ANIONIC TOLYLMETHYLIDYNE(CARBABORANE)TUNGSTEN COMPLEXES: PROTONATION AND REACTION WITH TRIMETHYLPHOSPHINE

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Summary

Protonation of the closely related salts $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}1,2\text{-}C_2B_9H_9R_2)]$ (Ia, R = H; Ib, R = Me) affords structurally different products: $[N(PPh_3)_2][W_2(\mu\text{-}H)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}1,2\text{-}C_2B_9H_{11})_2]$ (III) and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}1,2\text{-}C_2B_9H_{10}Me_2)]$ (V), respectively. Treatment of Ib, with PMe_3 gives the ketenyl complex $[N(PPh_3)_2][W(CO)(PMe_3)\{\eta^2\text{-}C(C_6H_4Me\text{-}4)C(O)\}(\eta\text{-}1,2\text{-}C_2B_9H_9Me_2)]$ (VI). Protonation and methylation of the latter yields the alkyne–tungsten compounds $[W(CO)(PMe_3)\{\eta\text{-}C_2(OR')(C_6H_4Me\text{-}4)\}(\eta\text{-}1,2\text{-}C_2B_9H_9Me_2)]$ (IXa, R' = H; IXb, R' = Me).
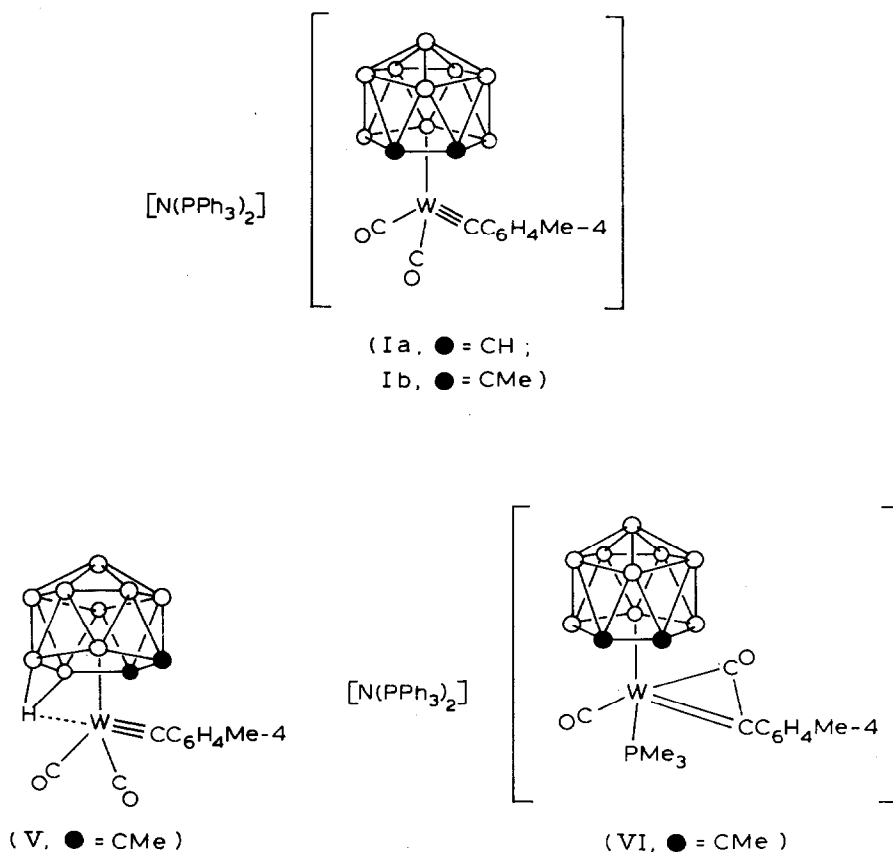
Introduction

