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Synthesis and Reactivities of Tungsten Complexes with Disubstituted Trimethylenemethane Ligands

Iuan-Yuan Wu, Ming-Chu Cheng, Ying-Chih Lin,* and Yu Wang

Department of Chemistry, National Taiwan University, Taipei,
Taiwan 10764, Republic of China

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Treatment of the tungsten carbonyl β-(chlorocarbonyl)allyl complex $Cp(CO)_2W(\eta^3\text{-}CH_2C(COCl)CH_2)$ with 2 equiv of organolithium reagent followed by hydrolysis affords the allyl complex $Cp(CO)_2W(\eta^3\text{-}CH_2C(CR_2OH)CH_2)$ (**2a**, R = Me; **2b**, R = C_6H_5). Treatment of complex **2** with HBF_4 causes dehydration and produces the cationic tungsten disubstituted-trimethylenemethane complexes $[Cp(CO)_2W(\eta^4\text{-}CH_2C(CR_2)CH_2)]BF_4$ (**3a**, R = Me; **3b**, R = C_6H_5). Hydride regiospecifically attacks the disubstituted peripheral carbon atom of **3a**, producing $Cp(CO)_2W(\eta^3\text{-}CH_2C(C(H)Me_2)CH_2)$ (**4**). The methyl protons of complex **3a**, being acidic, are readily exchanged by deuterium in the presence of NaBr and acetone-d_6. Thus, the stable β-isopropenylallyl complex $Cp(CO)_2W(\eta^3\text{-}CH_2C(C(=CH_2)CH_3)CH_2)$ (**5**) is prepared from deprotonation of **3a** by a number of bases, including $Cp(CO)_3W^-$. Reaction of **5** with tetracyanoethylene proceeds via a [4 + 2] cycloaddition to yield a complex with a cyclohexyl moiety. Complexes **3a** and **3b** have been characterized by single-crystal X-ray diffraction analysis. Crystal data for **3a**: space group $P2_1/n$, $a = 7.465(4)$ Å, $b = 14.177(5)$ Å, $c = 14.242(7)$ Å, $\beta = 96.99(4)°$, $V = 1496(1)$ Å^3, $Z = 4$, $R = 0.043$, $R_w = 0.039$ based on 2109 reflections with $I > 3\sigma(I)$. Crystal data for **3b**: space group $Pna2_1$, $a = 10.000(3)$ Å, $b = 14.306(3)$ Å, $c = 14.747(6)$ Å, $V = 2110(1)$ Å^3, $Z = 4$, $R = 0.036$, $R_w = 0.028$ based on 1433 reflections with $I > 2\sigma(I)$.

Introduction

Free organic trimethylenemethane has been generated at low temperature by matrix photolysis.[1] This triplet diradical is highly reactive and is stable only below −185 °C. In contrast, the iron trimethylenemethane complex $(CO)_3Fe[\eta^4\text{-}C(CH_2)_3]$ reported by Emerson et al. is stable and can be easily handled at room temperature.[2] Trost and his co-workers developed palladium-catalyzed reactions of the bifunctional allyl acetate with activated olefins into a very efficient cyclopentanoid synthesis.[3] The mechanism for this reaction is thought to proceed via the generation of a zwitterionic trimethylenemethane complex. Theoretical calculations show that the η^3-trimethylenemethane structure is electronically favored over an η^4-trimethylenemethane geometry.[4] This is not the situation for the coordination of trimethylenemethane to d^8 metal complexes. In this case all three methylene carbons are strongly coordinated to the metal center, thus exhibiting much less reactivity.[5]

We are interested in exploring the steric effects that bias the coordination of the trimethylenemethane ligand to a metal center. (Trimethylenemethane)metal complexes are synthesized mainly via the following routes:[6] (1) the ring opening of alkylidenecyclopropanes, (2) the dehalogenation of α,α′-dihalo-substituted precursors, (3) the elimination of Me_3SiX from functionalized allylsilanes, and (4) the thermal extrusion of XY from η^3-methylallyl complexes. In exploring the chemistry of the tungsten β-(chlorocarbonyl)allyl complex $Cp(CO)_2W(\eta^3\text{-}CH_2C(COCl)CH_2)$ (**1**),[7d] we found that such a complex is also a good starting material for the preparation of substituted-trimethylenemethane complexes.[7b] Despite the extensive use of the trimethylenemethane complex, the number of systems of this type for which structural information is available is quite limited. Only six structures have been found in the literature, and none of them is of the 1,1-disubstituted type. A comparison of the structural parameters of organometallic trimethylenemethane complexes differing in their substituents details features of particular interest. Accordingly, we report here the synthesis and the crystal structures of two disubstituted-trimethylenemethane complexes and compare the structural parameters of these compounds to previously published structures of trimethylenemethane complexes of Fe, Ir, and Mo.[8]

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk

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techniques. NMR spectra were recorded on a Bruker AM-300WB spectrometer and are reported in units of parts per million with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93; C_6D_6, δ 7.15; C_2D_6CO, δ 2.04). IR spectra were measured on a Perkin-Elmer 983 instrument and referenced to a polystyrene standard. Electron impact mass spectra were determined with a Finnigan TSQ-46C spectrometer. Diethyl ether and CH_2Cl_2 were distilled from CaH_2. Benzene and THF were distilled from sodium–benzophenone. All other solvents and reagents were of reagent grade and used without further purification. $W(CO)_6$ was purchased from Strem Chemical. Propargyl bromide was purchased from Merck and distilled in small quantities before use. MeLi in ether and PhLi in cyclohexane were purchased from Merck and used as received. The complexes $[CpW(CO)_3]_2$,[9] $Cp(CO)_3WCH_2C{\equiv}CH$,[10] and $Cp(CO)_2W(\eta^3\text{-}CH_2C(COCl)CH_2)$[7] (**1**) were prepared according to the literature methods. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

