Synthesis, protonation, and electrophilic reactions of Tp′(CO)₂W≡C– OMe, a tungsten methoxycarbyne complex

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Abstract

The synthesis and characterization of the terminal methoxycarbyne complex Tp′(CO)₂W≡C–OMe is described. Nucleophiles attack Tp′(CO)₂W≡C–OMe at the methyl group of the methoxide substituent. The carbyne complex undergoes reversible protonation at the carbyne carbon in the presence of [H(Et₂O)₂][BAr₄] to generate the α-agostic carbene complex [Tp′(CO)₂W= C(H)OMe][BAr₄].

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1. Introduction

The first transition metal carbyne complex, Cl(CO)₄W≡C–Me [1], retains the methyl substituent from the (CO)₅W=CMe(OMe) carbene precursor [2]. Although methoxide abstraction to form carbyne complexes remains a primary route to carbynes (Scheme 1), the complementary reaction of methyl anion abstraction to prepare a methoxycarbyne complex has not been reported. Indeed the absence of alkoxycarbyne complexes was noted as early as 1987 [3]. No terminal methoxycarbyne complex has previously been isolated and structurally characterized, although a number of bridging di- and tri-nuclear 'methoxycarbyne' complexes have been reported [4–7]. These COMe ligands are generally synthesized by methylating a bridging carbonyl ligand.

Monomeric thiocarbonyl complexes have been converted to carbyne complexes by alkylation at sulfur. Two routes to the methylthiocarbyne complex Tp(CO)₂W≡C–SMe were developed by Angelici, and both involve derivatization of a thiocarbonyl ligand [8,9]. The anionic complex [Tp(CO)₂W(CS)]⁻ reacts with MeI to form Tp(CO)₂W≡C–SMe; the same complex can be made by reacting *trans*-Tp(CO)₂W(CS)I with MeLi (Scheme 2). In contrast, the related anionic carbonyl complex [Tp(CO)₂W(CO)]⁻ reacts with MeI to produce the η²-acyl complex Tp(CO)₂W(η²-C(O)CH₃ (Scheme 3), presumably by alkylation at metal (c.f. Cp(CO)₃WMe) followed by migratory insertion [10–12].

An important radical route to carbyne ligands was developed by Lalor with the synthesis of Tp′(CO)₂M≡ C–Cl (M = Mo, W) (Scheme 4) [13]. Lalor immediately recognized the potential of the anionic chloride substituent to act as a leaving group in reactions with nucleophiles to synthesize derivative carbyne ligands. The previously reported complex Tp′(CO)₂Mo≡C–SMe was synthesized by reacting the chlorocarbyne complex Tp′(CO)₂Mo≡C–Cl with methylthiolate anion (Scheme 5). Tp′(CO)₂Mo≡C–TeMe was synthesized by reaction of the chlorocarbyne complex with Na₂Te to generate the anionic chalcogenocarbonyl complex [Tp′(CO)₂Mo-(CTe)]⁻ that was subsequently alkylated with MeI [14]. Organothiocarbyne complexes typically react with nucleophiles either at the carbyne-carbon or at the metal center [15,16]. A proton source can add to the carbyne-carbon to form an η²-carbene ligand in which the sulfur is datively bound to the metal center [17].

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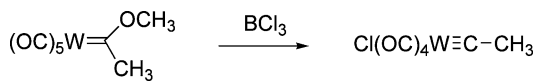
Scheme 1. Synthesis of Cl(CO)₄W≡C–Me.
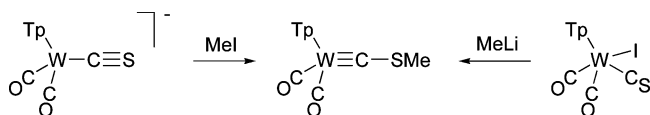
Scheme 2. Synthesis of Tp(CO)₂W≡C–SMe.

Scheme 4. Synthesis of Tp′(CO)₂W≡C–Cl.

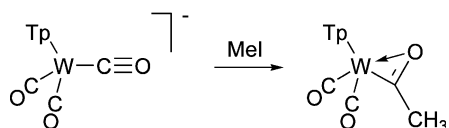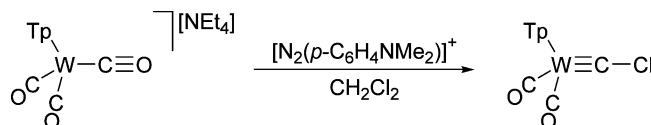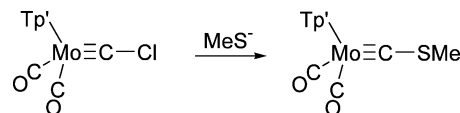Scheme 5. Synthesis of Tp′(CO)₂Mo≡C–SMe by nucleophilic displacement.

