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# X-ray structure and electrophilic reactivity of a cationic, chiral tungsten(II) methylene complex

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**Abstract**

The structure of a tungsten(II) methylene complex, $[Tp'(CO)(PhCCMe)W{=}CH_2][BAr'_4]$ (**2a**), was obtained by taking advantage of the stabilizing, weakly coordinating counterion, $BAr'_4{}^-$, to form X-ray quality single crystals. The electrophilic reactivity of $[Tp'(CO)(PhCCMe)W{=}CH_2][PF_6]$ (**2b**) was surveyed with both neutral nucleophiles (triphenylphosphine and pyridine) and anionic nucleophiles (formed by deprotonation of phthalimide, diethyl malonate, *t*-butyl acetoacetate, and acetophenone) to give derivatives of the form $[Tp'(CO)(PhCCMe)W{-}CH_2{-}Nu]^{+,0}$. Crystal structures obtained for the phthalimide (**5**) and diethyl malonate (**6**) adducts are compatible with attack of the nucleophile from along the metal CO axis. The stereochemistry of the *t*-butyl acetoacetate adduct was determined by 2-D NOESY-NMR. Reaction of methylene carbene **2b** with cyclohexene sulfide results in sulfur atom transfer to form a rare π-bound thioformaldehyde complex (**9**). 

*Keywords:* Hydridotris(3,5-dimethylpyrazolyl)borate; Tungsten; Methylene; Electrophilic; Carbene; Thioformaldehyde

## 1. Introduction

Discovery of the heteroatom stabilized, electrophilic carbene complex, $(CO)_5W{=}C(OCH_3)Ph$, in 1964 [1] has been followed by utilization of carbene complexes [2] as carbene transfer reagents [3–6], as catalysts in both olefin metathesis [7–12] and ROMP [13–16], and as proposed intermediates in the Fischer–Tropsch synthesis [17,18]. Pettit and Jolly suggested the presence of an electrophilic methylene carbene, $[CpFe(CO)_2{=}CH_2]^+$, in the reaction of $CpFe(CO)_2(CH_2OCH_3)$ with acid in the presence of cyclohexene to produce norcarane [19]. In 1975, Schrock reported the first isolable methylene complex, $Cp_2(CH_3)Ta{=}CH_2$ [20]. Unlike the electrophilic Fisher carbenes, this complex exhibited nucleophilic behavior. Although methylene complexes remain relatively rare [21–40], both nucleophilic [37–40] and electrophilic [28–36] methylene complexes have been reported.

The chiral carbene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)][PF_6]$ (R = H, alkyl, or phenyl) investigated by Gladysz et al. display extensive chemistry at the carbene carbon [28,41,42]. This cationic rhenium carbene complex serves as a paradigm for Fischer reactivity patterns. Nucleophiles attack the benzylidene carbene stereospecifically to give one set of diastereomers [43]. Diazo compounds add stereoselectively to form olefin complexes [44].

We have reported the chiral methylene complex, $[Tp'(CO)(PhCCMe)W{=}CH_2][PF_6]$ (**2b**) (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) [45]. The $[Tp'(CO)(PhCCMe)W{=}CH_2]^+$ cation was shown to transfer the methylene fragment to olefins, and it also catalyzed the formation of aziridines from *N*-arylimines and ethyl diazoacetate [46]. Reaction of carbene **2b** with excess base forms a $C_3H_5$ bridged dimer [47]. Here we report the X-ray crystal structure of the parent, cationic methylene carbene complex with the bulky $BAr'_4{}^-$ (tetrakis(bis (3,5-trifluoromethyl)phenyl)borate) counterion [48,49]. In addition, we have surveyed the reactivity of the electrophilic carbene, $[Tp'(CO)(PhCCMe)W{=}CH_2][PF_6]$ (**2b**), with neutral nucleophiles, anionic nucleophiles, and the sulfur atom transfer reagent, cyclohexene sulfide.

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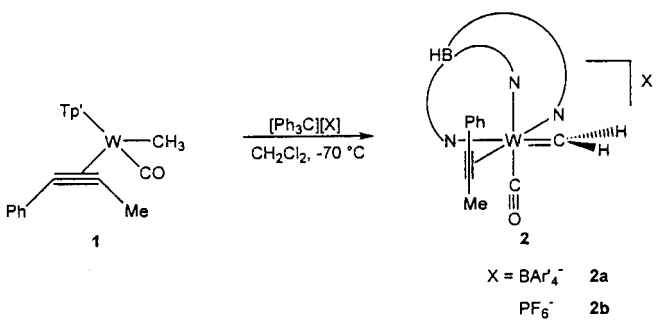
Table 1
Crystallographic data and collection parameters for [Tp′(CO)(PhCCMe)W=$CH_2$][$BAr'_4$] (**2a**), Tp′(CO)(PhCCMe)W$CH_2$-phthalimide (**5**), and Tp′(CO)(PhCCMe)W$CH_2CH(COOEt)_2$ (**6**)

| | **2a** | **5** | **6** |
|---|---|---|---|
| Formula | $C_{58}H_{44}N_6OB_2F_{24}W$ | $C_{34}H_{36}N_7O_3BW$ | $C_{33}H_{43}N_6O_5BW$ |
| Molecular weight (g $mol^{-1}$) | 1502.44 | 785.35 | 798.39 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Crystal dimensions (mm) | $0.30\times0.20\times0.20$ | $0.40\times0.20\times0.05$ | $0.35\times0.20\times0.10$ |
| Space group | $P\bar{1}$ | $P2_1/n$ | $P2_1/c$ |
| $a$ (Å) | 12.7471(6) | 14.4533(7) | 15.3286(7) |
| $b$ (Å) | 13.2602(6) | 14.7039(7) | 17.7713(8) |
| $c$ (Å) | 18.6748(9) | 15.2072(7) | 12.6318(6) |
| α (°) | 87.294(1) | | |
| β (°) | 80.273(1) | 95.5050(10) | 93.496(1) |
| γ (°) | 76.125(1) | | |
| $V$ ($Å^3$) | 3020.35(25) | 3216.9(3) | 3634.6(3) |
| $Z$ | 2 | 4 | 4 |
| $D_{calc}$ (g $cm^{-3}$) | 1.652 | 1.622 | 1.544 |
| $F$(000) | 1484.25 | 1566.64 | 1606.69 |
| Temperature (°C) | −100 | −100 | −100 |
| Radiation ($\lambda$, Å) | Mo–$K_\alpha$ (0.71073) | Mo–$K_\alpha$ (0.71073) | Mo–$K_\alpha$ (0.71073) |
| $2\theta$ range (°) | $3.00<\theta<55$ | $3.00<\theta<60.00$ | $3.00<\theta<60.00$ |
| $\mu$ ($mm^{-1}$) | 2.03 | 3.64 | 3.42 |
| $h$, $k$, $l$ ranges | −15, 16; 0, 17; −24, 24 | −19, 19; 0, 20; 0, 20 | −21, 21; 0, 23; 0, 16 |
| Scan mode | $\omega$ | $\omega$ | $\omega$ |
| Total no. of data | 37196 | 41519 | 43993 |
| Total no. of unique data | 13902 | 8677 | 9131 |
| No. of observed data ($I>3.0\sigma(I)$) | 9312 | 6044 | 6584 |
| $R_F$ | 0.059 | 0.041 | 0.051 |
| $R_w$ | 0.071 | 0.031 | 0.051 |
| Goodness-of-fit | 1.85 | 1.07 | 1.66 |
| Parameters | 829 | 415 | 416 |
| Max. shift (σ) | 0.020 | 0.000 | 0.002 |

## 2. Results and discussion

### 2.1. Carbene structure

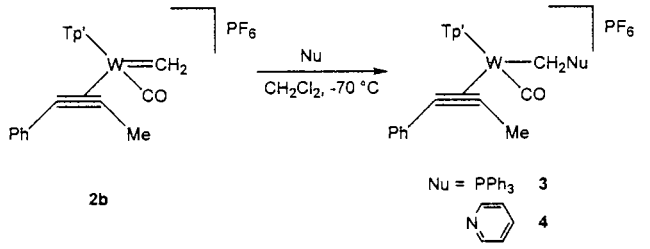
Replacement of the $PF_6^-$ counterion with $BAr'_4{}^-$ in the preparation of the methylene complex was accomplished by reaction of the carbene precursor tungsten methyl complex (**1**) with [$Ph_3C$][$BAr'_4$] [50] (Eq. (1)). The large $BAr'_4{}^-$ anion has been reported to stabilize electrophilic cations [51], and indeed, this anion afforded X-ray quality crystals of the complex cation from slow diffusion of hexanes into a $CH_2Cl_2$ solution of [Tp′(CO)(PhCCMe)W=$CH_2$][$BAr'_4$] (**2a**) (Table 1). A labeled ORTEP of **2a** is shown in Fig. 1, and selected bond distances and angles are shown in Table 2. The W–C(1) bond distance is 2.018(8) Å, which is in the middle of the range for a tungsten carbene bond [52–55]. The alkyne is oriented parallel to the CO as is seen in other complexes of this type [56]. Due to the complementary π bonding interactions of the alkyne and carbonyl ligand, the methylene protons will strongly prefer to be perpendicular to the W–CO axis [46].