Reaction of 1 with MeLi. A diethyl ether solution of MeLi (3.0 mL, 1.6 M, 4.8 mmol) was added dropwise to a solution of **1** (0.41 g, 1.0 mmol in 40 mL of C_6H_6) at room temperature. The solution was stirred for 20 min, and white precipitate formed. As aqueous hydrochloric acid solution (1.5 mL, 0.2 N) was added to quench the reaction, the solution turned yellow and the precipitate redissolved into the aqueous layer. The solution was stirred for another 10 min, and the organic and aqueous layers were separated. The organic part was dried over $MgSO_4$ and then filtered. Removal of the solvent under vacuum followed by washing with 3 × 10 mL portions of cold *n*-pentane gave $Cp(CO)_2W(\eta^3\text{-}CH_2C(C(CH_3)_2OH)CH_2)$ (**2a**; 0.34 g, 0.84 mmol) as an orange microcrystalline solid in 84% yield. Spectroscopic data for **2a**: IR ($CHCl_3$) 1948 (s), 1862 (s) (ν_{CO}) cm^{-1}; ^1H NMR (C_2D_6CO, δ) 5.40 (s, 5H, Cp), 2.98 (br, allyl syn CH), 1.88 (br, allyl anti CH), 1.39 (s, 6H, 2Me); ^{13}C NMR (C_2D_6CO, δ) 221.0 (2 terminal CO), 90.9 (Cp), 73.4(CMe_2OH), 32.3 (Me), 23.2 (2 allyl terminal C); mass spectrum *m/z* 406 (M^+), 378 ($M^+ - CO$), 350 ($M^+ - 2CO$). Anal. Calcd for $C_{13}H_{16}O_3W$: C, 38.64; H, 3.99. Found. C, 38.36; H, 4.12.

Reaction of 1 with PhLi. The synthesis and workup were similar to those used in the preparation of complex **2a**, except a solution of **1** (0.45 g, 1.1 mmol) in 60 mL of benzene and a solution of C_6H_5Li (3.0 mL, 2.0 M, 6.0 mmol) were used. The pure complex $Cp(CO)_2W[\eta^3\text{-}CH_2C(CPh_2OH)CH_2]$ (**2b**) as a yellow microcrystalline solid was isolated in 80% yield by slow evaporation of the solution under N_2. Spectroscopic data for $Cp(CO)_2W(\eta^3\text{-}CH_2C(CPh_2OH)CH_2)$ (**2b**): IR (THF) 1957 (s), 1886 (s) (ν_{CO}) cm^{-1}; ^1H NMR (CD_3CN, δ) 7.48, 7.26 (m, 10H, Ph), 5.27 (s, 5H, Cp), 3.64 (s, 1H, OH), 2.87 (br, 2H, allyl syn CH), 2.13 (br, 2 H, allyl anti CH); ^{13}C NMR (C_2D_6CO, δ) 228.5 (2 terminal CO), 148.9, 129.0, 128.2, 127.7 (Ph), 112.2 (allyl center C), 89.0 (Cp), 81.9 (CMe_2OH), 24.9 (2 allyl terminal C); mass spectrum *m/z* 530 (M^+), 502 ($M^+ - CO$), 474 ($M^+ - 2CO$). Anal. Calcd for $C_{23}H_{20}O_3W$: C, 52.29; H, 3.82. Found. C, 52.40; H, 3.98.

Direct Synthesis of $[Cp(CO)_2W(\eta^4\text{-}CH_2C({=}CMe_2)CH_2)]BF_4$ (3a) from 1. Freshly prepared complex **1** (0.414 g, 1.01 mmol, in 40 mL of C_6H_6) was treated with 3.0 mL of MeLi (1.6 N in ether) at 0 °C. As the mixture was stirred and warmed to room temperature over a 2-h period, a white precipitate formed. An aliquot of HCl solution (20 mL, 0.2 N) was added to quench the reaction. The organic layer was separated, and a 0.15-mL solution of HBF_4 in ether was added, yielding a light green precipitate. The precipitate was filtered and washed with 2 × 25 mL of THF. Excess solvent was removed under vacuum to give the crude product. Recrystallization by diffusion of hexane vapor into a CH_2Cl_2 solution of the crude product gave the yellow crystalline complex $[Cp(CO)_2W(\eta^4\text{-}CH_2C({=}CMe_2)CH_2)]BF_4$ (**3a**; 0.44 g, 0.93 mmol, 92% yield). Spectroscopic data for **3**: IR (KBr) 2040 (s), 1985 (s, br) (ν_{CO}) cm^{-1}; ^1H NMR (C_2D_6CO, δ) 5.94 (s, 5H, Cp), 3.24 (t, br, 2H, syn CH), 2.92 (t, br, 2H, anti CH), 2.16 (s, 6H, 2Me); ^{13}C NMR (C_2D_6CO, δ) 204.8 (2 terminal CO), 110.1 (CMe_2), 108.4 ($C{=}CMe_2$), 89.3 (Cp), 46.9 (CH_2), 23.4 (2 Me); mass spectrum *m/z* 388 ($M^+ - BF_4$, H), 360 ($M^+ - CO$, BF_4, H), 332 ($M^+ - 2CO$, BF_4, H). Anal. Calcd for $C_{13}H_{15}O_2WBF_4$: C, 32.95; H, 3.19. Found. C, 32.88; H, 4.06. Crystals suitable for X-ray diffraction analysis were grown from a saturated acetone solution maintained at −5 °C.