Considerations based on the isolobal model [1,2] recently led us to prepare the salts $[N(PPh_3)_2][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}1,2\text{-}C_2B_9H_9R_2)]$ (Ia, R = H; Ib, R = Me) [3]. These species are related to the neutral complex $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (II) [4] by substitution of the ligand $C_5H_5^-$ in the latter by $C_2B_9H_9R_2^{2-}$ groups in the former. Anionic metal complexes containing alkylidyne ligands are relatively rare [5], and yet are likely to be useful reagents for preparative work. Indeed, the salts I have been employed in the synthesis of dimetal compounds containing bonds between tungsten and other metals, e.g. Mo [6], Ru [7], Rh and Au [3]. The non-innocent behaviour of the carbaborane ligand in several of the syntheses has added a novel dimension to the work.
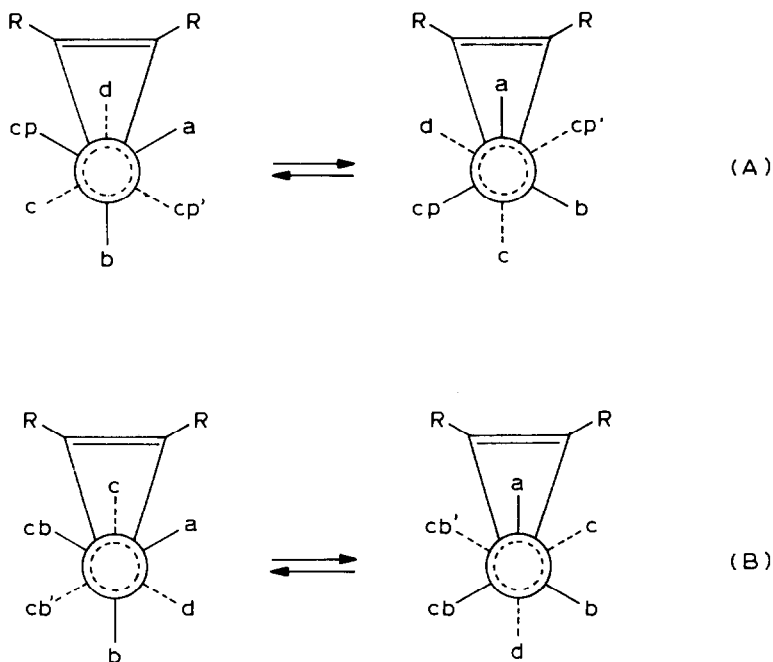
In this paper we report studies on the protonation of the complexes I, as well as the reaction between Ib and PMe_3. Previously similar investigations have been carried out with II, thus allowing comparisons to be made between the behaviour towards common reagents of these neutral and anionic carbyne–tungsten species.

Results and discussion

Treatment of Ia with $HBF_4 \cdot Et_2O$ in CH_2Cl_2 at room temperature afforded the ditungsten complex $[N(PPh_3)_2][W_2(\mu\text{-}H)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}1,2\text{-}C_2B_9H_{11})_2]$ (III). Earlier we showed [8] that protonation of II yields the ditungsten compound $[W_2(\mu\text{-}H)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$ (IV). The relationship between the salts III and IV is apparent on the basis of the isolobal model [1]. Both compounds have tungsten–tungsten bonds bridged by the alkyne $C_2(C_6H_4Me\text{-}4)_2$ and the hydrido ligand, but the difference in formal charge between $C_2B_9H_{11}{}^{2-}$ and $C_5H_5{}^{-}$ necessitates that III be an anionic complex and that IV be a cationic complex. The synthesis of III by protonation of Ia probably proceeds via a similar pathway to that proposed for the formation of IV [8].

The IR spectrum of III shows three bands in the carbonyl stretching region at 2024, 2001 and 1937 cm^{-1}, and a broad band at 2548 cm^{-1} due to the B–H groups. The presence of the bridging hydrido ligand in III was firmly established by the appearance in the ^{1}H NMR spectrum of a resonance at δ -13.32 which showed

$[N(PPh_3)_2]$

$OC\text{—}W\equiv CC_6H_4Me\text{-}4$

(Ia, ● = CH ;
  Ib, ● = CMe)

$H\cdots\cdots W\equiv CC_6H_4Me\text{-}4$

(V, ● = CMe)

$[N(PPh_3)_2]$

$OC\text{—}W\text{=}CC_6H_4Me\text{-}4$

PMe_3

(VI, ● = CMe)

SCHEME 1. R = C_6H_4Me-4, cp = η-C_5H_5, cb = η-1,2-$C_2B_9H_{11}$, a–d are CO ligands, and the μ-H ligand *trans* to the μ-C_2R_2 group is omitted for clarity.