(1)

### 2.2. Reactions with neutral nucleophiles

Carbene **2b** has been shown to add $PMe_3$ at the electrophilic carbene carbon [46]. To extend the range of neutral nucleophiles that form cationic adducts, the bulkier triphenylphosphine phosphorus donor and the nitrogen donor, pyridine, were allowed to react with carbene **2b** (Eq. (2)). Triphenylphosphine reacts with carbene **2b** ($\nu_{CO}=2066$ $cm^{-1}$, KBr) to give [Tp′(CO)(PhCCMe)W–$CH_2PPh_3$][$PF_6$] (**3**) which has a




(2)

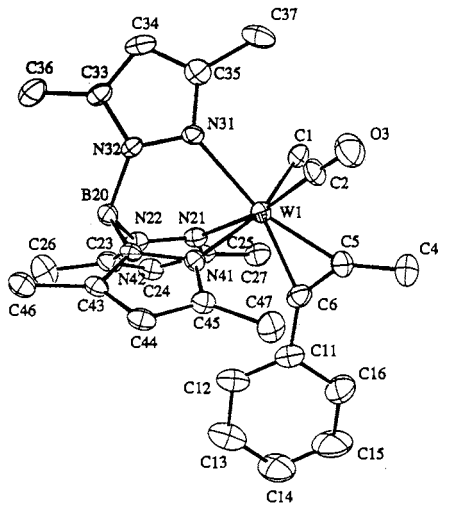



Fig. 1. ORTEP diagram of $[Tp'(CO)(PhCCMe)W{=}CH_2][BAr'_4]$ (**2a**).

Table 2
Selected bond distances (Å) and angles (°) for $[Tp'(CO)(PhCCMe)W{=}CH_2][BAr'_4]$ (**2a**)

| | | | |
|---|---|---|---|
| *Bond distances* | | | |
| W(1)–C(1) | 2.018(8) | W(1)–N(41) | 2.232(6) |
| W(1)–C(2) | 2.048(8) | C(2)–O(3) | 1.131(11) |
| W(1)–C(5) | 2.089(9) | C(4)–C(5) | 1.461(13) |
| W(1)–C(6) | 2.040(8) | C(5)–C(6) | 1.302(13) |
| W(1)–N(21) | 2.182(6) | C(6)–C(11) | 1.455(13) |
| W(1)–N(31) | 2.247(6) | | |
| *Bond angles* | | | |
| C(1)–W(1)–C(2) | 89.6(3) | C(5)–W(1)–N(41) | 101.8(3) |
| C(1)–W(1)–C(5) | 93.2(3) | C(6)–W(1)–N(21) | 85.8(3) |
| C(1)–W(1)–C(6) | 105.4(3) | C(6)–W(1)–N(31) | 163.8(3) |
| C(1)–W(1)–N(21) | 89.8(3) | C(6)–W(1)–N(41) | 88.5(3) |
| C(1)–W(1)–N(31) | 86.6(3) | N(21)–W(1)–N(31) | 83.33(23) |
| C(1)–W(1)–N(41) | 164.7(3) | N(21)–W(1)–N(41) | 84.75(21) |
| C(2)–W(1)–C(5) | 70.5(4) | N(31)–W(1)–N(41) | 78.59(21) |
| C(2)–W(1)–C(6) | 105.2(4) | W(1)–C(2)–O(3) | 176.1(8) |
| C(2)–W(1)–N(21) | 168.7(3) | W(1)–C(5)–C(4) | 149.7(7) |
| C(2)–W(1)–N(31) | 85.4(3) | W(1)–C(5)–C(6) | 69.6(5) |
| C(2)–W(1)–N(41) | 92.9(3) | C(4)–C(5)–C(6) | 140.6(9) |
| C(5)–W(1)–C(6) | 36.7(4) | W(1)–C(6)–C(5) | 73.7(6) |
| C(5)–W(1)–N(21) | 120.8(3) | W(1)–C(6)–C(11) | 146.3(7) |
| C(5)–W(1)–N(31) | 155.9(3) | C(5)–C(6)–C(11) | 139.8(9) |

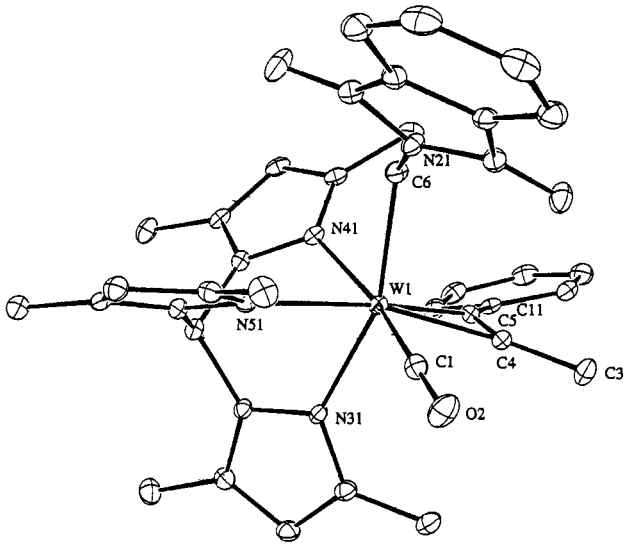
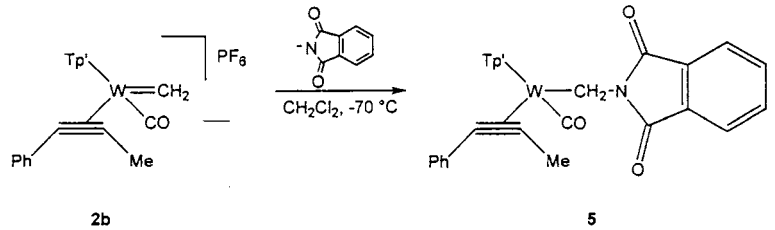



Fig. 2. ORTEP diagram of $Tp'(CO)(PhCCMe)W{-}CH_2$-phthalimide (**5**).

carbonyl stretch of 1895 $cm^{-1}$ in the IR spectrum, slightly higher than in $[Tp'(CO)(PhCCMe)W{-}CH_2PMe_3][PF_6]$ ($\nu_{CO} = 1888$ $cm^{-1}$, KBr). The $^1$H-NMR spectrum of the triphenylphosphine adduct **3** shows the diastereotopic methylene hydrogens as a coincidental triplet at 2.55 ppm ($^2J_{HH} = {}^2J_{PH} = 14$, $^2J_{WH} = 10$ Hz, $^{183}$W, 14% abundance) and a doublet of doublets at 1.38 ppm ($^2J_{HH} = 14$, $^2J_{PH} = 22$ Hz). Reaction of carbene **2b** with excess pyridine forms $[Tp'(CO)(PhCCMe)W{-}CH_2{-}NC_5H_5][PF_6]$ (**4**). The carbonyl stretching frequency of the pyridine adduct is at 1881 $cm^{-1}$, slightly lower than in the phosphine adducts, and the diastereotopic hydrogens resonate as doublets at 4.47 ($^2J_{HH} = 14$, $^2J_{WH} = 11$ Hz) and 4.06 ppm ($^2J_{HH} = 14$, $^2J_{WH} = 7$ Hz) in the $^1$H-NMR spectrum. The directions of the terminal metal carbonyl shifts are in accord with expectations, but the $CH_2$ spacer between the metal and the Lewis base buffers the influence of the donor group dramatically compared to the effect of direct metal ligation by either phosphorus or nitrogen donors on metal carbonyl frequencies.