Reaction of 2b with HBF_4. To a solution of **2b** (1.50 g, 2.8 mmol, in 150 mL of benzene) was added dropwise a 1.0-mL solution of 54% HBF_4 in diethyl ether. The solution turned yellowish brown, and precipitate formed. The mixture was stirred for 5 min. The precipitate was collected by filtration, washed with 2 × 50 mL of water, 2 × 30 mL of THF, and 30 mL of diethyl ether, and then dried under vacuum. This product is insoluble in CH_3CN and is identified as $[Cp(CO)_2W(\eta^4\text{-}CH_2C({=}CPh_2)CH_2)]BF_4$ (**3b**; 1.43 g, 2.39 mmol, 85% yield). Spectroscopic data for **3b**: IR (KBr) 2051 (s), 1991 (s) (ν_{CO}), 1631 (m, br) cm^{-1}; ^1H NMR (CD_6CN, δ) 7.50, 7.27 (m, 10H, Ph), 5.57 (s, 5H, Cp), 3.30 (br, 2H, 2 syn CH), 2.90 (br, 2H, 2 anti CH); ^{13}C NMR (CD_3CN, δ) 220.5 (2 terminal CO), 141.0, 130.7, 128.3, 127.7 (Ph), 112.0 (CPh_2), 109.0 (allyl center C), 91.5 (Cp), 48.0 (br, CH_2); mass spectrum *m/z* 514 ($M^+ + H - BF_4$), 513 ($M^+ - BF_4$), 486 ($M^+ + H - CO$, BF_4), 458 ($M^+ + H - 2CO$, BF_4), 457 ($M^+ - CO$, BF_4). Anal. Calcd for $C_{23}H_{19}O_2WBF_4$: C, 46.19; H, 3.20. Found. C, 46.87; H, 3.07.

Reaction of 3a with MeLi. To a suspension of **3a** (0.30 g, 0.63 mmol) in 25 mL of THF was added dropwise a 1.0-mL solution of MeLi (1.6 M) in diethyl ether at 0 °C. The precipitate dissolved, and the solution turned yellowish brown. After 5 min, water was added to quench the reaction. The solvent was removed under reduced pressure, and the residue was extracted with benzene. After removal of benzene in vacuo, the byproducts were washed away with cold hexane and the residue was dried under vacuum. This product was finally purified by recrystallization from CH_2Cl_2 at 0 °C and was identified as $Cp(CO)_2W(\eta^3\text{-}CH_2C(C({=}CH_2)Me)CH_2)$ (**5**; 0.20 g, 0.52 mmol, 82% yield). Spectroscopic data for **5**: IR (THF) 1947 (s), 1875 (s) (ν_{CO}), 1640 (m, br) cm^{-1}; ^1H NMR (C_2D_6CO, δ) 5.46 (s, 5H, Cp), 5.03 (s, 1H, ${=}CH$), 4.56 (s, 1H, ${=}CH$), 2.97 (br, 2H, 2 syn CH), 2.69 (br, 2H, 2 anti CH), 1.63 (s, 3H, Me); ^{13}C NMR (C_2D_3CO, δ) 232.6 (2 terminal CO), 143.8 (CMe), 119.0 (allyl center C), 109.6 (${=}CH_2$), 90.2 (Cp), 23.6 (br, CH_2), 19.5 (CH_3); mass spectrum *m/z* 338 (M^+), 360 ($M^+ - CO$), 332 ($M^+ - 2CO$). The same product was isolated from the reactions of **3a** with a base such as amine, phosphine, or $Cp(CO)_3W^-$, with I_2, or even with air. The best yield is obtained from the reaction of **3a** with MeLi reagent.

Synthesis of $Cp(CO)_2W(\eta^3\text{-}CH_2C(C(H)Me_2)CH_2)$ (4). Complex **3a** (0.15 g, 0.32 mmol, in 10 mL of CH_3CN) was treated with $NaBH_4$ (15 mg, 0.40 mmol, in 5 mL of CH_3CN) at 0 °C, and the resulting mixture was stirred at this temperature for 10 min. After removal of the solvent in vacuo, the residue was extracted with 2 × 10 mL of benzene to give a yellow product, identified as $Cp(CO)_2W(\eta^3\text{-}CH_2C(C(H)Me_2)CH_2)$ (**4**; 0.093 g, 0.24 mmol, 75% based on **3a**). Spectroscopic data for **4**: IR ($CHCl_3$) 1943 (s), 1860 (s, br) (ν_{CO}) cm^{-1}; ^1H NMR (C_6D_6, δ) 4.54 (s, 5H, Cp), 2.95 (br, 2H, syn CH), 2.35 (m, 1H, J_{H-H} = 6.85 Hz, CH), 1.48 (br, 2 H, anti CH), 1.14 (d, 6H, J_{H-H} = 6.85 Hz, 2 Me); ^{13}C NMR (C_6D_6, δ) 230.1 (2 terminal CO), 88.8 (Cp), 35.9 (CH_2), 30.5 (CH), 24.8 (Me); mass spectrum *m/z* 390 (M^+), 362 ($M^+ - CO$), 334 ($M^+ - 2CO$). Anal. Calcd for $C_{13}H_{16}O_2W$: C, 40.23; H, 4.16. Found. C, 40.12; H, 4.08.

Reaction of 5 with Tetracyanoethene. To a solution of **5** (0.37 g, 0.96 mmol) in 10 mL of acetone was added dropwise a solution of $(NC)_2C{=}C(CN)_2$ (0.12 g, 0.96 mmol, in 5 mL of acetone). The solution turned from yellow to dark brown. The mixture was stirred for 5 min, and then the solvent was removed to give a greenish brown oily residue. The residue was subjected to column chromatography on silica gel, and the second band eluted by 1:1 acetone/hexane gave $Cp(CO)_2W(\eta^3\text{-}CH_2C(C_4H_4\text{-}$

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Table I. Crystal and Intensity Collection Data for $[Cp(CO)_2W(\eta^4-C(CH_2)_2(C(CH_3)_2))]BF_4$ (3a) and $[Cp(CO)_2W(\eta^4-C(CH_2)_2(C(C_6H_5)_2))]BF_4$ (3b)