^{183}W satellite peaks [J(WH) 33 Hz]; this signal appearing as a quintet in the expected 0.04/1/6/1/0.04 ratio [9].

The ^{13}C-$\{^1$H$\}$ NMR spectrum of III was also informative, particularly when compared with that of IV [8,10]. The spectra of both compounds show two resonances for the carbonyl groups (III, δ 218.5 and 210.5; IV, 209.1 and 203.3 ppm). In contrast, however, the ligated carbon nuclei of the transversely bridging alkyne ligand gave rise to two signals in the spectrum of III (δ 69.5 and 61.7 ppm) but only one peak in the spectrum of IV (δ 60.7 ppm). We have previously suggested [8] that the data for IV may be understood in terms of the occurrence of a dynamic process in solution in which isomers with *trans* η-C_5H_5 groups interconvert (Scheme 1(A)) via a low energy pathway similar to that described in detail earlier for the closely related neutral complexes [M_2(μ-alkyne)(CO)$_4$(η-C_5H_5)$_2$] (M = Mo or W) [11–13]. Evidently a similar process might explain the ^{13}C-$\{^1$H$\}$ NMR data for III, but for this species the inequivalence of the carbon atoms of the ligated μ-C_2 group dictates a *cis* configuration for the carbaborane cage ligands (Scheme 1(B)). It will be appreciated that a number of alternative isomers could be envisaged to replace those depicted in Scheme 1. Those shown have been chosen to minimise steric interactions between the bulky pentahapto bound ligands and the μ-$C_2(C_6H_4Me$-4)$_2$ and μ-H groups, since it has been established that this feature tends to control the dynamic behaviour observed in the compound [$Mo_2\{\mu$-C_2-(SiMe$_3$)$_2\}$(CO)$_4$(η-C_5H_5)$_2$], containing the sterically demanding alkyne Me$_3$-SiC≡CSiMe$_3$ [11].

Protonation of Ib was next investigated, with interesting results, since the expected ditungsten compound similar to III was not formed. Reaction of Ib with

either $HBF_4 \cdot Et_2O$ or aqueous HI afforded a yellow oil which unfortunately resisted repeated attempts to crystallise. However, the spectroscopic properties of the product led to its formulation as the mononuclear tungsten tolylmethylidyne complex V shown. The IR spectrum showed the required two bands (2008 and 1912 cm^{-1}) in the carbonyl stretching region. These absorptions occur at higher frequency than those in the spectrum of Ib (1956 and 1874 cm^{-1}), as expected, since V is a neutral compound. The ^1H NMR spectrum of V showed a resonance at δ -2.68 characteristic for a $B(\mu\text{-}H)B$ bridge system. Thus in the spectrum of the compound [exo-nido-6,10-{Rh(PPh_3)(PCy_3)}-6,10-μ-(H)$_2$-7,8-μ-(1',2'-$CH_2C_6H_4CH_2$)-10,11-μ-(H)-7,8-$C_2B_9H_7$] the signal for the $B(\mu\text{-}H)B$ proton which is sited on the face of the carbaborane cage occurs at δ -2.8 [14]. Two peaks were observed for the carbaborane cage methyl groups in both the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of V (see Experimental), indicating a degree of asymmetry in the molecule. Likewise, the $^{13}C\text{-}\{^1H\}$ spectrum showed two different CO environments [δ 220.9 and 220.6 ppm]. A resonance at 230.9 ppm [$J(WC)$ 128 Hz] is assigned to the ligated carbon of the terminally bound tolylmethylidyne group. In agreement, in a fully coupled ^{13}C NMR spectrum this signal remained a singlet. There was thus no evidence for the presence of a $W=CH(C_6H_4Me\text{-}4)$ group. An unusual feature of this resonance is its appearance at such a relatively high field. In the $^{13}C\text{-}\{^1H\}$ NMR spectra of compounds Ib and II the resonances for the alkylidyne–carbon nuclei are at 298.3 and 300.1 ppm, respectively [3,4]. Generally alkylidyne groups terminally bound to tungsten show signals for their ligated carbon atoms in the range ca. 270–330 ppm [15]. There are only a few known mononuclear metal species having resonances for the alkylidyne carbon nuclei more shielded, e.g. [$W(\equiv CC\equiv CPh)Br(CO)_4$], δ 230.5 ppm [16].