### 2.3. Reactions with anionic nucleophiles

Carbene **2b** reacts with anionic nucleophiles to form neutral adducts by addition of the nucleophile to the carbene carbon. Deprotonation of phthalimide with *n*-butyl lithium in THF provides an anionic nitrogen donor, and subsequent reaction with carbene **2b** leads to the formation of $Tp'(CO)(PhCCMe)W{-}CH_2$–phthalimide (**5**) (Eq. (3)). The terminal metal carbonyl stretch in the IR spectrum is at 1883 $cm^{-1}$, nearly identical to the frequency of the cationic pyridine adduct. The phthalimide C=O infrared absorption is at 1692 $cm^{-1}$. Crystals of **5** suitable for X-ray analysis

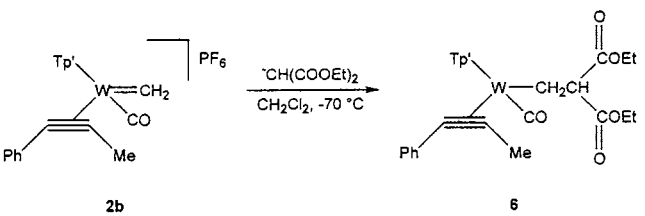



(3)

were obtained by slowly cooling a saturated solution of the phthalimide adduct (**5**) in acetone. The crystal structure of Tp′(CO)(PhCCMe)W–$CH_2$-phthalimide (**5**) is shown in Fig. 2, and selected bond distances and angles are listed in Table 3. The W–C(6) bond length of 2.223(4) Å, is significantly longer than the tungsten carbon double bond distance of 2.018(8) Å in carbene reagent **2b** and is typical of W–C single bonds [57–59]. The C(6)–N(21) bond length is 1.467(5) Å and the W–C(6)–N(21) angle is 124.7(3)°. This large bond angle indicates a distorted tetrahedral geometry at C(6) to accommodate the large W and N substituents along with the two hydrogens. The location of the added nucleophile in the solid state positions the large phthalimide substituent on the metal bound carbon near the CO rather than near the sterically bulky Tp′. This geometry is compatible with the incoming nucleophile attacking the carbene carbon from along the CO axis, since attack from the opposite carbene face would be hindered by the projecting 3-methyl substituents on Tp′. Although the solid state structure need not reflect the site of nucleophilic attack, the preference for locating the bulky substituents away from the pendant Tp′ methyl groups is clear.

Table 3
Selected bond distances (Å) and angles (°) for Tp′(CO)(PhCCMe)W$CH_2$-phthalimide (**5**)

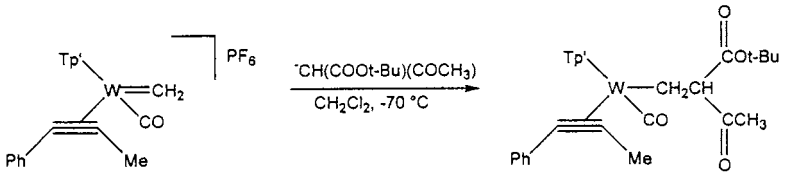
| | | | |
|---|---|---|---|
| *Bond distances* | | | |
| W(1)–C(1) | 1.945(4) | W(1)–N(51) | 2.278(3) |
| W(1)–C(4) | 2.055(4) | C(1)–O(2) | 1.174(5) |
| W(1)–C(5) | 2.031(4) | C(3)–C(4) | 1.493(6) |
| W(1)–C(6) | 2.223(4) | C(4)–C(5) | 1.310(6) |
| W(1)–N(31) | 2.221(3) | C(5)–C(11) | 1.462(6) |
| W(1)–N(41) | 2.272(3) | C(6)–N(21) | 1.467(5) |
| *Bond angles* | | | |
| C(1)–W(1)–C(4) | 70.16(17) | C(6)–W(1)–N(31) | 160.09(13) |
| C(1)–W(1)–C(5) | 106.87(16) | C(6)–W(1)–N(41) | 81.63(13) |
| C(1)–W(1)–C(6) | 95.97(15) | C(6)–W(1)–N(51) | 86.37(13) |
| C(1)–W(1)–N(31) | 95.42(14) | N(31)–W(1)–N(41) | 83.82(12) |
| C(1)–W(1)–N(41) | 167.88(14) | N(31)–W(1)–N(51) | 78.35(11) |
| C(1)–W(1)–N(51) | 85.25(14) | N(41)–W(1)–N(51) | 82.75(11) |
| C(4)–W(1)–C(5) | 37.39(16) | W(1)–C(1)–O(2) | 176.3(3) |
| C(4)–W(1)–C(6) | 99.32(15) | W(1)–C(4)–C(3) | 149.7(3) |
| C(4)–W(1)–N(31) | 99.89(13) | W(1)–C(4)–C(5) | 70.32(23) |
| C(4)–W(1)–N(41) | 121.92(14) | C(3)–C(4)–C(5) | 139.9(4) |
| C(4)–W(1)–N(51) | 155.15(14) | W(1)–C(5)–C(4) | 72.29(24) |
| C(5)–W(1)–C(6) | 102.52(15) | W(1)–C(5)–C(11) | 146.5(3) |
| C(5)–W(1)–N(31) | 89.70(13) | C(4)–C(5)–C(11) | 141.1(4) |
| C(5)–W(1)–N(41) | 85.24(14) | W(1)–C(6)–N(21) | 124.7(3) |
| C(5)–W(1)–N(51) | 163.87(14) | | |




(4)

Reaction of carbene **2b** with deprotonated diethyl malonate yields a carbon–carbon bond in adduct **6** (Eq. 4), and the metal carbonyl infrared stretch drops to 1866 $cm^{-1}$, well below other adducts. The malonate ester C=O infrared absorption is observed at 1725 $cm^{-1}$. Crystals for X-ray analysis were obtained from slow diffusion of hexanes into a methylene chloride solution of the malonate adduct (**6**). The ORTEP diagram is shown in Fig. 3 and selected bond distances and angles are listed in Table 4. The W–C(21) bond length is 2.197(7) Å and the W–C(21)–C(22) bond angle is 121.9(4)°, similar to the parameters observed for the phthalimide product. The $^1$H-NMR spectrum of malonate adduct **6** shows the diastereotopic methylene hydrogens of the W–$CH_2$–C linkage as doublets of doublets at 0.95 and 1.84 ppm. Likewise, the ethyl groups of the malonate moiety are inequivalent with the two distinct $CH_3$ groups appearing as triplets at 1.14 and 1.25 ppm. One of the $CH_2$ groups is a coincidental quartet, but the other diastereotopic ethyl $CH_2$ group is a multiplet. A selective decoupling experiment was performed by saturating the methyl signal at 1.25 ppm. This revealed an AB spin system for the adjacent methylene with resonances at 4.150 and 4.146 ppm. The geminal coupling between these protons is 17 Hz, while coupling to the adjacent methyl group is 7 Hz in this $ABX_3$ spin system.

Deprotonation of *t*-butyl acetoacetate with *n*-butyl lithium and subsequent reaction of the stabilized carbanion with carbene **2b** yields adduct **7** (Eq. (5)). The metal carbonyl stretch appears at 1877 $cm^{-1}$ in the IR spectrum, slightly higher than the metal carbonyl frequency in the malonate adduct. The ketone and ester C=O infrared stretches of the *t*-butyl acetoacetate appear at 1715 and 1696 $cm^{-1}$. The diastereotopic methylene protons in the $^1$H-NMR spectrum of **7** are doublets of doublets at 1.68 and 1.07 ppm ($^2J_{HH} = 14$




(5)

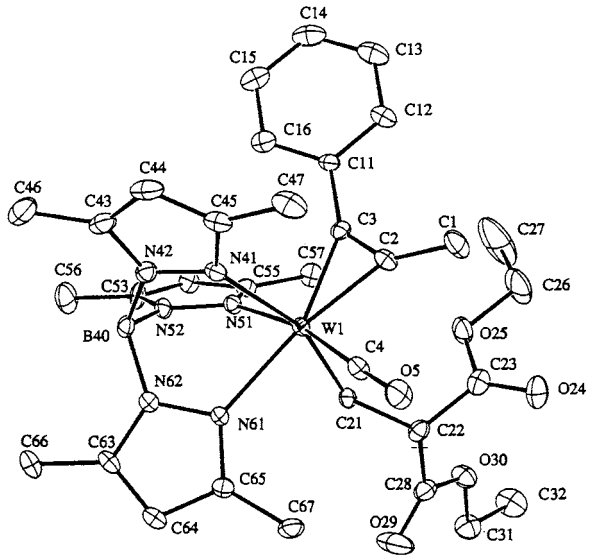



Fig. 3. ORTEP of Tp′(CO)(PhCCMe)$WCH_2CH(COOEt)_2$ (**6**).