	3a	3b
mol formula	$C_{13}H_{15}O_2BF_4W$	$C_{23}H_{19}O_2BF_4W$
mol wt	473.91	598.03
space group	$P2_1/n$	$Pna2_1$
a, Å	7.465(4)	10.000(3)
b, Å	14.177(5)	14.306(3)
c, Å	14.242(7)	14.747(6)
β, deg	96.99(4)	90.00
V, Å^3	1496(1)	2110(1)
Z	4	4
cryst dimens, mm	0.40 × 0.2 × 0.50	0.3 × 0.4 × 0.4
radiation	Mo Kα (λ = 0.7107 Å)	
2θ range, deg	2–50	2–50
scan type	$2\theta/\omega$	
total no. of rflns	2621	1918
no. of unique rflns	2109 ($I > 3\sigma(I)$)	1433 ($I > 2\sigma(I)$)
R	0.043	0.036
R_w	0.039	0.028
GOF	4.11	2.12

$(CN)_4)CCH_3)$ (**6**; 0.27 g, 0.52 mmol, 55% yield). Spectroscopic data for **6**: IR ($CHCl_3$) 1957 (s), 1882 (s, br) (ν_{CO}) cm^{-1}; ^{1}H NMR (C_2D_6CO, 223 K, δ) 5.75 (s, 5H, Cp), 4.82 (d, 1H, J_{H-H} = 17.3 Hz), 4.19 (d, 1H, J_{H-H} = 17.3 Hz), 3.78 (d, 1H, J_{H-H} = 15.6 Hz, CH), 3.22 (d, 1H, J_{H-H} = 15.6 Hz, CH), 2.48 (d, 1H, J_{H-H} = 4.1 Hz, syn CH), 1.56 (s, 3H, CH_3), 1.29 (d, 1H, J_{H-H} = 4.1 Hz, anti CH); ^{13}C NMR (C_6D_6, δ) 210.0 (2 terminal CO), 111.7 (center C), 112.1, 111.6, 111.5, 110.6 (CN), 91.7 (Cp), 88.3, 42.6, 39.5, 39.2, 38.1, 68.8 (cyclohexyl), 39.8 (allyl CH_2), 27.5 (Me); mass spectrum m/z 516 (M$^+$), 488 (M$^+$ – CO), 460 (M$^+$ – 2CO).

Single-Crystal X-ray Diffraction Analysis of 3a and 3b. Single crystals of **3a** and **3b** suitable from X-ray diffraction analysis were grown by recrystallization from acetone and acetonitrile, respectively. The diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.7107 Å) radiation. The raw intensity data were converted to structure factor amplitudes and their esd's after correction for scan speed, background, Lorentz, and polarization effects. An empirical absorption correction, based on the azimuthal scan data, was applied to the data. Crystallographic computations were carried out on a Microvax III computer using the NRCC-SDP-VAX structure determination package.[11]

A suitable single crystal of **3a** was mounted on the top of a glass fiber with glue. Initial lattice parameters were determined from 24 accurately centered reflections with 2θ values in the range from 19.50 to 24.38°. Cell constants and other pertinent data were collected and are recorded in Table I. Reflection data were collected using the ω-2θ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2 to 7° min^{-1}. The ω scan angle was determined for each reflection according to the equation $0.75 \pm 0.25 \tan\theta$. Three check reflections were measured every 30 min throughout the data collection and showed no apparent decay. The merging of equivalent and duplicate reflections gave a total of 2621 unique measured data in which 2109 reflections with $I > 3\sigma(I)$ were considered observed. The structure was first solved by using the heavy-atom method (Patterson synthesis), which revealed the positions of metal atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The quantity minimized by the least-squares program was $w(|F_o| - |F_c|)^2$, where w is the weight of a given operation. The analytical forms of the scattering factor tables for the neutral atoms were used.[12] The non-hydrogen atoms were refined anisotropically.

Table II. Fractional Coordinates and Isotropic Temperature Factors for 3a

	x	y	z	B_{iso},[a] Å^2
W	0.27314(7)	0.31233(3)	0.12114(3)	2.783(20)
C(1)	0.4324(21)	0.2863(10)	0.2672(9)	6.0(8)
C(2)	0.3182(23)	0.2109(8)	0.2501(9)	5.8(9)
C(3)	0.1393(22)	0.2439(10)	0.2415(9)	6.4(8)
C(4)	0.1548(20)	0.3459(9)	0.2580(10)	5.7(8)
C(5)	0.3308(20)	0.3710(9)	0.2718(9)	5.1(7)
C(6)	0.1936(19)	0.4468(8)	0.0935(9)	5.1(7)
O(6)	0.1613(15)	0.5244(5)	0.0839(7)	7.0(6)
C(7)	0.5224(19)	0.3500(8)	0.0954(9)	4.9(7)
O(7)	0.6631(14)	0.3720(8)	0.0812(9)	9.4(8)
C(11)	0.1819(19)	0.2375(7)	–0.0105(8)	4.0(6)
C(12)	0.2976(18)	0.1665(7)	0.0250(8)	3.9(6)
C(13)	0.0168(19)	0.2537(8)	0.0289(10)	4.6(7)
C(14)	0.2534(20)	0.3242(9)	–0.0426(8)	5.1(7)
C(15)	0.2312(23)	0.0773(8)	0.0651(10)	6.2(9)
C(16)	0.4791(20)	0.1512(8)	–0.0106(10)	5.3(7)
B	0.787(5)	0.0372(24)	0.2169(24)	19.6(14)
F(1)	0.9190(12)	0.0474(5)	0.3008(6)	6.91(21)
F(2)	0.6188(16)	0.0304(7)	0.2649(8)	11.1(3)
F(3)	0.7501(19)	0.1360(9)	0.2019(9)	14.6(4)
F(4)	0.803(3)	–0.0029(11)	0.1637(12)	18.7(6)
F(4′)	0.729(15)	–0.065(7)	0.208(7)	7.9(28)
F(4″)	0.850(15)	0.073(7)	0.120(8)	7.9(28)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table III. Selected Interatomic Distances (Å) and Bond Angles (deg) for 3a