Lalor reported that phenyl lithium reacted with Tp′(CO)₂Mo≡C–Cl to produce Tp′(CO)₂Mo≡C–Ph in modest yields [14]. Later work demonstrated that aryloxides and phosphines could successfully replace the chloride substituent on the carbyne carbon in both molybdenum and tungsten chlorocarbyne complexes [18]. The neutral triphenylphosphine substituent in the cationic complex [Tp′(CO)₂W≡C–PPh₃]⁺ was found to be an excellent leaving group, and this trait allowed exploration of the chemistry of the parent terminal methylidyne complex Tp′(CO)₂W≡C–H (Scheme 6) [19]. Aryloxides were also observed to replace phosphine in the cationic phosphonium carbyne complex [20]. Could addition of methoxide to the phosphonium carbyne complex allow isolation of an elusive methoxycarbyne ligand?

We report here the synthesis of the terminal methoxycarbyne complex Tp′(CO)₂W≡C–OMe (1). Reactions of the methoxycarbyne complex with nucleophiles and with a proton source are included.

2. Results and discussion

2.1. Synthesis of Tp′(CO)₂W≡C–O–Me (1)

The methoxycarbyne complex Tp′(CO)₂W≡C–OMe (1) was observed by infrared spectroscopy in a solution of the phosphonium carbyne complex [Tp′(CO)₂W≡C–PPh₃][PF₆] and methoxide (Scheme 7). The purple phosphonium carbyne complex and Na[OMe] were combined in cold THF and IR absorbances for the unreacted starting material at 2023 and 1938 cm⁻¹ diminished as the solution was allowed to warm to room temperature. New IR absorbances appeared at 1958 and 1862 cm⁻¹ as the solution turned first pink and then orange over half an hour. The reaction was quenched with excess methyl iodide, and then the THF solution

was added to hexanes and the total solution volume was quickly reduced by rotary evaporation. The resulting orange solid was chromatographed on silica which afforded separation of the desired Tp′(CO)₂W≡C–OMe (1) and the contaminating Tp′(CO)₂W≡C–Ph as yellow and orange bands. The methoxycarbyne complex was recovered as a light and heat sensitive yellow solid in 48% yield after solvent removal. The complex can be stored for 2 weeks at −35 °C under inert atmosphere if protected from light.

Although electrophiles have been successfully added to isonitrile ligands and chalcogenocarbonyl ligands to form carbyne complexes [3], terminal carbonyl ligands resist methylation. The microscopic reverse of a carbonyl–oxygen alkylation reaction may be facile for methoxycarbyne ligands. Previous attempts at methoxide substitution of the chloride substituent in Tp′(CO)₂W≡C–Cl did not result in isolation of an alkoxycarbyne complex [18]. An electrophilic methyl group in the methoxycarbyne complex would not persist in the presence of alkoxide in a reaction similar to the conversion of Tp′(CO)₂W≡C–Cl to Tp′(CO)₂W≡C–OPh with aryloxide. Of course the aryl substituent in the W≡C–OAr fragment is not susceptible to nucleophilic attack. The cationic complex [Tp′(CO)₂W≡C–PPh₃][PF₆] evidently reacts with methoxide fast enough to generate the desired methoxycarbyne complex
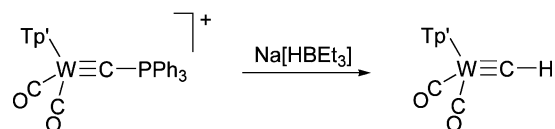
Scheme 6. Synthesis of Tp′(CO)₂W≡C–H.

Scheme 3. Synthesis of Tp(CO)₂W(η²-C(O)CH₃).
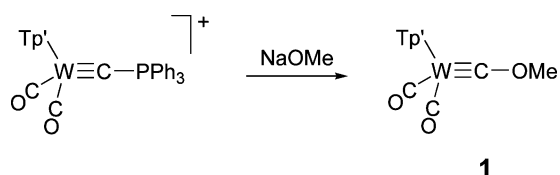
Scheme 7. Synthesis of the methoxycarbyne complex Tp′(CO)₂W≡C–OMe (1).
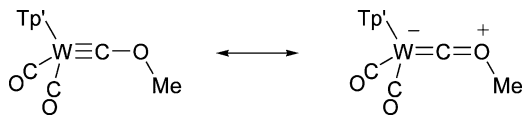
Fig. 2. Resonance forms for Tp′(CO)₂W≡C–OMe (**1**).

Tp′(CO)₂W≡C–OMe (**1**) before the methoxycarbyne complex reacts with nucleophiles in solution to transfer the methyl group with the [Tp′(CO)₃W]⁻ anion serving as an excellent leaving group. If the reaction is not quenched with MeI, the IR absorbances at 1958 and 1862 cm⁻¹ due to Tp′(CO)₂W≡C–OMe diminish as new IR absorbances at 1880 and 1749 cm⁻¹ appear due to conversion of methoxycarbyne complex **1** to the tricarbonyl anion [Tp′(CO)₃W]⁻.