Table 4
Selected bond distances (Å) and angles (°) for Tp′(CO)(PhCCMe)-$WCH_2CH(COOEt)_2$ (**6**)

| | | | |
|---|---|---|---|
| *Bond distances* | | | |
| W(1)–C(2) | 2.052(6) | C(1)–C(2) | 1.488(10) |
| W(1)–C(3) | 2.014(6) | C(2)–C(3) | 1.310(9) |
| W(1)–C(4) | 1.934(6) | C(3)–C(11) | 1.473(8) |
| W(1)–C(21) | 2.197(7) | C(4)–O(5) | 1.175(8) |
| W(1)–N(41) | 2.232(5) | C(21)–C(22) | 1.542(9) |
| W(1)–N(51) | 2.267(5) | C(22)–C(23) | 1.504(10) |
| W(1)–N(61) | 2.280(5) | C(22)–C(28) | 1.530(10) |
| *Bond angles* | | | |
| C(2)–W(1)–C(3) | 37.6(3) | C(21)–W(1)–N(61) | 85.19(20) |
| C(2)–W(1)–C(4) | 69.7(3) | N(41)–W(1)–N(51) | 85.34(19) |
| C(2)–W(1)–C(21) | 100.96(24) | N(41)–W(1)–N(61) | 76.70(17) |
| C(2)–W(1)–N(41) | 99.27(22) | N(51)–W(1)–N(61) | 81.43(17) |
| C(2)–W(1)–N(51) | 121.02(21) | W(1)–C(2)–C(1) | 150.4(5) |
| C(2)–W(1)–N(61) | 157.12(21) | W(1)–C(2)–C(3) | 69.6(4) |
| C(3)–W(1)–C(4) | 106.8(3) | C(1)–C(2)–C(3) | 139.9(6) |
| C(3)–W(1)–C(21) | 106.82(24) | W(1)–C(3)–C(2) | 72.8(4) |
| C(3)–W(1)–N(41) | 88.43(21) | W(1)–C(3)–C(11) | 147.4(5) |
| C(3)–W(1)–N(51) | 84.46(22) | C(2)–C(3)–C(11) | 138.8(6) |
| C(3)–W(1)–N(61) | 160.21(21) | W(1)–C(4)–O(5) | 177.2(5) |
| C(4)–W(1)–C(21) | 89.9(3) | C(3)–C(11)–C(12) | 120.9(6) |
| C(4)–W(1)–N(41) | 98.53(24) | W(1)–C(21)–C(22) | 121.9(4) |
| C(4)–W(1)–N(51) | 168.06(22) | C(21)–C(22)–C(23) | 116.0(5) |
| C(4)–W(1)–N(61) | 88.45(21) | C(21)–C(22)–C(28) | 109.3(5) |
| C(21)–W(1)–N(41) | 159.72(20) | C(23)–C(22)–C(28) | 109.3(6) |
| C(21)–W(1)–N(51) | 82.98(20) | | |

Hz, $^3J_{HH} = 7$ Hz) and the methyne proton is a triplet at 3.50 ppm ($^3J_{HH} = 7$ Hz). Although adduct **7** has two stereogenic centers, the metal and the β carbon, only one diastereomer is evident by $^1$H-NMR in the crude reaction mixture.

The structure of adduct **7** was assigned by 2-D NOESY and comparison with the crystal structure of the malonate adduct **6**. NOESY has been shown to be quite useful for determination of orientation and stereochemistry in complexes involving Tp′. This is due to the close proximity of three of the Tp′ methyl groups to the ancillary ligands. These methyl groups act as reporters that help determine the location of the other ligands [60,61].

In the crystal structure of **6**, one ester group is between the Tp′ methyl groups and the other is near the alkyne, not the metal carbonyl. This gave a good first approximation of the structure of the major diastereomer of **7**. The *t*-butyl ester should prefer to be between the Tp′ methyl groups because of its size and the acyl group should then be near the alkyne by analogy to the malonate adduct. This structure was confirmed by NOESY. The phenyl and methyl signals from the alkyne give strong correlations to the Tp′ methyl groups at 1.67 and 1.35 ppm. The acyl protons give strong correlations to the Tp′ methyl group at 1.35 ppm and to the alkyne. Correlations of the *t*-butyl ester with the Tp′ methyl signals at 2.95 and 1.35 allow for complete assignment of the orientation and stereochemistry of the single diastereomer of adduct **7**. Fig. 4 shows a Newman projection along the Cα–Cβ bond with the Tp′ methyl groups shown as small circles and the NOE correlations indicated by arrows.

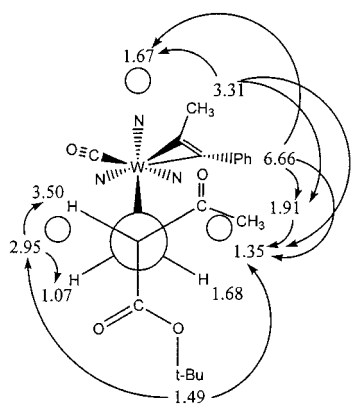
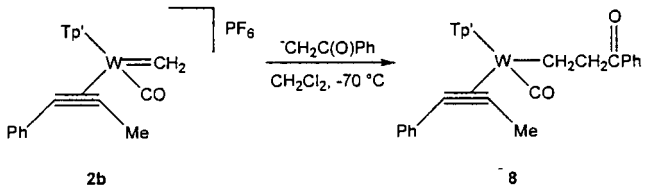



Fig. 4. Newman projection of **7** showing NOE correlations.

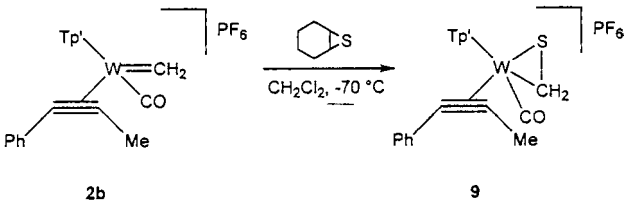
Reaction of carbene **2b** with deprotonated acetophenone gives product **8** (Eq. (6)). The metal carbonyl stretch in the IR spectrum is at 1847, and the acetophenone ketone infrared absorption is at 1671 $cm^{-1}$. Both methylene groups have diastereotopic hydrogens, and each hydrogen could appear as a doublet of doublets of doublets if all of the coupling constants differ significantly. A typical pattern for one hydrogen of these four is seen at 3.64 ppm ($^2J_{HH} = 14$, $^3J_{HH} = 12$, $^3J_{HH} = 4$ Hz) and shown in Fig. 5. The other protons appear at 2.10 (ddd), 1.71 (ddd), and 0.90 (m) ppm.




**2b** **8** (6)

### 2.4. Reaction with cyclohexene sulfide

Thioformaldehyde complexes are rare [29,39,62–65]. Reaction of carbene **2b** with cyclohexene sulfide (Eq. (7)) gives the thioformaldehyde complex, [Tp′(CO)-(PhCCMe)W($\eta^2$-S=$CH_2$)][$PF_6$] (**9**), and is accompanied by only a slight shift of the CO frequency from the cationic carbene value of 2078 to 2057 $cm^{-1}$ in the IR spectrum of the product. This frequency is comparable to that found for the π-bound acetaldehyde complex, [Tp(CO)(PhCCMe)W(O=CHMe)][$BAr'_4$], at 2042 $cm^{-1}$ [66]. It is significant to note that only σ bound aldehyde and ketone adducts have been reported previously for alkyne complexes with the bulky Tp′ in the coordination sphere; complexes of the smaller parent Tp (hydridotris(pyrazolyl)borate) ligand gave both σ and π-bound aldehydes [67,68]. The $^1$H-NMR spectrum of the thioformaldehyde complex **9** shows the two diastereotopic methylene protons as singlets at 6.09 and 4.83 ppm. The absence of geminal $J_{HH}$ coupling is not surprising; [CpRe(NO)($PPh_3$)($\eta^2$-S=$CH_2$)][$PF_6$] shows a coupling between the methylene protons of only 0.9 Hz [62]. The proton coupled $^{13}$C-NMR spectrum of the thioformaldehyde complex **9** shows the methylene carbon as a triplet at 60.3 ppm ($^1J_{CH} = 166$ Hz). The magnitude of $^1J_{CH}$ indicates that p character at the methylene carbon is used for the strained ring bonds, leaving more s character for the C–H bonds. The lack of geminal coupling between the protons is also indicative of utilization of carbon p character in the cyclopropane-like ring structure of a π-bound thioformaldehyde.




**2b** **9** (7)

## 3. Summary

Utilization of the $BAr'_4{}^-$ counterion produced a stable, crystalline sample of the cationic carbene complex **2a**. The structure of the prototype methylene tungsten carbene was determined. The electrophilic nature of carbene **2b** has been shown in reactions with phosphorus and nitrogen based neutral nucleophiles as well as