W–C(1)	2.297(13)	C(4)–C(5)	1.353(21)
W–C(2)	2.324(12)	C(6)–O(6)	1.132(14)
W–C(3)	2.300(12)	C(7)–O(7)	1.137(16)
W–C(4)	2.285(12)	C(11)–C(12)	1.382(17)
W–C(5)	2.292(13)	C(11)–C(13)	1.433(19)
W–C(6)	2.021(12)	C(11)–C(14)	1.436(17)
W–C(7)	2.012(13)	C(12)–C(15)	1.497(17)
W–C(11)	2.189(12)	C(12)–C(16)	1.518(18)
W–C(12)	2.499(10)	B–F(1)	1.46(4)
W–C(13)	2.338(13)	B–F(2)	1.51(4)
W–C(14)	2.324(12)	B–F(3)	1.44(4)
C(1)–C(2)	1.370(21)	B–F(4)	0.97(4)
C(1)–C(5)	1.426(19)	B–F(4′)	1.51(10)
C(2)–C(3)	1.406(24)	B–F(4″)	1.60(11)
C(3)–C(4)	1.466(20)		

C(6)–W–C(7)	88.3(5)	C(11)–C(12)–C(15)	122.2(12)
C(6)–W–C(11)	103.7(5)	C(11)–C(12)–C(16)	121.7(10)
C(6)–W–C(12)	135.5(5)	C(15)–C(12)–C(16)	110.9(10)
C(6)–W–C(13)	91.4(5)	W–C(13)–C(11)	66.0(7)
C(6)–W–C(14)	75.8(5)	W–C(14)–C(11)	66.4(6)
C(7)–W–C(11)	99.9(5)	F(1)–B–F(2)	98.7(20)
C(7)–W–C(12)	89.4(4)	F(1)–B–F(3)	97.0(22)
C(7)–W–C(13)	134.7(5)	F(1)–B–F(4)	124(4)
C(7)–W–C(14)	75.2(5)	F(1)–B–F(4′)	108(5)
W–C(6)–O(6)	173.8(12)	F(1)–B–F(4″)	115(5)
W–C(7)–O(7)	179.5(10)	F(2)–B–F(3)	88.5(21)
W–C(11)–C(12)	85.7(8)	F(2)–B–F(4)	120(3)
W–C(11)–C(13)	77.3(7)	F(2)–B–F(4′)	74(4)
W–C(11)–C(14)	76.7(7)	F(2)–B–F(4″)	139(5)
C(12)–C(11)–C(13)	120.2(11)	F(3)–B–F(4)	119(3)
C(12)–C(11)–C(14)	120.0(12)	F(3)–B–F(4′)	150(5)
C(13)–C(11)–C(14)	111.0(10)	F(3)–B–F(4″)	68(4)
W–C(12)–C(11)	60.9(6)	F(4)–B–F(4′)	55(4)
W–C(12)–C(15)	116.1(8)	F(4)–B–F(4″)	55(4)
W–C(12)–C(16)	115.4(8)	F(4′)–B–F(4″)	110(6)

Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares. All hydrogens were assigned isotropic thermal parameters 1–2 Å^2 larger then the equivalent B_{iso} value of the atom to which they were bonded. The final residuals of this refinement were R = 0.043 and R_w = 0.039. Final values of all refined atomic positional parameters and selected bond distances and angles are listed in Tables II and III, respectively.

The procedures for **3b** were similar to those for **3a**. The unit cell constants were also determined from 24 accurately centered

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[11] Gabe, E. J.; Lee, F. L.; LePage, Y. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; p 167.

[12] *International Tables for X-ray Crystallography*; D. Reidel: Dordrecht, The Netherlands, and Boston, MA, 1974; Vol. IV.

Table IV. Fractional Coordinates and Isotropic Temperature Factors for 3b

	x	y	z	B_{iso},[a] Å^2
W	0.37086(5)	0.51640(3)	0.41883	2.99(4)
C(1)	0.5048(16)	0.6003(13)	0.3558(13)	5.1(10)
O(1)	0.5726(11)	0.6477(10)	0.3150(11)	7.8(8)
C(2)	0.2254(16)	0.5756(10)	0.3443(12)	4.0(8)
O(2)	0.1439(12)	0.6096(9)	0.3045(10)	7.2(8)
C(3)	0.2706(13)	0.3714(10)	0.3932(11)	3.6(9)
C(4)	0.3973(15)	0.3821(11)	0.3520(10)	3.6(8)
C(5)	0.3962(14)	0.4466(11)	0.2764(10)	4.0(8)
C(6)	0.5217(11)	0.3772(9)	0.4029(10)	2.0(7)
C(11)	0.5335(13)	0.3132(10)	0.4850(11)	2.8(7)
C(12)	0.4672(14)	0.2283(10)	0.4884(14)	4.1(9)
C(13)	0.4867(14)	0.1673(11)	0.5605(13)	4.3(9)
C(14)	0.5739(14)	0.1907(13)	0.6278(14)	5.5(10)
C(15)	0.6449(17)	0.2732(11)	0.6254(12)	4.8(9)
C(16)	0.6246(14)	0.3331(10)	0.5537(10)	3.3(7)
C(21)	0.6533(14)	0.3956(10)	0.3565(9)	2.7(7)
C(22)	0.6873(13)	0.3355(10)	0.2879(11)	3.0(7)
C(23)	0.8115(16)	0.3440(13)	0.2442(12)	4.7(9)
C(24)	0.8975(15)	0.4174(13)	0.2712(12)	5.1(10)
C(25)	0.8626(15)	0.4726(11)	0.3377(11)	4.3(8)
C(26)	0.7396(14)	0.4674(10)	0.3831(10)	3.6(7)
C(31)	0.4641(15)	0.5414(14)	0.5599(11)	5.7(10)
C(32)	0.4182(16)	0.6269(12)	0.5269(13)	5.3(10)
C(33)	0.2770(16)	0.6217(10)	0.5240(13)	4.5(9)
C(34)	0.2425(15)	0.5332(12)	0.5458(12)	5.1(10)
C(35)	0.3554(16)	0.4819 (12)	0.5648(12)	5.5(9)
B	0.8416(18)	0.6268(13)	0.5686(14)	3.9(10)
F(1)	0.8704(13)	0.6794(7)	0.6393(8)	8.6(7)
F(2)	0.9503(10)	0.6254(10)	0.5107(10)	10.0(9)
F(3)	0.8211(10)	0.5387(7)	0.5981(8)	7.1(7)
F(4)	0.7373(9)	0.6565(7)	0.5220(10)	8.0(8)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