2.2. Spectral data for Tp′(CO)₂W≡C–OMe (1)

The methoxy group is electron rich and the IR absorptions at 1958 and 1862 cm⁻¹ for methoxycarbyne complex **1** are at the low end of the range for neutral Tp′ dicarbonyl tungsten carbyne complexes. For comparison note that the yellow aryloxycarbyne complex Tp′(CO)₂W≡C–OPh exhibits carbonyl ligand absorbances at 1967 and 1870 cm⁻¹ [18], and peaks were observed at 1968 and 1867 cm⁻¹ for the yellow methylcarbyne complex Tp′(CO)₂W≡C–Me [21]. Less electron rich are the chlorocarbyne complex which has absorptions at 1987 and 1894 cm⁻¹ [18] and the parent C–H carbyne complex with absorptions at 1989 and 1893 cm⁻¹ [19].

The protons of the methoxycarbyne methyl group resonate at 4.15 ppm in the ^{1}H-NMR spectrum. The ^{1}H- and ^{13}C-NMR signals resulting from the Tp′ ligand reflect the mirror symmetry of the complex in a 2:1 pattern. The resonance assigned to the carbyne-carbon at 228.2 ppm in the ^{13}C-NMR spectrum possesses ^{183}W satellites ($^1J_{WC} = 235$ Hz) similar to the carbon resonances observed for Tp′(CO)₂W≡C–OPh (219.3 ppm, $^1J_{WC} = 242$ Hz) [18]. The methyl–carbon resonance at 62.6 ppm was observed to have ^{183}W satellites with a coupling constant of 3 Hz.

2.3. X-ray structure of Tp′(CO)₂W≡C–OMe (1)

The methoxycarbyne complex Tp′(CO)₂W≡C–OMe (**1**) crystallized as yellow needles from a dichloromethane/methanol solution. X-ray structure determination confirmed the formation of a terminal methoxycarbyne ligand (Fig. 1, Table 1). The W≡C bond distance (1.86(1) Å) is within the normal range of values for a tungsten–carbon triple bond distance (1.8–1.9 Å) [3]. The C–O bond distance (1.27(1) Å) is significantly less than the value expected for a carbon–oxygen single bond (1.43 Å) [22]. The partial C–O double bond character reflects some contribution from
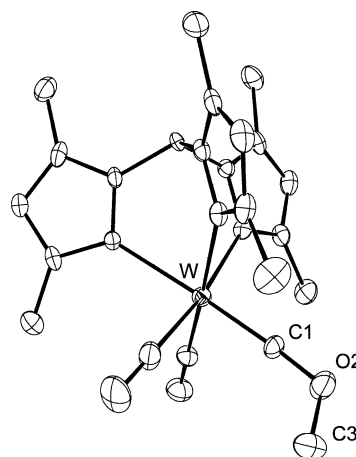

Fig. 1. ORTEP of Tp′(CO)₂W≡C–OMe (**1**).

an oxonium resonance form in addition to the methoxycarbyne resonance form (Fig. 2). A similar bonding arrangement has been previously observed between the carbyne-carbon and the heteroatom substituent in aminocarbyne complexes [23].

2.4. Addition of nucleophiles to Tp′(CO)₂W≡C–OMe (1)

Anionic transition metal complexes of the form [Et₄N][Tp′(CO)₃M] (M = Cr, Mo, W) react with alkylating agents at the metal instead of the carbonyl–oxygen [10–12]. One explanation for the failure to observe methylation at oxygen may simply be that [Tp′(CO)₃W]⁻ is such a good leaving group that an S_N2 reaction at the methoxycarbyne methyl–carbon of Tp′(CO)₂W≡C–OMe invariably generates [Tp′-(CO)₃W]⁻ and MeNuc. A partial positive charge at oxygen suggested by the crystal structure (vide supra) would increase the electrophilicity of the methoxycarbyne methyl group. As representative nucleophiles,

Table 1
Selected bond distances (Å), bond angles (°), and torsion angles (°) for Tp′(CO)₂W≡COMe (**1**)

Bond distances			
W–C(1)	1.86(1)	C(1)–O(2)	1.27(1)
W–C(4)	1.96(1)	C(3)–O(2)	1.44(1)
W–C(6)	2.00(1)	C(4)–O(5)	1.16(1)
W–N(11)	2.30(1)	C(6)–O(7)	1.16(1)
W–N(21)	2.22(1)		
W–N(31)	2.22(1)		
Bond angles			
W–C(1)–O(2)	177(1)	C(1)–W–N(11)	175.4(3)
C(1)–O(2)–C(3)	116(1)	C(4)–W–N(31)	174.3(3)
C(1)–W–C(4)	86.6(4)	C(6)–W–N(21)	172.0(3)
C(1)–W–C(6)	84.8(4)	C(4)–W–C(6)	88.1(4)
Torsion angles			
C(6)–W–O(2)–C(3)	7(1)		

triethylphosphine and the sodium salt of diethylmalonate were used to explore the electrophilicity of methoxycarbyne complex **1**.