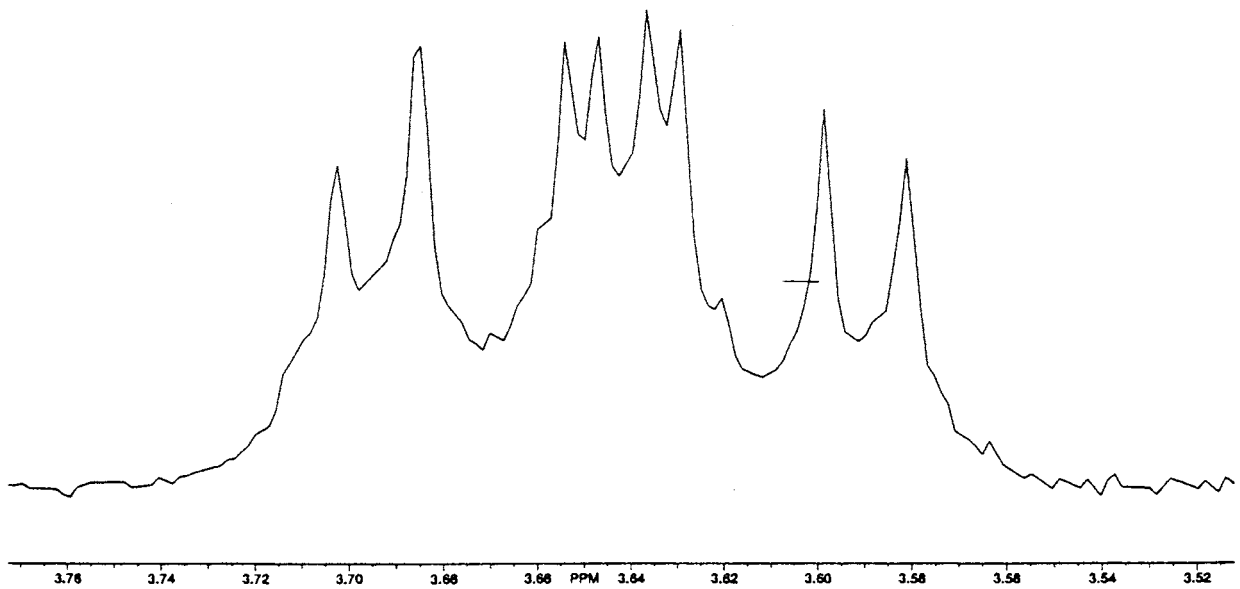



Fig. 5. $^1$H-NMR signal at 3.64 ppm for one diastereotopic hydrogen in adduct **8**.

nitrogen and carbon based anionic nucleophiles. The methylene group buffers the shifts in the metal carbonyl frequencies to a small range of about 30 wavenumbers as a function of the added nucleophile. Crystal structures of the phthalimide (**5**) and diethyl malonate (**6**) derivatives may reflect attack by nucleophiles along a path parallel to the carbonyl axis which avoids approach from between the bulky Tp′ methyl groups. The utility of the Tp′ methyl groups as reporter ligands for NOESY-NMR was shown in the determination of the stereochemistry of the *t*-butyl acetoacetate adduct (**7**). Neutral sulfur atom transfer from cyclohexene sulfide to the methylene carbene forms the $\eta^2$-thioformaldehyde complex (**9**).

## 4. Experimental

### 4.1. General considerations

Reactions (**2**–**9**) were carried out under a purified nitrogen atmosphere using standard Schlenk techniques. Solvents were purified as follows: hexanes, diethyl ether ($Et_2O$), methylene chloride, and pentane were degassed and passed through activated alumina [69]; tetrahydrofuran (THF) was distilled from Na–benzophenone. Methylene-$d_2$ chloride was degassed and stored over 4 Å molecular sieves. Tp′(CO)(PhCCMe)WMe [67], [Tp′(CO)(PhCCMe)W=$CH_2$][$PF_6$] [46], and [$Ph_3C$][$BAr'_4$] [50] were synthesized according to the literature.

$^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Bruker AC 200, a Bruker AC 250, a Bruker AMX 300, or a Bruker DRX 400 spectrometer. Infrared spectra for solutions were recorded on a Mattson Polaris FT-IR and solid state infrared spectra were recorded on an ASI ReactIR 1000 FT-IR. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

### 4.2. Representative $[BAr'_4]^-$

$^1$H-NMR and $^{13}$C-NMR data for the $[BAr'_4]^-$ counterion are reported separately for simplicity. $^1$H-NMR ($CD_2Cl_2$, $\delta$): 7.72 (br, 8H, *o*-Ar′), 7.55 (br, 4H, *p*-Ar′). $^{13}$C{H}-NMR ($CD_2Cl_2$, $\delta$): 162.1 (q, $^1J_{BC} = 50$ Hz, *ipso*), 135.2 (*o*-C), 129.3 (q, $^2J_{CF} = 30$ Hz, *m*-C), 125.0 (q, $^1J_{CF} = 273$ Hz, $CF_3$), 117.8 (m, *p*-C).

### 4.3. [Tp′(CO)(PhCCMe)W=$CH_2$][$BAr'_4$] (**2a**)

A solution of methyl complex **1** (38 mg, 0.06 mmol) in methylene chloride (10 ml) was cooled to −70°C and added to [$Ph_3C$][$BAr'_4$] (66 mg, 0.06 mmol). The resulting brown solution was stirred for 30 min at −70°C and then warmed to room temperature r.t. Solvent was removed under reduced pressure leaving a brown solid. Recrystallization was performed at −40°C with $CH_2Cl_2$–hexanes (90% yield). IR (neat solid): $\nu_{CO} = 2078$ cm$^{-1}$.$^1$H-NMR ($CD_2Cl_2$, $\delta$): 12.24 (d, 1H, $^2J_{HH} = 12$ Hz, [W]=C*H*H), 11.96 (d, 1H, $^2J_{HH} = 12$, $^2J_{WH} = 7$ Hz due to $^{183}$W (14% abundance, $I = \frac{1}{2}$), [W]=CH*H*), 7.44, 7.33, 6.80 (each a m, 5H, phenyl *H*s), 6.21, 6.00, 5.74 (each a s, 3H, 1:1:1, Tp′ C*H*), 4.08 (s, 3H, PhCCC$H_3$), 2.75, 2.60, 2.48, 2.45, 1.29, 1.20 (each a s, 18H, 3:3:3:3:3:3, Tp′ C$H_3$). $^{13}$C-NMR ($CD_2Cl_2$, $\delta$): 307.3 (t, $^1J_{CH} = 137$, $^1J_{WC} = 109$ Hz, [W]=*C*$H_2$), 213.6, 211.8 (Ph*CC*$CH_3$), 205.1 (*C*O), 154.9, 154.1, 151.4, 148.9, 148.0, 147.5 (Tp′ *C*$CH_3$), 134.1, 133.1, 131.0, 129.8 (phenyl *C*s), 110.4, 109.4, 108.7 (Tp′ *C*H), 17.5, 17.0, 14.9, 14.2, 13.2, 13.0, 12.6 (Tp′ C*C*$H_3$ and alkyne *C*$H_3$).

### 4.4. [Tp′(CO)(PhCCMe)W–$CH_2$–$PPh_3$][$PF_6$] (**3**)

A solution of methyl complex **1** (0.19 mmol) in methylene chloride was cooled to −70°C and added to [$Ph_3C$][$PF_6$] (0.19 mmol). The solution was stirred at −70°C for 30 min. Excess triphenylphosphine (0.22 mmol) in methylene chloride was cannulated to the carbene. The solution was stirred and warmed to r.t. and solvent was removed under reduced pressure leaving a blue solid. The crude product was purified by column chromatography on alumina with 2:1 ether–hexanes. Recrystallization was performed at −40°C with $CH_2Cl_2$–$Et_2O$ (15% yield). IR (neat solid): $\nu_{CO} =$ 1895 cm$^{-1}$. $^1$H-NMR ($CD_2Cl_2$, $\delta$): 7.32 − 7.85 (m, $PPh_3$ *H*s), 7.02, 6.85, 6.66 (each a m, phenyl *H*s), 6.03, 5.89, 5.64 (each a s, 3H, 1:1:1, Tp′ C*H*), 2.55 (t, 1H, $^2J_{WH} = {}^2J_{PH} = 14$, $^2J_{WH} = 10$ Hz, [W]–CH*H*–$PPh_3$), 1.38 (dd, 1H, $^2J_{HH} = 14$ Hz, $^2J_{PH} = 22$ Hz, [W]–C*H*H–$PPh_3$), 2.88, 2.62, 2.44, 2.40, 1.99, 1.54, 1.20 (each a s, 21H, 3:3:3:3:3:3:3, Tp′ C$H_3$ and alkyne C$H_3$). $^{13}$C-NMR ($CD_2Cl_2$, $\delta$): 237.4 ($^1J_{WC} = 142$ Hz, *C*O), 216.5, 214.5 (Ph*CC*$CH_3$) 153.1, 152.3, 150.3, 146.7, 145.8, 145.7 (Tp′ *C*$CH_3$), 136.7, 134.3, 134.0, 133.9, 130.3, 130.2, 129.2, 125.0, 124.2 (phenyl *H*s), 109.4, 108.7, 107.7 (Tp′ *C*H), 22.5 (q, $^1J_{CH} = 130$ Hz, alkyne C$H_3$), 14.9 ($^1J_{PC} = 31$ Hz, [W]–*C*$H_2$$PPh_3$), 15.9, 15.5, 15.4, 13.1, 13.0, 12.8 (Tp′ C*C*$H_3$). Anal. Calc. for $C_{43}H_{49}N_6OBF_6P_2W$: C, 49.93; H, 4.58; N, 8.12. Found: C, 49.99; H, 4.54; N, 7.72%.