reflections. Cell constants and other petinent data were collected and are also recorded in Table I. Procedures for data collection and refinement were similar to those used for **3a**. The final residuals of this refinement were $R = 0.036$ and $R_w = 0.028$. Final values of all refined atomic positional parameters (with esd's) and selected bond distances and bond angles are listed in Tables IV and V, respectively. Tables of thermal parameters are given in the supplementary material.

Table V. Selected Interatomic Distances (Å) and Bond Angles (deg) for 3b

W–C(1)	2.025(18)	C(12)–C(13)	1.39(3)
W–C(2)	2.010(16)	C(13)–C(14)	1.36(3)
W–C(3)	2.335(14)	C(14)–C(15)	1.378(24)
W–C(4)	2.175(15)	C(15)–C(16)	1.376(23)
W–C(5)	2.340(15)	C(21)–C(22)	1.370(20)
W–C(6)	2.509(13)	C(21)–C(26)	1.398(20)
W–C(31)	2.308(16)	C(22)–C(23)	1.404(21)
W–C(32)	2.294(18)	C(23)–C(24)	1.415(25)
W–C(33)	2.357(16)	C(24)–C(25)	1.307(23)
W–C(34)	2.283(16)	C(25)–C(26)	1.402(20)
W–C(35)	2.214(17)	C(31)–C(32)	1.39(3)
C(1)–O(1)	1.132(22)	C(31)–C(35)	1.38(3)
C(2)–O(2)	1.116(19)	C(32)–C(33)	1.414(23)
C(3)–C(4)	1.414(20)	C(33)–C(34)	1.352(23)
C(4)–C(5)	1.448(22)	C(34)–C(35)	1.376(23)
C(4)–C(6)	1.454(19)	B–F(1)	1.318(22)
C(6)–C(11)	1.522(21)	B–F(2)	1.382(22)
C(6)–C(21)	1.507(18)	B–F(3)	1.349(21)
C(11)–C(12)	1.385(20)	B–F(4)	1.320(21)
C(11)–C(16)	1.391(20)		
C(1)–W–C(2)	88.7(6)	W–C(4)–C(6)	85.0(9)
C(1)–W–C(3)	137.5(7)	C(3)–C(4)–C(5)	113.1(13)
C(1)–W–C(4)	103.6(7)	C(3)–C(4)–C(6)	122.7(14)
C(1)–W–C(5)	76.7(7)	C(5)–C(4)–C(6)	115.8(13)
C(1)–W–C(6)	91.7(6)	W–C(5)–C(4)	65.2(8)
C(2)–W–C(3)	88.6(6)	W–C(6)–C(4)	59.7(7)
C(2)–W–C(4)	102.3(6)	W–C(6)–C(11)	116.7(9)
C(2)–W–C(5)	76.5(6)	W–C(6)–C(21)	115.4(9)
C(2)–W–C(6)	135.9(6)	C(4)–C(6)–C(11)	120.4(11)
C(3)–W–C(4)	36.3(5)	C(4)–C(6)–C(21)	120.3(13)
C(3)–W–C(5)	61.4(5)	C(11)–C(6)–C(21)	113.5(10)
C(3)–W–C(6)	62.5(4)	C(6)–C(11)–C(12)	121.2(14)
C(4)–W–C(5)	37.2(6)	C(6)–C(11)–C(16)	120.4(12)
C(4)–W–C(6)	35.3(5)	C(6)–C(21)–C(22)	116.3(12)
C(5)–W–C(6)	60.8(5)	C(6)–C(21)–C(26)	122.7(12)
W–C(1)–O(1)	174.5(15)	F(1)–B–F(2)	109.0(15)
W–C(2)–O(2)	178.5(16)	F(1)–B–F(3)	108.1(16)
W–C(3)–C(4)	65.6(8)	F(1)–B–F(4)	113.6(15)
W–C(4)–C(3)	78.0(9)	F(2)–B–F(3)	107.8(15)
W–C(4)–C(5)	77.6(9)	F(2)–B–F(4)	107.8(16)
		F(3)–B–F(4)	110.4(14)