Addition of triethylphosphine to a solution of $Tp'(CO)_2W\equiv C-OMe$ in CD_2Cl_2 caused a yellow precipitate to form in the solution, consistent with the production of $[MePEt_3][Tp'W(CO)_3]$ (**2**) (Scheme 8). Resonance peaks in the ^1H-NMR at 5.76, 2.51, and 2.35 ppm (3:9:9H) were assigned to the $[Tp'(CO)_3W]^-$ anion based on literature values [24]. Resonances at 2.25 (6H), 1.83 (3H), and 1.27 (9H) ppm exhibited ^{31}P coupling and were assigned to the $[MePEt_3]^+$ cation [25]. An IR spectrum of the CD_2Cl_2 solution revealed absorption peaks at 1872 and 1741 cm^{-1} that are similar to absorbances obtained for $[Et_4N][Tp'(CO)_3W]$ in CH_2Cl_2 (1876, 1737 cm^{-1}).

A second reaction probing the reactivity of the methoxycarbyne complex utilized $Na[CH(CO_2Et)_2]$ as a nucleophile in THF. The IR absorbances due to starting material carbonyl ligands diminished as a new absorption grew at 1881 cm^{-1}. The absorbance was attributed to the formation of $Na[Tp'W(CO)_3]$ based on the reported IR absorbances for $[Et_4N][Tp'W(CO)_3]$ (1881, 1744 cm^{-1} in CH_3CN [12]); the region around 1744 cm^{-1} was obscured by absorptions due to diethylmalonate. A ^1H-NMR spectrum of the residue remaining after solvent removal revealed resonance peaks at 5.76, 2.49, and 2.33 ppm (3:9:9H) confirming formation of the $[Tp'W(CO)_3]^-$ anion [24]. A quartet at 3.42 ppm (1H) and a doublet at 1.38 ppm (3H) were assigned to the methylated product $MeCH(CO_2Et)_2$ (**3**) (Scheme 9).

Neutral carbyne complexes generally react at either the carbyne-carbon or the metal center [3]. The reactivity of the methoxycarbyne complex $Tp'(CO)_2W\equiv C-OMe$ with nucleophiles differs from the reactivity of the methylthiocarbyne complex $Tp'(CO)_2W\equiv C-SMe$. The complex $Tp'(CO)_2W\equiv C-SMe$ reacts with phosphines at the carbyne-carbon to undergo nucleophilic displacement of the methylsulfide substituent to produce phosphonium carbyne complexes [15]. The close structural similarities between these fraternal tungsten twins, the methylthiocarbyne and methoxycarbyne complexes, suggests that the difference in reactivity is due to the electronic differences between oxygen and sulfur.
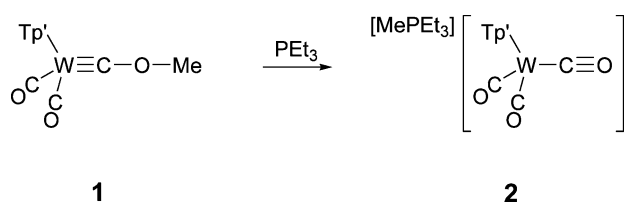
2.5. Protonation to form $[Tp'(CO)_2W=C(H)OMe][BAr_4']$

Protonation of $Tp(CO)_2W\equiv C-SMe$ with strong acids results in formation of the η^2-carbene complex $[Tp(CO)_2W=C(SMe)H][X]$ (X = OTf, BF$_4$, or O_2CCF_3) in which the sulfur is datively bound to the metal [17]. The complex $Tp'(CO)_2W\equiv C-OAr$ (Ar = p-C_6H_4OMe) undergoes protonation with $[H(Et_2O)_2]$-$[BAr_4']$ to yield the α-agostic η^2-carbene intermediate complex $[Tp'(CO)_2W=C(H)OAr][BAr_4']$ [26]. In the case of $[Tp'(CO)_2W=C(H)OMe]^+$, either the methoxycarbene–oxygen or the carbene C–H bond could donate electron density to the transition metal center to stabilize the formal 16 electron carbene species.

A CD_2Cl_2 solution containing $Tp'(CO)_2W\equiv C-OMe$ and one equivalent of $[H(Et_2O)_2][BAr_4']$ was prepared at low temperature, and a ^1H-NMR spectrum at $-57\,^\circ C$ revealed a 1:1 mixture of $Tp'(CO)_2W\equiv C-OMe$ (**1**) and $[Tp'(CO)_2W=C(H)OMe][BAr_4']$ (**4**) (Scheme 10). New $Tp'(methine)$–proton signals (6.06 and 6.04 ppm, 2:1H) confirmed the presence of the new species. A peak located at -0.45 ppm was observed with coupling to ^{183}W ($^2J_{WH}$ = 14 Hz) and ^{13}C ($^1J_{CH}$ = 89 Hz) that indicated an agostic C(H)OMe carbene. The α-agostic carbene complex $[Tp'(CO)_2W=C(H)H][BAr_4']$ possesses distinct α-agostic and terminal protons. The parameters of the CH_2 carbene complex allow definitive assignment of the bonding mode adopted by a C–H carbene of an unsaturated Tp' dicarbonyl tungsten complex. The α-agostic hydrogen in $[Tp'(CO)_2W=C(H)H][BAr_4']$ appears upfield in the ^1H-NMR spectrum at 1.92 ppm and displays relatively small coupling constants to ^{183}W and ^{13}C ($^2J_{WH}$ = 23 Hz, $^1J_{CH}$ = 93 Hz). The terminal proton appears downfield at 9.18 ppm and displays strong coupling to ^{183}W and ^{13}C ($^2J_{WH}$ = 63 Hz, $^1J_{CH}$ = 191 Hz) [19]. The carbene intermediate $[Tp'(CO)_2W=C(H)OMe][BAr_4']$ (**4**) is best described as an α-agostic carbene complex based on chemical shift and coupling constants of the proton bound to the carbene–carbon.