### 4.5. [Tp′(CO)(PhCCMe)W–$CH_2$–$NC_5H_5$][$PF_6$] (**4**)

A solution of methyl complex **1** (64 mg, 0.1 mmol) in methylene chloride (8 ml) was cooled to −70°C and added to a solution of [$Ph_3C$][$PF_6$] (39 mg, 0.1 mmol) in methylene chloride (7 ml). The solution was stirred at −70°C for 30 min. Excess pyridine (14.4 μl, 0.2 mmol) was added by syringe. The solution was warmed to r.t. and solvent was removed under reduced pressure. Recrystallization at ambient temperature with $CH_2Cl_2$–

$Et_2O$ yielded a green solid (81% yield). IR (neat solid): $\nu_{CO} = 1881 cm^{-1}$. $^1$H-NMR ($CD_2Cl_2$, $\delta$): 8.24, 7.86 (each a m, pyridine *H*s), 7.27, 6.69 (each a m, phenyl *H*s), 5.97, 5.95, 5.69 (each a s, 3H, 1:1:1, Tp′ C*H*), 4.47 (d, 1H, $^2J_{HH} = 14$, $^2J_{WH} = 11$ Hz, [W]–CH*H*–$NC_5H_5$), 4.06 (d, 1H, $^2J_{HH} = 14$, $^2J_{WH} = 7$ Hz, [W]–C*H*H–$NC_5H_5$), 3.33, 2.61, 2.45, 2.42, 2.29, 1.59, 1.30 (each a s, 21H, 3:3:3:3:3:3:3, Tp′ C$H_3$ and alkyne C$H_3$). $^{13}$C-NMR ($CD_2Cl_2$, $\delta$): 237.0 ($^1J_{WC} = 145$ Hz, *C*O), 212.9, 207.4 (Ph*CC*$CH_3$) 153.3, 152.9, 150.1, 146.9, 146.1, 145.3 (Tp′ *C*$CH_3$), 143.2, 141.7, 136.9, 129.7, 129.0, 127.8 (phenyl and pyridine *C*s), 109.3, 109.0, 107.3 (Tp′ *C*H), 75.6 (t, $^1J_{CH} = 134$ Hz, $^1J_{WC} =$ 94 Hz, [W]–*C*$H_2$–$NC_5H_5$), 21.7 (q, $^1J_{CH} = 129$ Hz, alkyne C$H_3$), 16.0, 15.8, 15.5, 13.1, 12.9, 12.8 (Tp′ C*C*$H_3$). Anal. Calc. for $C_{31}H_{37}N_7BF_6OPW$: C, 43.13; H, 4.32; N, 11.36. Found: C, 42.94; H, 4.24; N, 11.12%.

### 4.6. Tp′(CO)(PhCCMe)W–$CH_2$-phthalimide (5)

A solution of methyl complex **1** (256 mg, 0.4 mmol) in methylene chloride was cooled to −70°C and added to a solution of $[Ph_3C][PF_6]$ (155 mg, 0.4 mmol) in methylene chloride. The solution was stirred at −70°C while a solution of the deprotonated phthalimide was prepared. Phthalimide (70.6 mg, 0.48 mmol) was dissolved in a minimum amount of THF and cooled to −70°C. Then a hexane solution of *n*-BuLi (0.48 mmol) was added by syringe. The solution was stirred for 20 min at −70°C and then added to the tungsten carbene complex. The solution was then stirred for 30 min, then warmed to r.t. and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on alumina using $CH_2Cl_2$–hexanes. Recrystallization at −40°C with $CH_2Cl_2$–pentane yielded purple needles (40% yield). Crystals for X-ray crystallographic investigation were obtained by making a saturated solution of the solid in acetone and cooling it to −40°C. IR (neat solid): $\nu_{CO} = 1883$, 1692 $cm^{-1}$. $^1$H-NMR ($CD_2Cl_2$, $\delta$): 7.73, 7.64 (each a m, phthalimide *H*s), 7.24, 6.72 (each a m, phenyl *H*s), 5.90, 5.62 (each a s, 3H, 2:1, Tp′ C*H*), 3.47 (d, 1H, $^2J_{HH} = 14$, $^2J_{WH} = 6$ Hz, [W]–CH*H*-phthalimide), 3.07 (d, 1H, $^2J_{HH} = 14$, $^2J_{WH} = 13$ Hz, [W]–C*H*H-phthalimide), 3.18, 2.86, 2.58, 2.42, 2.37, 1.81, 1.31 (each a s, 21H, 3:3:3:3:3:3:3, Tp′ C$H_3$ and alkyne C$H_3$). $^{13}$C-NMR ($CD_2Cl_2$, $\delta$): 239.9 ($^1J_{WC} = 147$ Hz, *C*O), 211.0, 207.6 (Ph*CC*$CH_3$), 168.9 (phthalimide *C*O), 154.6, 154.0, 149.6, 145.6, 144.9, 144.5 (Tp′ *C*$CH_3$), 138.6, 133.3, 128.7, 128.5, 128.1, 122.2 (phenyl and phthalimide *C*s), 108.9, 108.0, 106.6 (Tp′ *C*H), 50.7 (t, $^1J_{CH} = 130$, $^1J_{WC} = 101$ Hz, [W]–*C*$H_2$-phthalimide), 21.4 (q, $^1J_{CH} =$ 130 Hz, alkyne C$H_3$), 16.6, 15.9, 15.2, 13.2, 13.0, 12.7 (Tp′ C*C*$H_3$). Anal. Calc. for $C_{34}H_{36}N_7O_3BW \cdot CH_2Cl_2$ ($CH_2Cl_2$ present by NMR): C, 48.30; H, 4.40; N, 11.27. Found: C, 48.03; H, 4.39; N, 10.99%.

### 4.7. Tp′(CO)(PhCCMe)W–$CH_2$–CH(COOEt)$_2$ (6)

A solution of methyl complex **1** (128 mg, 0.2 mmol) in methylene chloride was cooled to −70°C and added to a solution of $[Ph_3C][PF_6]$ (78 mg, 0.2 mmol) in methylene chloride. The solution was stirred at −70°C while the malonate was deprotonated. Malonate (45.6 μl, 0.3 mmol) was dissolved in a small amount of THF and cooled to −70°C. Then a hexane solution of *n*-BuLi (0.3 mmol) was added by syringe. The solution was stirred for 20 min at −70°C and then added to the tungsten carbene complex. The solution was then stirred for 30 min and then warmed to r.t. and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on alumina using $CH_2Cl_2$. Purple crystals suitable for X-ray crystallographic investigation were obtained by recrystallization at −40°C with $CH_2Cl_2$–hexanes (43% yield). IR (neat solid): $\nu_{CO} = 1866$, 1725 $cm^{-1}$. $^1$H-NMR ($CD_2Cl_2$, $\delta$): 7.21, 6.66 (each a m, phenyl *H*s), 5.92, 5.89, 5.63 (each a s, 3H, 1:1:1, Tp′ C*H*), 4.15 (2H, $ABX_3$ spin system, $^2J_{HH} = 17$, $^3J_{HH} = 7$ Hz, one malonate C$H_2$), 3.96 (q, 2H, $^3J_{HH} = 7$ Hz, one malonate C$H_2$), 3.76 (dd, 1H, $^3J_{HH} = 6.3$, $^3J_{HH} = 8.5$ Hz, [W]–CH–C*H*), 1.84 (dd, 1H, $^2J_{HH} = 14.4$, $^3J_{HH} = 8.5$ Hz [W]–CH*H*), 2.88, 2.55, 2.41,2.34, 1.71, 1.34 (each a s, 21H, 3:3:3:3:3:3:3, Tp′ C$H_3$ and alkyne C$H_3$), 1.25, 1.14 (each a t, 6H, $^3J_{HH} = 7$ Hz, malonate C$H_3$s), 0.95 (dd, 1H, $^2J_{HH} = 14.4$ Hz, $^3J_{HH} = 6.3$ [W]–C*H*H). $^{13}$C-NMR ($CD_2Cl_2$, $\delta$): 243.4 (*C*O), 213.0, 209.1 (Ph*CC*$CH_3$) 173.9, 172.2 (malonate *C*OO) 153.7, 153.6, 149.7, 145.1, 144.8, 144.4 (Tp′ *C*$CH_3$), 138.7, 128.5, 128.4, 128.1 (phenyl *C*s), 108.5, 108.1, 106.7 (Tp′ *C*H), 61.0, 60.7 (malonate *C*$H_2$), 60.5 (d, $^1J_{CH} = 134$ Hz, [W]–$CH_2$–*C*H) 39.8 (t, $^1J_{CH} = 122$, $^1J_{WC} = 96$ Hz, [W]–*C*$H_2$–malonate), 21.4 (alkyne C$H_3$), 14.2, 14.1 (malonate *C*$H_3$), 16.2, 15.8, 15.4, 13.0, 12.9, 12.7 (Tp′ C*C*$H_3$). Anal. Calc. for $C_{33}H_{43}N_6BO_5W$: C, 49.64; H, 5.43; N, 10.53. Found: C, 49.62; H, 5.53; N, 10.48%.