The formulation proposed for V is supported by an independent synthesis involving treatment of [$W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4$] in tetrahydrofuran (thf) at $-20°C$ with the sodium salt of the mono-anion $7,8\text{-}C_2B_9H_{10}Me_2^-$. Compound V may have a structural feature in common with the iron compex [$FeH(\eta\text{-}2,3\text{-}C_2B_4H_6)(\eta\text{-}C_5H_5)$]. It has been suggested [17] that in the latter a proton may cap a B_2Fe face of the closo pentagonal bipyramidal $FeC_2B_4H_6$ fragment. It is possible that in V the proton responsible for the NMR signal at δ -2.68 caps the B_2W face rather than edge-bridging a B–B bond of the tungsten-ligating $1,2\text{-}C_2B_9H_9Me_2$ fragment. However, if this were so the resonance for the unique proton would be expected to be somewhat more shielded than δ -2.68 ppm, in accord with the presence of hydrido-metal character [18].

Compound V may be deprotonated with $K[BH(CHMeEt)_3]$, in the presence of $[N(PPh_3)_2]Cl$, reforming Ib. The complex [$FeH(\eta\text{-}2,3\text{-}C_2B_4H_6)(\eta\text{-}C_5H_5)$] can also be deprotonated and, as with V, the process is reversible [17].

Treatment of a CH_2Cl_2 solution of Ib at $-30°C$ with PMe_3 affords the purple crystalline salt VI. The IR spectrum showed a band for the terminal CO group at 1843 cm^{-1} and an absorption at 1676 cm^{-1} attributable to the ketenyl-carbonyl group. The $^{13}C\text{-}\{^1H\}$ NMR spectrum of VI showed resonances at δ 223.6 [d, $J(PC)$ 9 Hz], 198.1 and 190.5 ppm [d, $J(PC)$ 5 Hz] which may be assigned to the WCO, ketenyl CO and $CC_6H_4Me\text{-}4$ groups, respectively. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a characteristic signal for the PMe_3 ligand at δ -7.6 ppm with $^{183}W\text{-}^{31}P$ satellite peaks [$J(WP)$ 412 Hz].

Compound VI is an analogue of the complex [$W(CO)(PMe_3)\{\eta^2\text{-}C(C_6H_4Me\text{-}$
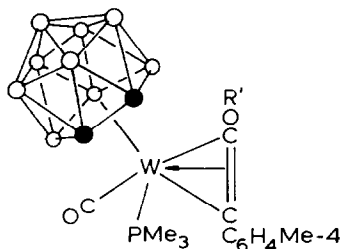
	●	R'
IXa	CMe	H
IXb	CMe	Me

4)C(O)}(η-C$_5$H$_5$)] (VII), prepared by treating II with PMe$_3$ [19]. Hence in reactions with the latter reagent, compounds Ib and II show a similar behavioural pattern but differ in affording anionic and neutral complexes, respectively. Protonation and methylation of VII occurs at the oxygen atom of the ketenyl ligand to yield the cationic tungsten–alkyne complexes [W(CO)(PMe$_3$){ η-C$_2$(C$_6$H$_4$Me-4)(OH)}(η-C$_5$H$_5$)][BF$_4$] (VIIIa) and [W(CO)(PMe$_3$){ η-C$_2$(C$_6$H$_4$Me-4)(OMe)}(η-C$_5$H$_5$)]-[SO$_3$CF$_3$] (VIIIb), respectively. In these species the alkynes function as four-electron donors [8]. It was therefore of interest to investigate the protonation and methylation of VI. Moreover if the products obtained were analogous to VIIIa and VIIIb they would be neutral complexes.

Treatment of VI with HBF$_4$ · Et$_2$O gave the purple compound IXa. Similarly, reaction of VI with CF$_3$SO$_3$Me yielded the related purple species IXb. These products each showed one carbonyl stretching band in their IR spectra (IXa, 1922; IXb, 1933 cm^{-1}); the absorptions being at higher frequency than the corresponding band (1843 cm^{-1}) in the spectrum of VI. The ^{1}H NMR spectrum of IXa showed a broad resonance at δ 9.50 which may be ascribed to the hydroxyl group, and the spectrum of IXb had a peak at δ 4.46 assigned to an OMe moiety. Both spectra showed two signals for the methyl substituents of the carbaborane cage, reflecting the asymmetry of the molecules. The ^{31}P-{^{1}H} NMR spectra displayed resonances at δ −10.9 [J(WP) 397 Hz] (IXa) and −11.0 ppm [J(WP) 395 Hz] (IXb).

