 21.7 (Me-4), and 21.6 ppm (d, MeP, *J*(PC) 39 Hz); ^1H (−50°C, in $((CD_3)_2CO)$, δ 13.9 (s,br, 1 H, OH). For compound VIb, ν_{max}(CO) at 1970s cm^{-1} (CH_2Cl_2). NMR $(CD_3)_2CO$: $^{31}P\text{-}\{^1H\}$, δ −14.4 ppm (*J*(WP) 400 Hz); $^{13}C\text{-}\{^1H\}$, 222.5 (MeC≡*C*OH), 222.1 (d, CO, *J*(PC) 10 Hz), 197.4 (Me*C*≡COH, *J*(WC) 50 Hz), 94.8 (C_5H_5), 21.2 (d, MeP, *J*(PC) 36 Hz), and 19.9 ppm (Me).

8 For the compound $[W(CO)(PMe_3)(\eta\text{-}MeC_2OMe)(\eta\text{-}C_5H_5)][SO_3CF_3]$, ν_{max}(CO) at 1975s cm^{-1} (CH_2Cl_2). NMR ($(CD_3)_2CO$): $^{31}P\text{-}\{^1H\}$, δ −16.6 ppm (*J*(WP) 400 Hz); $^{13}C\text{-}\{^1H\}$ (−20°C), δ 227.1 (MeC≡*C*OMe, *J*(WC) 70 Hz), 222.9 (d, CO, *J*(PC),4, *J*(WC) 143 Hz), 197.6 (d, Me*C*≡COMe, *J*(PC),7, *J*(WC) 55 Hz), 121.5 (q, CF_3SO_3, *J*(FC) 322 Hz), 94.2 (C_5H_5), 66.3 (OMe), 21.1 (d, MeP, *J*(PC) 37 Hz), and 19.9 19.9 ppm (Me).

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11 For VIa, *crystal data*. $C_{18}H_{22}BF_4O_2PW \cdot (OCMe_2)$, $M = 630.1$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.018(5)$, $b = 13.676(7)$, $c = 12.728(7)$ Å, $\alpha = 69.04(4)$, $\beta = 71.52(5)$, $\gamma = 89.53(5)^\circ$, $U = 1\ 227(1)$ Å^3, $Z = 2$, $D_c = 1.71$ g cm^{-3}, $F(000) = 616$, $\mu(\text{Mo-}K_\alpha) = 49.2$ cm^{-1}. Current $R = 0.033$ ($R' = 0.034$) for 3 887 absorption-corrected intensities (293 K, ω scans, $2\theta \leqslant 50^\circ$, $I \geqslant 2.5\sigma(I)$, Nicolet *P3m* diffractometer. Mo-K_α (λ = 0.710 69 Å)).

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by the full literature citation for this communication.

12 For compound VIIa, ν_{max}(CO) at 2004w and 1934s cm^{-1} (CH_2Cl_2). NMR: ^1H ($CDCl_3$), δ 13.08 (s, 1 H, C*H*R, *J*(WH) 10 Hz), 7.23 and 7.62 ($(AB)_2$, 4 H, C_6H_4, *J*(AB) 8 Hz), 6.01 (s, 5 H, C_5H_5), and 2.23 (s, 3 H, Me-4); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2 - CH_2Cl_2), δ 267.4 (*C*HR, *J*(WC) 75 Hz), 206.5 (CO, *J*(WC) 161 Hz), 146.9—129.2 (C_6H_4), 96.6 (C_5H_5) and 21.1 ppm (Me-4). For compound VIIb, ν_{max}(CO) at 2018 m and 1954s cm^{-1} (hexane). NMR: ^1H ($CDCl_3$), δ 13.42 (q, 1 H, C*H*Me, *J*(HH) 8 Hz), 5.95 (s, 5 H, C_5H_5), and 2.66 (d, 3 H, Me, *J*(HH) 8 Hz); $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), δ 287.2 (*C*HMe), 206.4 (CO), 97.9 (C_5H_5), and 36.6 ppm (Me).

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