### 4.8. Tp′(CO)(PhCCMe)W–$CH_2$–CH($COCH_3$)-(COO*t*-Bu) (7)

A solution of methyl complex **1** (128 mg, 0.2 mmol) in methylene chloride was cooled to −70°C and added to a solution of $[Ph_3C][PF_6]$ (78 mg, 0.2 mmol) in methylene chloride. The solution was stirred at −70°C while the *tert*-butyl acetoacetate was deprotonated. *tert*-Butyl acetoacetate (50.0 μl, 0.3 mmol) was dissolved in a small amount of THF and cooled to −70°C. Then a hexane solution of *n*-BuLi (0.3 mmol) was added by syringe. The solution was stirred for 20 min at −70°C and then added to the tungsten carbene complex. The solution was then stirred for 30 min, warmed to r.t. and the solvent was removed under reduced pressure. The crude product was purified by

column chromatography on alumina using $CH_2Cl_2$ (42% yield). Crystals were obtained by slow evaporation of a solution of the *t*-butyl acetoacetate adduct **7** in acetone. IR (neat solid): $\nu_{CO} = 1877$, 1715, 1696 $cm^{-1}$. $^1$H-NMR ($CD_2Cl_2$, $\delta$): 7.22, 6.66 (each a m, phenyl *H*s), 5.93, 5.91, 5.64 (each a s, 3H, 1:1:1, Tp′ C*H*), 3.50 (t, 1H, $^3J_{HH} = 7$ Hz, [W]–$CH_2$–C*H*), 3.31 (s, 3H, alkyne $CH_3$), 2.95, 2.57, 2.42, 2.36, 1.67, 1.35 (each a s, 18H, 3:3:3:3:3:3, Tp′ C$H_3$), 1.91 (s, 3H, COC$H_3$), 1.68 (dd, 1H, $^2J_{HH} = 14$, $^3J_{HH} = 7$ Hz, [W]–C*H*H), 1.49 (s, 9H, *t*-Bu *H*s) 1.07 (dd, 1H, $^2J_{HH} = 14$, $^3J_{HH} = 7$ Hz, [W]–CH*H*). $^{13}$C-NMR ($CD_2Cl_2$, $\delta$): 243.0 ($^1J_{WC} = 145$ Hz, *C*O), 212.5, 209.1 (Ph*CC*CH$_3$), 206.2 (*C*OCH$_3$), 173.4 (*C*OO*t*-Bu), 153.8, 153.4, 149.7, 145.1, 144.8, 144.4 (Tp′ *C*CH$_3$), 138.7, 128.6, 128.4, 128.1 (phenyl *C*s), 108.5, 108.2, 106.8 (Tp′ *C*H), 80.8 (*t*-Bu *C*(CH$_3$)$_3$), 70.5 (d, $^1J_{CH} = 136$ Hz, [W]–$CH_2$–*C*H), 40.6 (t, $^1J_{CH} = 121$, $^1J_{WC} = 94$ Hz, [W]–*C*H$_2$–), 28.2 (*t*-Bu *C*H$_3$), 26.6, 21.6, 16.4, 15.8, 15.6, 13.1, 13.0, 12.8 (Tp′ C*C*H$_3$, alkyne *C*H$_3$, and CO*C*H$_3$). Anal. Calc. for $C_{34}H_{46}N_6O_4BW$: C, 51.25; H, 5.69; N, 10.55. Found: C, 51.17; H, 5.84; N, 10.49%.

### 4.9. Tp′(CO)(PhCCMe)W–CH$_2$–CH$_2$C(O)Ph (8)

A solution of methyl complex **1** (161.0 mg, 0.25 mmol) in methylene chloride (10 ml) was cooled to −70°C and added to a solution of [$Ph_3C$][$PF_6$] (97 mg, 0.25 mmol) in methylene chloride (10 ml). The solution was stirred at −70°C while acetophenone was deprotonated in the following way: Acetophenone (43.8 μl, 0.375 mmol) was dissolved in a small amount of THF (3 ml) and cooled to −70°C. Then a hexane solution of *n*-BuLi (0.375 mmol) was added by syringe. The solution was stirred for 20 min at −70°C and then added to the tungsten carbene complex. The solution was stirred for 30 min, warmed to r.t. and the solvent was removed under reduced pressure. The crude product was collected as a blue band by column chromatography on alumina using $CH_2Cl_2$–hexanes (27% yield). IR (neat solid): $\nu_{CO} = 1847$, 1671 $cm^{-1}$. $^1$H-NMR ($CD_2Cl_2$, $\delta$): 7.82, 7.42 (each a m, 5 H, 2:3, acetophenone phenyl *H*s), 7.22, 6.70 (each a m, 5H, 3:2, phenyl *H*s), 5.89, 5.84, 5.65 (each a s, 3H, 1:1:1, Tp′ C*H*), 3.64 (ddd, 1H, $^2J_{HH} = 14$, $^3J_{HH} = 12$, $^3J_{HH} = 4$ Hz, [W]–$CH_2$–C*H*H), 2.10 (ddd, 1H, $^2J_{HH} = 14$, $^3J_{HH} = 5$, $^3J_{HH} = 13$ Hz, [W]–$CH_2$–CH*H*), 3.36, 2.81, 2.53, 2.42, 2.32, 1.59, 1.38 (each a s, 21H, 3:3:3:3:3:3:3, Tp′ C$H_3$, alkyne C$H_3$ and COC$H_3$), 1.71 (ddd, 1H, $^2J_{HH} = 14$, $^3J_{HH} = 5$ Hz, $^3J_{HH} = 12$, [W]–C*H*H–$CH_2$), 0.90 (m, 1H, [W]–CH*H*–$CH_2$). $^{13}$C-NMR ($CD_2Cl_2$, $\delta$): 245.0 ($^1J_{WC} = 145$ Hz, *C*O), 210.2, 207.3 (Ph*CC*CH$_3$), 205.0 (*C*OPh), 153.2, 149.5, 145.0, 144.9, 144.3 (Tp′ *C*CH$_3$), 138.5, 137.8, 132.2, 128.7, 128.6, 128.5, 128.1 (phenyl *C*s), 108.3, 108.0, 106.7 (Tp′ *C*H), 47.4 (t, $^1J_{CH} = 128$ Hz, *C*H$_2$COPh), 38.5 (t, $^1J_{CH} = 120$, $^1J_{WC} = 88$ Hz, [W]–*C*H$_2$), 21.2 (alkyne C*H*$_3$), 16.4, 15.9, 15.3, 12.9, 12.7 (1:1:1:1:2:1, Tp′ C*C*H$_3$). Anal. Calc. for $C_{34}H_{39}N_6BO_2W$: C, 53.85; H, 5.18; N, 11.08. Found: C, 53.57; H, 5.32; N, 11.04%.

### 4.10. [Tp′(CO)(PhCCMe)W(η$^2$–S=CH$_2$)][PF$_6$] (9)

A solution of methyl complex **1** (133 mg, 0.21 mmol) in methylene chloride (10 ml) was cooled to −70°C and added to [$Ph_3C$][$PF_6$] (80 mg, 0.21 mmol). The solution was stirred for 15 min. Then cyclohexene sulfide (50 μl, 0.4 mmol) was added by syringe and the yellow–brown solution was stirred for 30 min. Solvent was removed in vacuo and the brown solid was washed with hexanes and ether to give a mustard yellow powder (81% yield). IR (KBr): $\nu_{CO} = 2057$ $cm^{-1}$. $^1$H-NMR ($CD_2Cl_2$, $\delta$): 7.37 (t, 1H, phenyl *p*-*H*), 7.27 (t, 2H, phenyl m-Hs), 6.44 (d, 2H, phenyl *o*-Hs), 6.09 (s, 1H, S=C*H*H), 6.12, 5.99, 5.83 (each a s, 1:1:1, Tp′ C*H*), 4.83 (s, 1H, S=CH*H*), 3.60 (s, 3H, alkyne C*H*$_3$), 2.67, 2.47, 2.41, 1.58, 1.56 (each a s, 3:6:3:3:3, Tp′ C$H_3$). $^{13}$C-NMR ($CD_2Cl_2$, $\delta$): 205.5 (*C*O), 192.3, 179.74 (Ph*CC*Me), 156.65, 155.1, 151.9, 147.8, 147.1, 146.9 (Tp′ *C*CH$_3$), 134.0, 131.7, 129.6, 129.4, 128.6 (phenyl *C*s), 111.2, 111.0, 110.0 (Tp′ *C*H), 60.3 (t, S=*C*H$_2$, $^1J_{CH} = 166$ Hz), 20.5 (alkyne *C*H$_3$), 17.2, 16.2, 15.6, 13.2, 13.1, 13.0 (Tp′ *C*H$_3$).