The ^{13}C-{^{1}H} NMR spectra of the complexes IX are also informative, since the chemical shifts observed for the ligated carbon atoms of the alkyne groups are in accord with the latter functioning as four-electron donors. For IXa the resonances occur at δ 222.9 ($\equiv$COH) and 194.1 ($\equiv$CC$_6$H$_4$Me-4) ppm, and for IXb the signals are at 225.2 ($\equiv$COMe) and 186.7 ppm ($\equiv$CC$_6$H$_4$Me-4). All the resonances appear as doublets due to ^{31}P–^{13}C coupling. These chemical shifts are ca. 100 ppm more deshielded that those observed in complexes in which alkyne ligands act as two-electron donors. This effect has been discussed in detail by Templeton et al. [20].

The compounds IX appear to be the first examples of mononuclear metal complexes containing both carbaborane and alkyne groups, however, dimetal com-

pounds [MoW{μ-σ,η^3-CH(C_6H_4Me-4)($C_2B_9H_8Me_2$)}(CO)$_3$(η-RC$_2$R)(η-C_9H_7)] (R = Me or Et) containing this combination of ligands have been prepared [6]. Related to the synthesis of IXb is that of the compound [W(CN)(CO)(η-C_2(OMe)Me}(η-C_5H_5)], prepared by methylation of the salt [NBu$_4^n$][W(CN)(CO){η^2-C(Me)C(O)}-(η-C_5H_5)] [21], which like VI contains an anionic tungsten centre ligated by a ketenyl group.

Experimental

Solvents were rigorously dried before use, and all reactions were carried out in Schlenk tubes, under oxygen-free nitrogen. Light petroleum refers to the fraction of b.p. 40–60°C. Alumina used for chromatography columns (20 × 2 cm) was B.D.H. aluminium oxide (Brockman activity II). The infrared spectra were recorded in CH_2Cl_2 with a Nicolet 10-MX FT spectrophotometer, and the NMR measurements were made with JNM FX 90Q and FX 200 instruments. All coupling constants listed are in Hz. Phosphorus-31 chemical shifts (ppm) are positive to high frequency of 85% H_3PO_4 (external). The NMR spectra were measured in CD_2Cl_2 (^{1}H and ^{31}P-{^{1}H}) or CD_2Cl_2/CH_2Cl_2 (^{13}C-{^{1}H}). The reagents [W($\equiv$CC$_6H_4$Me-4)Br(CO)$_4$] [22] and Na$_2$[7,8-$C_2B_9H_9R_2'$] (R' = H or Me) [23] used to obtain Ia and Ib were prepared by methods previously described.

Protonation of the salts [N(PPh$_3$)$_2$][W($\equiv$CC$_6H_4$Me-4)(CO)$_2$(η-1,2-$C_2B_9H_9R_2$)] (R = H or Me)

(i) Treatment of Ia (0.26 g, 0.25 mmol) in CH_2Cl_2 (10 cm^3) with HBF$_4$ · Et$_2$O (0.05 cm^3) afforded a yellow solution. Solvent was removed in vacuo, after which the residue was dissolved in CH_2Cl_2/Et$_2$O (20 cm^3, 1/1) and chromatographed. Elution with the same solvent mixture gave a yellow solution. Removal of solvent in vacuo, and crystallisation of the residue from CH_2Cl_2/light petroleum (5 cm^3, 1/1) at −20°C gave yellow microcrystals of [N(PPh$_3$)$_2$][W$_2$(μ-H){μ-C_2(C_6H_4Me-4)$_2$} (CO)$_4$(η-1,2-$C_2B_9H_{11}$)$_2$] (III) (0.09 g, 47%) (Found: C, 48.5; H, 5.4. $C_{60}H_{67}B_{18}NO_4$-P$_2$W$_2$ calcd.: C, 48.2; H, 4.5%); ν_{max} (BH) at 2548 cm^{-1}; ν_{max} (CO) at 2024m, 2001m and 1937s cm^{-1}. NMR: ^{1}H, δ −13.32 [s, 1H, μ-H, J(WH) 33], 2.33 (s, 6H, Me-4), and 6.95–7.67 (m, 38H, C_6H_4 and Ph); ^{13}C-{^{1}H}, δ 218.5, 210.5 (CO), 138.6–125.3 (C_6H_4 and Ph), 69.5, 61.7 (CC$_6H_4$Me-4), 46.7, 45.6 ($C_2B_9H_{11}$), and 20.8 ppm (Me-4).