The peak at -0.45 ppm due to the agostic proton was observed to correlate to a peak in the carbon spectrum at 204 ppm in a 2D HMQC experiment. The carbene–carbon peak at 204 ppm is near the chemical shift of 201 ppm observed for the carbene–carbon in $[Tp'(CO)_2W=C(H)OAr][BAr_4']$ [26]. The methyl–carbon of the methoxy group in the cationic carbene intermediate $[Tp'(CO)_2W=C(H)OMe]^+$ shifted downfield to 66.8 ppm from 62.6 ppm in the carbyne precursor.

2.6. Reactivity of $[Tp'(CO)_2W=C(H)OMe][BAr_4']$ (4) with diethyl ether

When the CD_2Cl_2 solution with the 1:1 mixture of $Tp'(CO)_2W\equiv C-OMe$ (**1**) and $[Tp'(CO)_2W=$

Scheme 8. S_N2 displacement of $[Tp'(CO)_3W]^-$ by PEt_3.

Scheme 9. Methylation of Na[CH(COOEt)$_2$] to form CH$_3$CH(COOEt)$_2$ (3).

C(H)OMe][BAr$_4'$] (4) at $-57\,^{\circ}$C was warmed to $-25\,^{\circ}$C the amount of carbene 4 increased such that the ratio of carbyne complex to carbene complex was 1:2. The temperature of the solution was returned to $-57\,^{\circ}$C, and a ^{1}H-NMR spectrum revealed that the carbyne and carbene species were again present in an ca. 1:1 ratio, indicating the reaction in Scheme 10 is reversible. The [Tp$'$(CO)$_2$W = C(H)OMe][BAr$_4'$] complex is sufficiently acidic that it is deprotonated by diethyl ether at low temperatures to regenerate [H(Et$_2$O)$_2$][BAr$_4'$]. A temperature dependent equilibrium is present between methoxycarbyne complex 1 and cationic methoxycarbene complex 4 in the presence of [H(Et$_2$O)$_2$][BAr$_4'$] (Scheme 10). Warming the solution to room temperature results in the almost complete disappearance of Tp$'$(CO)$_2$W≡C–OMe due to an equilibrium shift and proton exchange between the carbene and carbyne complexes that results in broadening of the proton resonances from the methoxycarbyne complex.

While the temperature was maintained at $-25\,^{\circ}$C, peaks appeared in the ^{1}H-NMR spectrum at 5.88, 2.56, and -2.42 ppm (3:9:1H), diagnostic for Tp$'$(CO)$_3$WH (5) [24]. Concurrently, proton signals appeared at 4.66, 4.20, and 1.61 ppm (4:3:6H) due to formation of the [MeOEt$_2$]$^+$ cation. When the reaction solution was warmed to room temperature, demethylation of the methoxycarbene intermediate accelerated such that after an hour the major species in solution were Tp$'$(CO)$_3$WH (5), [MeOEt$_2$][BAr$_4'$] (6), and diethyl ether.

3. Conclusions

Isolation and structural characterization of a terminal methoxycarbyne complex have been achieved. The methoxycarbyne complex Tp$'$(CO)$_2$W≡C–OMe (1) readily transfers Me$^+$ to nucleophiles with [Tp$'$W(CO)$_3$]$^-$ serving as the leaving group. This monomeric methoxycarbyne complex reacts with acid at the carbyne carbon to form an α-agostic methoxycarbene complex [Tp$'$(CO)$_2$W = C(H)OMe]$^+$.
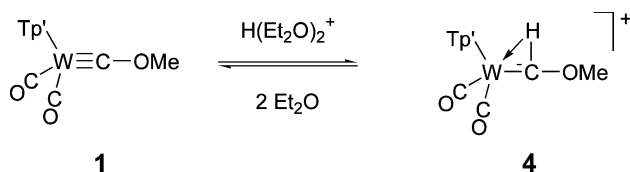
Scheme 10. Synthesis of [Tp$'$(CO)$_2$W = C(H)OMe][BAr$_4'$].