## 5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 148457 for complex **6**, 148458 for complex **5**, and 148459 for complex **2a**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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## References

[1] E.O. Fischer, A. Maasbol, Angew. Chem. Int. Ed. Engl. 3 (1964) 580.
[2] F.Z. Dörwald, Metal Carbenes in Organic Synthesis, Wiley-VCH, Weinheim, 1999.

[3] M. Brookhart, Y. Liu, E.W. Goldman, D.A. Timmers, G.D. Williams, J. Am. Chem. Soc. 113 (1991) 927.
[4] A.F. Noels, A. Demonceau, J. Phys. Org. Chem. 11 (1998) 602.
[5] D.H. Berry, T.S. Koloski, P.J. Carroll, Organometallics 9 (1990) 2952.
[6] M.P. Doyle, D.C. Forbes, Chem. Rev. 98 (1998) 911.
[7] J.W. Herndon, Coord. Chem. Rev. 181 (1999) 177.
[8] R.H. Grubbs, S. Chang, Tetrahedron 54 (1998) 4413.
[9] M. Schuster, S. Blechert, Angew. Chem. Int. Ed. Engl. 36 (1997) 2037.
[10] R.R. Schrock, Tetrahedron 55 (1999) 8141.
[11] H.G. Schmalz, Angew. Chem. Int. Ed. Engl. 34 (1995) 1833.
[12] R.H. Grubbs, S.J. Miller, G.C. Fu, Acc. Chem. Res. 28 (1995) 446.
[13] R.H. Grubbs, W. Tumas, Science 243 (1989) 907.
[14] C. Pariya, K.N. Jayaprakash, A. Sarkar, Coord. Chem. Rev. 168 (1998) 1.
[15] R.R. Schrock, Acc. Chem. Res. 23 (1990) 158.
[16] K.J. Ivin, A.M. Kenwright, E. Khosravi, J.G. Hamilton, J. Organomet. Chem. 606 (2000) 37.
[17] R.B. Anderson, The Fischer–Tropsch Synthesis, Academic Press, New York, 1984, p. 174.
[18] G. Proulx, R.G. Bergman, Science 259 (1993) 661.
[19] P.W. Jolly, R. Pettit, J. Am. Chem. Soc. 88 (1966) 5044.
[20] R.R. Schrock, J. Am. Chem. Soc. 97 (1975) 6577.
[21] P. Schwab, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 110.
[22] D.S. Bohle, G.R. Clark, C.E.F. Rickard, W.R. Roper, L.J. Wright, J. Organomet. Chem. 358 (1988) 411.
[23] M.D. Fryzuk, S.A. Johnson, S.J. Rettig, Organometallics 18 (1999) 4059.
[24] S.J. Holmes, R.R. Schrock, J. Am. Chem. Soc. 103 (1981) 4599.
[25] H. Werner, W. Stüer, M. Laubender, C. Lehmann, R. Herbst-Irmer, Organometallics 16 (1997) 2236.
[26] H. Werner, W. Stüer, J. Wolf, M. Laubender, B. Weberndörfer, R. Herbst-Irmer, C. Lehmann, Eur. J. Inorg. Chem. (1999) 1889.
[27] J.Y. Thépot, V. Guerchais, L. Toupet, C. Lapinte, Organometallics 12 (1993) 4843.
[28] A.T. Patton, C.E. Strouse, C.B. Knobler, J.A. Gladysz, J. Am. Chem. Soc. 105 (1983) 5804.
[29] D.M. Heinekey, C.E. Radzewich, Organometallics 17 (1998) 51.
[30] M. Brookhart, J.R. Tucker, R.C. Flood, J. Jensen, J. Am. Chem. Soc. 102 (1980) 1203.
[31] W.B. Studabaker, M. Brookhart, J. Organomet. Chem. 310 (1986) C39.
[32] M.N. Mattson, E.J. O'Connor, P. Helquist, Org. Synth. 70 (1992) 177.
[33] S.E. Kegley, M. Brookhart, G.R. Husk, Organometallics 1 (1982) 760.
[34] S.M. Mullins, R.G. Bergman, J. Arnold, Organometallics 18 (1999) 4465.
[35] J.L. Brumaghim, G.S. Girolami, J. Chem. Soc. Chem. Commun. (1999) 953.
[36] W.K. Wong, W. Tam, J.A. Gladysz, J. Am. Chem. Soc. 101 (1979) 5440.
[37] J. Schwartz, K.I. Gell, J. Organomet. Chem. 184 (1980) C1.
[38] F.N. Tebbe, G.W. Parshall, G.S. Reddy, J. Am. Chem. Soc. 100 (1978) 3611.
[39] A.F. Hill, W.R. Roper, J.M. Waters, A.H. Wright, J. Am. Chem. Soc. 105 (1983) 5939.
[40] A.K. Burrell, G.R. Clark, C.E.F. Rickard, W.R. Roper, A.H. Wright, J. Chem. Soc. Dalton Trans. (1991) 609.
[41] W.A. Kiel, G.Y. Lin, J.A. Gladysz, J. Am. Chem. Soc. 102 (1980) 3299.
[42] W.A. Kiel, G.Y. Lin, G.S. Bodner, J.A. Gladysz, J. Am. Chem. Soc. 105 (1983) 4958.
[43] W.A. Kiel, G.Y. Lin, A.G. Constable, F.B. McCormick, C.E. Strouse, O. Eisenstein, J.A. Gladysz, J. Am. Chem. Soc. 104 (1982) 4865.
[44] Y. Wang, J.A. Gladysz, Chem. Ber. 128 (1995) 213.
[45] T.B. Gunnoe, P.S. White, J.L. Templeton, L. Casarrubios, J. Am. Chem. Soc. 119 (1997) 3171.
[46] T.B. Gunnoe, M. Surgan, P.S. White, J.L. Templeton, L. Casarrubios, Organometallics 16 (1997) 4865.
[47] T.B. Gunnoe, P.S. White, J.L. Templeton, Organometallics 16 (1997) 3794.
[48] M. Brookhart, B. Grant, A.F. Volpe, Jr., Organometallics 11 (1992) 3920.
[49] W.V. Konze, B.L. Scott, G.J. Kubas, J. Chem. Soc. Chem. Commun. (1999) 1807.
[50] S.R. Bahr, P. Boudjouk, J. Org. Chem. 57 (1992) 5545.
[51] L.W. Francisco, P.S. White, J.L. Templeton, Organometallics 16 (1997) 2547.
[52] C.M. Bastos, K.S. Lee, M.A. Kjelsberg, A. Mayr, D. Van Engen, S.A. Koch, J.D. Franolic, W.T. Klooster, T.F. Koetzle, Inorg. Chim. Acta 279 (1998) 7.
[53] P.A. van der Shaaf, R.A.T.M. Abbenhuis, W.P.A. van der Noort, R. de Graaf, D.M. Grove, W.J.J. Smeets, A.L. Spek, G. van Koten, Organometallics 13 (1994) 1433.
[54] A.J. Shultz, J.M. Williams, R.R. Schrock, S.J. Holmes, Acta Crystallogr., Sect. C 40 (1984) 590.
[55] J.A. Marsella, K. Folting, J.C. Huffman, K.G. Caulton, J. Am. Chem. Soc. 103 (1981) 5596.
[56] J.L. Templeton, Adv. Organomet. Chem. 29 (1989) 1.
[57] M.R. Churchill, W.J. Youngs, Inorg. Chem. 18 (1979) 2454.
[58] R.R. Schrock, T.E. Glassman, M.G. Vale, M. Kol, J. Am. Chem. Soc. 115 (1993) 1760.
[59] M.B. O'Regan, A.H. Liu, W.C. Finch, R.R. Schrock, W.M. Davis, J. Am. Chem. Soc. 112 (1990) 4331.
[60] P.S. Pregosin, A. Macchioni, J.L. Templeton, P.S. White, S. Feng, Magn. Reson. Chem. 32 (1994) 415.
[61] D.S. Frohnapfel, P.S. White, J.L. Templeton, H. Rüegger, P.S. Pregosin, Organometallics 16 (1997) 3737.
[62] W.E. Buhro, M.C. Etter, S. Georgiou, J.A. Gladysz, F.B. McCormick, Organometallics 6 (1987) 1150.
[63] H. Werner, M. Steinmetz, K. Peters, H.G. von Schnering, Eur. J. Inorg. Chem. (1998) 1605.
[64] J.W. Park, L.M. Henling, W.P. Schaefer, R.H. Grubbs, Organometallics 9 (1990) 1650.
[65] T.J. Collins, W.R. Roper, J. Organomet. Chem. 159 (1978) 73.
[66] D.M. Schuster, P.S. White, J.L. Templeton, Organometallics 19 (2000) 1540.
[67] J.L. Calderelli, L.E. Wagner, P.S. White, J.L. Templeton, J. Am. Chem. Soc. 116 (1994) 2878.
[68] D.M. Schuster, J.L. Templeton, Organometallics 17 (1998) 2707.
[69] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, Organometallics 15 (1996) 1518.