Results and Discussion

Syntheses of Tungsten Trimethylenemethane Complexes. We have reported the synthesis of the β-(chlorocarbonyl)allyl complex $Cp(CO)_2W(\eta^3\text{-}CH_2C(COCl)CH_2)$ (**1**)[7] from the reaction of $AlCl_3$ with the tungsten propargyl complex $Cp(CO)_3W(\eta^1\text{-}CH_2C{\equiv}CH)$,[10] in the presence of a Brøsted acid. In an analogous Mo propargyl complex, alkoxycarbonylation at the β-carbon of the propargyl ligand has been reported.[13] In the reaction of amine with the tungsten propargyl complex, C–C bond formation with the same regiosepcificity was observed.[7] Formation of **1** may thus proceed through the same intermediate, i.e., an η^2-allene complex from the protonation of the propargyl complex. Treatment of **1** with 2 equiv of MeLi in benzene followed by acid hydrolysis resulted in the formation of $Cp(CO)_2W(\eta^3\text{-}CH_2C(CMe_2OH)CH_2)$ (**2a**) in 84% isolated yield. In **2a**, the 2-propanol group is attached to the β-carbon of the allylic ligand. From the reaction of 2 equiv of C_6H_5Li with **1**, the diphenyl-substituted complex $Cp(CO)_2W(\eta^3\text{-}CH_2C(CPh_2)OH)CH_2)$ (**2b**), in 80% isolated yield, was similarly obtained. Use of the organolithium reagent always resulted in products where two nucleophiles were added to the allylic carbonyl position. Characterization of complexes **2a** and **2b** was accomplished through a combination of elemental analysis, mass spectrometry, and IR and ^1H and ^{13}C NMR spectroscopy. The sp^2 hybridization at the terminal CH_2 carbon of the allylic ligand of **2** is readily apparent upon inspection of the ^1H and ^{13}C NMR spectra. The allylic methylene protons of **2a** appeared as two well-resolved broad resonances at δ 2.98 and 1.88 assignable to the syn and anti protons, respectively. For **2b**, the corresponding syn and anti protons appear at δ 2.87 and 2.13, respectively.[7] On the basis of the chemical shift of these protons,[8] the endo conformation, which is generally observed in the β-substituted allylic compound, is assumed for both complexes **2a** and **2b**. In the ^1H NMR of **2a**, the hydroxyl proton is not observed due to exchange with trace D_2O in the solvent, and the resonance for the two equivalent methyl protons is a singlet.

In the reaction of nucleophiles with the metal allylic compound, the site of nucleophilic attack depends on metal and nucleophile. Attacks at the terminal and at the central carbon atom of the allylic ligand have both been observed.[14] The more electrophilic carbon center of the chlorocarbonyl group of **1** causes the nucleophilic attack to occur exclusively at the chlorocarbonyl carbon atom.

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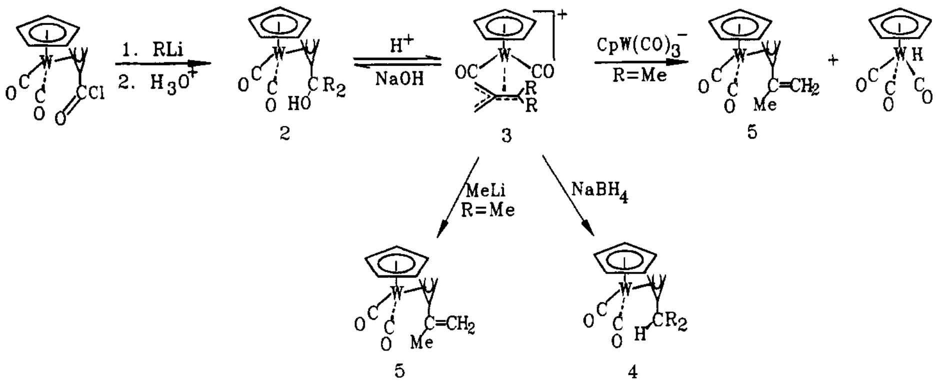
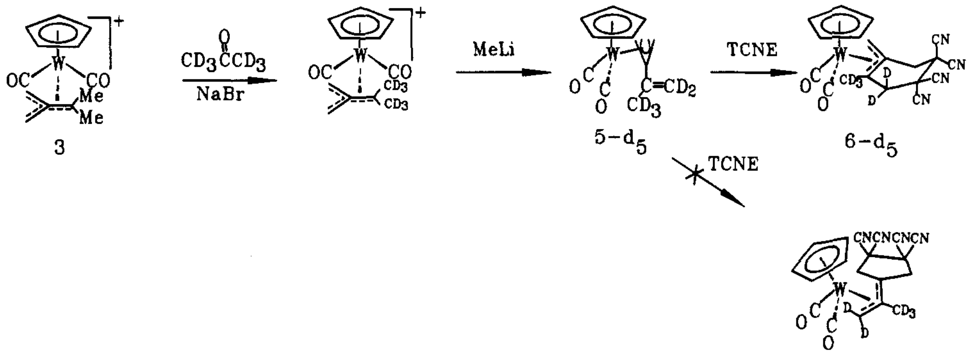
(13) (a) Roustan, J. L.; Guinot, A.; Cadiot, P. *J. Organomet. Chem.* **1980**, *194*, 357. (b) Collin, J.; Roustan, J. L.; Cadiot, P. *J. Organomet. Chem.* **1978**, *162*, 67.

(14) (a) Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887. (b) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *106*, 7272.

Scheme I



Scheme II



When complex **2a** was treated with HBF_4, an immediate dehydration reaction occurred, producing the orange, cationic complex $[Cp(CO)_2W(\eta^4\text{-}CH_2C(CMe_2)CH_2)]BF_4$ (**3a**) in high yield. The complex $[Cp(CO)_2W(\eta^4\text{-}CH_2C(CPh_2)CH_2)]BF_4$ (**3b**) is obtained from **2b** in a similar manner. Complexes **3a** and **3b**, in the solid state, are air-stable, and each contains an η^4-1,1-disubstituted trimethylenemethane ligand. Substituted-trimethylenemethane complexes of Mo,[8b] Fe,[15] and Ir[16] have been prepared from the ring opening of 2-substituted methylenecyclopropane. The ^1H and ^{13}C NMR spectral data for **3a** are consistent with that of an η^4-trimethylenemethane complex. Unequivocal confirmation of the structures of **3a** and **3b** was obtained by the X-ray diffraction analysis described below. In the ^1H NMR spectrum, the two methylene protons of **3a** appear as two broad signals at δ 3.24 and 2.92 which are assigned to the protons syn and anti with respect to the methyl groups, respectively. The methyl protons appear as a broad resonance at δ 2.16. From the 2D-COSY spectrum of **3a**, the long-range spin–spin couplings between the syn/anti ($^4J_{H-H}$) and anti/methyl ($^5J_{H-H}$) protons are clearly revealed.