[Tp$'$(CO)$_2$W = C(H)OMe][BAr$_4'$] (4) exists in equilibrium with [H(Et$_2$O)$_2$][BAr$_4'$] and methoxycarbyne complex (1). Above $-25\,^{\circ}$C the cationic carbene complex methylates diethyl ether to form the diethylmethyloxonium cation [MeOEt$_2$]$^+$ and the hydride complex Tp$'$(CO)$_3$WH.

4. Experimental

4.1. Tp$'$(CO)$_2$W≡C–O–Me (1)

[Tp$'$(CO)$_2$W≡C–PPh$_3$][PF$_6$] (0.600 g, 0.627 mmol) and Na[OMe] (0.068 g, 1.26 mmol) were added to a Schlenk flask and the flask was cooled in an ice-water bath. THF (15 ml) was added slowly to the purple and white solids, resulting in a purple solution with IR absorbances at 2023 and 1938 cm^{-1}. The mixture was stirred for 25 min while warming to room temperature before IR absorbances due to starting material were absent and 1958 and 1862 cm^{-1} were the major absorptions in the IR spectrum. Methyl iodide (78 μl, 1.25 mmol) was added to the yellow–orange THF solution before the solution was transferred via cannula to an open flask containing 100 ml of stirring hexanes. Solvent was removed by rotary evaporation until a non-dry orange solid remained. The damp orange solid was taken up in 3:1 hexanes:CH$_2$Cl$_2$, added to a silica column, and eluted with 3:1 hexanes:CH$_2$Cl$_2$. An orange band (Tp$'$(CO)$_2$W≡CPh) was eluted before a yellow band from which Tp$'$(CO)$_2$W≡COMe (0.174 g) was recovered as a yellow powder after solvent removal and drying in vacuo. Yellow needles of Tp$'$(CO)$_2$W≡COMe (1) were grown from MeOH/CH$_2$Cl$_2$ solution at 0 °C. Yield: 47.7%. IR (THF): ν_{CO} = 1958, 1862 cm^{-1}. ^{1}H-NMR (CD$_2$Cl$_2$, 293 K): δ 5.90, 5.84 (s, 2:1H, Tp$'$CH), 4.15 (s, $^1J_{CH}$ = 150 Hz, W≡COMe), 2.48, 2.47, 2.36, 2.34 (s, 6:3:6:3H, Tp$'$CMe). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 293 K): δ 228.2 (s, $^1J_{WC}$ = 235 Hz, W≡COMe), 222.4 (s, $^1J_{WC}$ = 164 Hz, W(CO)$_2$), 152.7, 151.8, 145.4, 145.0 (s, 1:2:1:2 C, Tp$'$$C$Me), 106.7, 106.4 (s, 1:2 C, Tp$'$$C$H), 62.6 (s, $^3J_{WC}$ = 3 Hz, W≡COMe), 16.6, 15.4, 12.71, 12.70 (s, 2:1:1:2 C, Tp$'$CMe). ^{13}C-NMR (CD$_2$Cl$_2$, 293 K): δ 228.2 (q, $^2J_{CH}$ = 4 Hz, W≡COMe), 62.6 (q, $^1J_{CH}$ = 150 Hz, W≡COMe). Anal. Calc. for C$_{19}$H$_{25}$N$_6$BO$_3$W–W≡C: C, 37.27; H, 4.34; N, 14.49. Found: C, 37.69; H, 4.50; N, 14.19%.

4.2. [MePEt₃][Tp′W(CO)₃] (2)

A CD_2Cl_2 solution of Tp′$(CO)_2W≡COMe$ (34 mg, 0.059 mmol) was prepared before PEt_3 (11 μl, 0.076 mmol) was added to the solution. The solution turned cloudy yellow upon mixing. A ^{1}H-NMR spectrum revealed the clean formation of [MePEt₃][Tp′W(CO)₃], and that the methoxycarbyne complex had been completely consumed. Literature values were used to ascertain which peaks resulted from the phosphonium cation [25] and which peaks resulted from the tricarbonyl anion [24]. The IR spectrum of [MePEt₃][Tp′W(CO)₃] in CD_2Cl_2 compared well with the spectrum of [Et₄N][Tp′W(CO)₃] obtained in CH_2Cl_2. [MePEt₃][Tp′W(CO)₃]: IR (CD_2Cl_2): $\nu_{CO} = 1872$, 1741 cm^{-1}. ^{1}H-NMR (CD_2Cl_2, 293 K): δ 5.76 (s, 3H, Tp′CH), 2.51, 2.35 (s, 9:9H, Tp′CH_3), 2.25 (d of q, 6H, $^2J_{PH} = 13$ Hz, PCH_2CH₃), 1.83 (d, 3H, $^2J_{PH} = 13$ Hz, PCH_3), 1.27 (d of t, $^3J_{PH} = 19$ Hz, PCH₂CH_3). [Et₄N][Tp′W(CO)₃]: IR (CH_2Cl_2): $\nu_{CO} = 1876$, 1737 cm^{-1}.