(ii) A 57% aqueous solution of HI was added dropwise to a CH_2Cl_2 (10 cm^3) solution of Ib (0.52 g, 0.50 mmol) until an IR spectrum of the mixture showed that all of the salt had been consumed. Solvent was removed in vacuo, and the oily residue was extracted with thf/light petroleum (20 cm^3, 1/1). Removal of solvent in vacuo afforded [W($\equiv$CC$_6H_4$Me-4)(CO)$_2$(η-1,2-$C_2B_9H_{10}Me_2$)] (V) as a dark yellow oil, ν_{max} (BH) at 2549 cm^{-1}; ν_{max} (CO) at 2008s and 1912s cm^{-1}. NMR: ^{1}H, δ −2.68 [br, 1H, B(μ-H)B], 1.58 (s, 3H, Me), 1.92 (s, 3H, Me), 2.22 (s, 3H, Me-4), 6.72 and 6.88 [(AB)$_2$, 4H, C_6H_4, J(AB) 8]; ^{13}C-{^{1}H}, δ 230.9 [C$\equiv$W, J(WC) 128], 220.9 [WCO, J(WC) 137], 220.6 [WCO, J(WC) 130], 145.8 [C^1(C_6H_4)], 133.8–125.9 (C_6H_4), 32.5, 30.3 (Me), and 20.7 ppm (Me-4).

Reaction of [N(PPh$_3$)$_2$][W$\equiv$CC$_6H_4$Me-4)(CO)$_2$(η-1,2-$C_2B_9H_9Me_2$)] with PMe$_3$

Trimethylphosphine (2.5 cm^3 of a 0.50 mol dm^{-3} solution in light petroleum) was

added to Ib (1.04 g, 1.0 mmol) in CH_2Cl_2 (10 cm^3) at $-30°C$. The solution turned purple, and the reactants were stirred for 10 min. Solvent was removed in vacuo, and the residue washed with Et_2O (3 × 10 cm^3). In this manner, purple microcrystals of $[N(PPh_3)_2][W(CO)(PMe_3)\{\eta^2\text{-}C(C_6H_4Me\text{-}4)C(O)\}(\eta\text{-}1,2\text{-}C_2B_9H_9Me_2)]$ (VI) (0.97 g, 87%) were obtained (Found: C, 38.1; H, 5.7; N, 0.8. $C_{53}H_{61}B_9NO_2P_3W$ calcd.: C, 37.6; H, 5.5; N, 1.0%); ν_{max} (BH) at 2525cm^{-1}; ν_{max} (CO) at 1843s and 1676 m cm^{-1}. NMR (measured at $-40°C$): ^1H, δ 1.52 [d, 9H, MeP, J(PH) 10], 2.12 (s, 3H, Me-4), 2.31 (s, 6H, Me), and 7.26–7.81 (m, 34H, C_6H_4 and Ph); $^{13}C\text{-}\{^1H\}$, δ 223.6 [d, CO, J(PC) 9], 198.1 [$C(C_6H_4Me\text{-}4)C(O)$], 190.5 [d, $C(C_6H_4Me\text{-}4)C(O)$, J(PC) 5], 136.7–120.1 (C_6H_4 and Ph), 30.5, 29.2 (Me), 20.8 (Me-4), and 18.4 ppm [d, MeP, J(PC) 37]; $^{31}P\text{-}\{^1H\}$, δ -7.6 ppm [J(WP) 412].