4.3. MeCH(CO₂Et)₂ (3)

Diethyl malonate (60 ml, 0.40 mmol) was dissolved in THF (20 ml) and a piece of sodium was added to deprotonate the malonate reagent. After an hour the remaining sodium pellet was removed. Tp′$(CO)_2W≡$COMe (0.020 g, 0.034 mmol) was dissolved in THF (3 ml) and transferred to the Na[CH(CO₂Et)₂] solution. IR absorbances at 1960 and 1862 cm^{-1} decreased as a new absorbance at 1881 cm^{-1} increased due to the formation of Na[Tp′(CO)₃W]. IR absorbances for the tricarbonyl anion in acetonitrile were previously observed near 1881 and 1744 cm^{-1} [12,24], however, the region from 1760 to 1710 cm^{-1} was obscured by absorbances due to diethyl malonate. The reaction was quenched by the addition of 50 μl of water. The solvent was removed by rotary evaporation, and the resulting yellow oil was dried under vacuum. The oil was dissolved in CD_2Cl_2 to confirm by ^{1}H-NMR the formation of Na[Tp′(CO)₃W] based on literature values [24]. The formation of MeCH(CO₂Et)₂ (3) was determined by comparison of the ^{1}H-NMR spectrum to that of diethylmalonate. Na[Tp′(CO)₃W]: IR (THF): $\nu_{CO} = 1881$ cm^{-1}. ^{1}H-NMR (CD_2Cl_2, 293 K): 5.76 (s, 3H, Tp′CH), 2.49, 2.33 (s, 9:9H, Tp′CH_3). MeCH(CO₂Et)₂: ^{1}H-NMR (CD_2Cl_2, 293 K): δ 3.42 (q, 1H, MeCH(CO₂Et)₂), 1.38 (d, 3H, CH_3CH(CO₂Et)₂). The peaks expected near 4.18 ppm (q, 4H, OCH_2CH₃) and 1.26 ppm (t, 6H, OCH₂CH_3) were obscured by excess diethylmalonate. CH₂(CO₂Et)₂: ^{1}H-NMR (CD_2Cl_2, 293 K): δ 4.18 (q, 4H, OCH_2CH₃), 3.35 (s, 2H, CH_2(CO₂Et)₂), 1.26 (t, 6H, OCH₂CH_3).

Table 2
Crystal and data collection parameters for Tp′$(CO)_2W≡$COMe (1)

	1
Formula	$C_{19}H_{25}N_6BO_3W\cdots CH_2Cl_2$
Formula weight	665.03
Color	Yellow
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	7.9597(10)
b (Å)	17.0959(19)
c (Å)	18.9040(22)
V (Å^3)	2572.3(5)
D_{calc} (g cm^{-3})	1.717
Z	4
Temperature (K)	173
R_{int}	0.041
No. of parameters refined	298
Final R indices ($I > 2\sigma(I)$)	$R_f = 0.045$, $R_w = 0.049$
R indices (all data)	$R_f = 0.045$, $R_w = 0.049$
Goodness-of-fit on F^2	1.7292

4.4. [Tp′(CO)₂W=C(H)OMe][B(2,4-(CF₃)₂C₆H₃)₄] (4)

An oven dried J-Young NMR tube was charged with Tp′$(CO)_2W≡$COMe (30 mg, 0.05 mmol) and [H(Et₂O)₂][BAr′₄] (50 mg, 0.05 mmol) before CD_2Cl_2 was introduced via vacuum transfer. After the solvent was melted and the solution was mixed at -78 °C, the tube was introduced to the NMR at 216 K. The solution was warmed in the NMR to obtain optimal spectra. A similar technique was used to obtain an IR spectrum. IR (CH_2Cl_2, 293 K): $\nu_{CO} = 2057$, 1980 cm^{-1}. ^{1}H-NMR (CD_2Cl_2, 259 K): δ 7.73, 7.57 (s, 8:4H, B$-$CH_{ortho}, B$-$CH_{para}), 6.06, 6.04 (s, 2:1H, Tp′CH), 4.57 (s, W= C(H)OMe), 2.37, 2.35 (br s, 9:9H, Tp′CH_3), -0.50 (s, 1H, $^2J_{WC} = 14$ Hz, $^1J_{CH} = 89$ Hz, W=C(H)OMe). ^{13}C{^{1}H} NMR (CD_2Cl_2, 248 K): δ 208.9 (s, W($CO)_2$), 204.0 (s, W=C), 161.7 (q (80%), $^1J(^{11}BC) = 50$ Hz, hp (20%), $^1J(^{10}BC) = 16$ Hz, B$-$C$_{ipso}$H), 154.0, 151.9, 148.8, 147.8 (s, 1:2:1:2 C, Tp′CMe), 134.7 (s, B$-$C$_{ortho}$H), 128.7 (q of q, $^2J_{FC} = 31$ Hz, $^4J_{FC} = 3$ Hz, B$-$C$_{meta}$CF₃), 124.5 (q, $^1J_{FC} = 272$ Hz, CF₃), 117.5 (hp, $^3J_{FC} = 4$ Hz, B$-$C$_{para}$H), 108.9, 108.0 (s, 2:1 C, Tp′CH), 66.8 (s, W=C(H)OMe), 15.94, 15.86, 13.3, 12.4 (s, 2:1:1:2 C, Tp′CMe). HMQC NMR (CD_2Cl_2, 216 K): δ -0.5 and 204 ppm (W=C(H)OMe), 4.6 and 67 ppm (W=C(H)OCH_3).

4.5. [MeOEt₂][B(2,4-(CF₃)₂C₆H₃)₄] (6)

A CD_2Cl_2 solution containing 4 was warmed to room temperature. ^{1}H-NMR (CD_2Cl_2, RT): δ 4.69 (q, 4H, OCH_2CH₃), 4.22 (s, 3H, OMe), 1.65 (t, 6H, OCH₂CH_3). The ^{1}H-NMR resonances from the [B(2,4-

$(CF_3)_2C_6H_3)_4]^-$ anion were identical to those observed in the ^{1}H-NMR spectrum of **4**.

5. X-ray crystal structure determination

A crystal of Tp′(CO)$_2$W≡COMe (**1**) measuring $0.25 \times 0.25 \times 0.05$ mm was placed on a Bruker SMART 1K diffractometer, and the intensity data were collected using the omega scan mode. Data was collected in the $\pm h$, $\pm k$, $\pm l$ hemisphere. Additional crystal and data collection parameters are listed in Table 2.

Acknowledgements

References

[1] E.O. Fischer, G. Kreis, C.G. Kreiter, J. Mueller, G. Huttner, H. Lorenz, Angew. Chem. Int. Ed. 12 (1973) 564.

[2] E.O. Fischer, A. Maasboel, Angew. Chem. Int. Ed. 3 (1964) 580.

[3] H.P. Kim, R.J. Angelici, Adv. Organomet. Chem. 27 (1987) 51.

[4] M.A. Alvarez, M.E. Garcia, V. Riera, M.A. Ruiz, F. Robert, Organometallics 21 (2002) 1177.

[5] J.R. Torkelson, O. Oke, J. Muritu, R. McDonald, M. Cowie, Organometallics 19 (2000) 854.

[6] C.A. Collins, I.D. Salter, V. Sik, S.A. Williams, T. Adatia, J. Chem. Soc. Dalton Trans. (1998) 1107.

[7] W. Luo, R.H. Fong, W.H. Hersh, Organometallics 16 (1997) 4192.

[8] W.W. Greaves, R.J. Angelici, Inorg. Chem. 20 (1981) 2983.

[9] B.D. Dombek, R.J. Angelici, Inorg. Chem. 15 (1976) 2397.

[10] H. Adams, R.J. Cubbon, M.J. Sarsfield, M.J. Winter, Chem. Commun. (1999) 491.

[11] M.D. Curtis, K.B. Shiu, W.M. Butler, J. Am. Chem. Soc. 108 (1986) 1550.

[12] S. Trofimenko, J. Am. Chem. Soc. 91 (1969) 588.

[13] T. Desmond, F.J. Lalor, G. Ferguson, M. Parvez, J. Chem. Soc. Chem. Commun. (1983) 457.

[14] T. Desmond, F.J. Lalor, G. Ferguson, M. Parvez, J. Chem. Soc. Chem. Commun. (1984) 75.

[15] A.E. Bruce, A.S. Gamble, T.L. Tonker, J.L. Templeton, Organometallics 6 (1987) 1350.

[16] H.P. Kim, S. Kim, R.A. Jacobson, R.J. Angelici, Organometallics 5 (1986) 2481.

[17] H.P. Kim, S. Kim, R.A. Jacobson, R.J. Angelici, Organometallics 3 (1984) 1124.

[18] G.M. Jamison, P.S. White, J.L. Templeton, Organometallics 10 (1991) 1954.

[19] A.E. Enriquez, P.S. White, J.L. Templeton, J. Am. Chem. Soc. 123 (2001) 4992.

[20] K.C. Stone, G.M. Jamison, P.S. White, J.L. Templeton, Inorg. Chim. Acta 330 (2002) 161.

[21] B.E. Woodworth, D.S. Frohnapfel, P.S. White, J.L. Templeton, Organometallics 17 (1998) 1655.

[22] L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaca, New York, 1960, p. 246.

[23] A.C. Filippou, E.O. Fischer, H.G. Alt, U. Thewalt, J. Organomet. Chem. 326 (1987) 59.

[24] A.J.M. Caffyn, S.G. Feng, A. Dierdorf, A.S. Gamble, P.A. Eldredge, M.R. Vossen, P.S. White, J.L. Templeton, Organometallics 10 (1991) 2842.

[25] J.B. Hendrickson, M.L. Maddox, J.J. Sims, H.D. Kaesz, Tetrahedron 20 (1964) 449.

[26] K.C. Stone, G.M. Jamison, P.S. White, J.L. Templeton, Organometallics, ASAP, July, 2003.