Protonation and methylation of $[N(PPh_3)_2][W(CO)(PMe_3)(\eta^2\text{-}C(C_6H_4Me\text{-}4)C(O)\}$-$(\eta\text{-}1,2\text{-}C_2B_9H_9Me_2)]$

(i) Excess of $HBF_4 \cdot Et_2O$ (0.1 cm^3) was added to VI (0.52 g, 0.50 mmol) in CH_2Cl_2 (10 cm^3) at $-40°C$, and the mixture was warmed to room temperature. Solvent was removed in vacuo, the residue extracted with Et_2O (2 × 10 cm^3) and the extracts filtered through a Celite pad (ca. 3 cm). Solvent was removed in vacuo, and the solid remaining was crystallised from Et_2O/light petroleum (10 cm^3, 1/1) at $-78°C$ to give purple crystals of $[W(CO)(PMe_3)\{\eta\text{-}C_2(OH)(C_6H_4Me\text{-}4)\}(\eta\text{-}1,2\text{-}C_2B_9H_9Me_2)] \cdot Et_2O$ (IXa) (0.46 g) (Found: C, 36.9; H, 6.6. $C_{17}H_{32}B_9O_2PW.C_4H_{10}O$ calcd.: C, 36.8; H, 6.0%); ν_{max} (BH) at 2532m cm^{-1}; ν_{max} (CO) at 1922s cm^{-1}. NMR (measured at $-40°C$): ^1H, δ 1.46 [d, 9H, MeP, J(PH) 10], 1.82 (s, 3H, Me), 2.17 (s, 3H, Me-4), 2.33 (s, 3H, Me), 7.17 and 7.38 [(AB)$_2$, 4H, C_6H_4, J(AB) 8], and 9.50 [s(br), 1H, OH]; $^{13}C\text{-}\{^1H\}$, δ 230.5 [d, CO, J(PC) 9], 222.9 [d, COH, J(PC) 6], 194.1 [d, $CC_6H_4Me\text{-}4$, J(PC) 6], 140.9 [$C^1(C_6H_4)$], 132.3, 129.6, 127.5 (C_6H_4), 30.8, 29.9 (Me), 21.4 (Me-4), and 19.7 ppm [d, MeP, J(PC) 39]; $^{31}P\text{-}\{^1H\}$, δ -10.9 ppm [J(WP) 397].

(ii) Compound VI (0.52 g, 0.50 mmol) in CH_2Cl_2 (15 cm^3) at $-40°C$ was treated with CF_3SO_3Me (0.2 cm^3). The resulting purple solution was stirred for 10 min, and then allowed to warm to room temperature. Solvent was removed in vacuo, and the residue extracted with Et_2O (2 × 10 cm^3). The extracts were filtered through a Celite pad (ca. 5 cm). Removal of solvent, and crystallisation of the solid from Et_2O/light petroleum (10 cm^3, 1/1) at $-78°C$ gave purple crystals of $[W(CO)(PMe_3)\{\eta\text{-}C_2(OMe)(C_6H_4Me\text{-}4)\}(\eta\text{-}1,2\text{-}C_2B_9H_9Me_2)]$ (IXb) (0.21 g, 79%) (Found: C, 36.2; H, 5.7; $C_{18}H_{34}B_9O_2PW$ calcd.: C, 35.9; H, 6.1%); ν_{max} (BH) at 2530 cm^{-1}; ν_{max} (CO) at 1933s cm^{-1}. NMR (measured at $-40°C$): ^1H, δ 1.60 [d, 9H, MeP, J(PH) 10], 2.06 (s, 3H, Me), 2.14 (s, 3H, Me-4), 2.42 (s, 3H, Me), 4.46 (s, 3H, OMe) 7.72 and 7.47 [(AB)$_2$, 4H, C_6H_4, J(AB) 8]; $^{13}C\text{-}\{^1H\}$, δ 228.8 [d, CO, J(PC) 9 J(WC) 136], 225.2 [d, COMe, J(PC) 10], 186.7 [d, $CC_6H_4Me\text{-}4$, J(PC) 6], 139.8 [$C^1(C_6H_4)$], 134.8, 129.2, 128.9 (C_6H_4), 64.9 (OMe), 30.1, 29.8 (Me), 20.7 (Me-4), and 20.3 ppm [d, MeP, J(PC) 31].

Acknowledgement

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