Chemical Reaction of 1,1-Dimethyltrimethylenemethane Complex 3a. Cationic substituted-trimethylenemethane complexes are known to react readily with nucleophiles.[6,8b] Complex **3a** presents several possible sites for nucleophilic attack: i.e. the metal center, the coordinated CO, and the cyclopentadienyl and trimethylenemethane ligands. Attack at the trimethylenemethane ligand could occur either at one of the three peripheral carbons or at the central carbon atom. The reaction of **3a** with NaOH results in an addition of an OH unit to the more substituted peripheral carbon atom and reverses the reaction to give **2a** quantitatively (see Scheme I). The reaction proceeds in a regiospecific manner. Also, complex **3a** reacts with $NaBH_4$ in CH_3CN, giving the η^3-allyl complex $Cp(CO)_2W(\eta^3\text{-}CH_2C(CMe_2H)CH_2)$ (**4**), where the hydride attack also occurs specifically at the dimethyl-substituted peripheral carbon. In the ^1H NMR spectrum, the methyl protons of **4** appear as a doublet resonance at δ 1.14, and in the ^{13}C NMR spectrum, the tertiary carbon atom of the isopropyl group appears as a resonance at δ 30.5. In the reaction of a carbon nucleophile with an Mo unsubstituted trimethylenemethane complex, the C–C bond formation also takes place at the peripheral carbon atom. In contrast, nucleophilic attack occurs at the terminal CO in an Ir trimethylenemethane carbonyl complex.[6] The Mo analogue of **4** has been prepared in a different manner.[8b] Attempted alkylation of complex **3a** using methyllithium does not result in any methylation. Instead, methyllithium acts as a strong base and deprotonates one of the methyl protons to yield the η^3-β-(isopropenyl)allyl complex $Cp(CO)_2W(\eta^3\text{-}CH_2C(C(Me)(=CH_2))CH_2)$ (**5**). In the ^1H NMR spectrum of **5**, two resonances at δ 4.51 and 5.02 are assigned to the terminal vinyl protons and two broad resonances at δ 3.02 and 1.75 are typical for the syn and anti protons of the allylic group. The single resonance at δ 1.60 is assigned to the unique methyl group. In addition, in the IR spectrum of **5**, an absorption at 1640 cm^{-1} is assigned to the stretching of the double bond and, in the mass spectrum, the parent peak is 1 mass unit smaller than that of **4**. Weak bases such as amine and phosphine also cause deprotonation of **3a** and change the η^4-trimethylenemethane ligand to a β-substituted η^3-allylic ligand to give the same product. This deprotonation process is clearly revealed by the presence of the hydride $Cp(CO)_3WH$ in the reaction of **3a** with $Cp(CO)_3W^-$.

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(15) (a) Noyori, R.; Nishimura, T.; Takaya, H. *J. Chem. Soc. D* **1969**, 89. (b) Billups, W. E.; Lin, L. P.; Gansow, O. A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 637.

(16) Jones, M. D.; Kemmitt, R. D. W.; Platt, A. W. G.; Russell, D. R.; Sherry, L. J. S. *J. Chem. Soc., Chem. Commun.* **1984**, 673.

When **3a** was treated with a catalytic amount of NaBr in acetone-d_6, exchange of the methyl protons with deuterium atom of the solvent with $t_{1/2}$ = 5 min occurred, indicating high kinetic acidity of the methyl protons (see Scheme II). In this reaction, NaBr is required as a catalyst. No deuterium exchange can be observed in the absence of NaBr. The role of NaBr is not yet clear. No proton–deuterium exchange was found for the methylene protons of **3a**. The methyl protons of **4**, unlike those in **3a**, are no longer acidic.

Reaction of β-Isopropenylallyl Complex 5 with TCNE. Transition-metal allyl complexes with unsaturated functional groups at the α-carbon were found to have a rich chemistry in organic reactions.[6] Thus, we believed complex **5**, with a vinyl group at the β-carbon, should behave similarly. The cycloaddition of trimethylenemethane to alkenes can be envisaged as the Diels–Alder reaction for the synthesis of five-membered rings. This is an attractive ring system to synthesize due to the abundance of five-membered rings found in natural products such as the prostaglandins.[6] We use an activated olefin to explore the cycloaddition reaction of complex **5**. Two modes of cycloaddition are possible for **5**, namely [3 + 2] or [4 + 2] cycloaddition[7,8] to give a five- or a six-membered ring, respectively. Reaction of **5** with tetracyanoethylene (TCNE) in acetone at room temperature yields $Cp(CO)_2W(\eta^3\text{-}CH_2C(C_4H_4(CN)_4)CCH_3)$ (**6**). This reaction proceeds via a [4 + 2] cycloaddition pathway. The proposed product from [3 + 2] cycloaddition cannot be observed. In the ^1H NMR spectrum of **6**, a set of inequivalent geminal protons on th six-membered ring system appears at δ 3.22, 3.78 with a coupling constant $^2J_{H-H}$ = 15.6 Hz. Another set of geminal protons appears at δ 4.19, 4.82 with $^2J_{H-H}$ = 17.3 Hz. Two broad resonances at δ 1.29 and 2.48 are assigned as the anti and syn protons on the allylic terminal carbon. As mentioned before, the complex **5**-d_5 with deuterium labeled only at the β-isopropenyl group can be easily prepared. This D-labeled compound was used to distinguish two types of cycloaddition. As shown in Scheme II, the [3 + 2] cycloaddition of this D-labeled compound involves only the allylic ligand and is supposed to give a five-membered ring product in which both methylene units are CH_2. In contrast, the [4 + 2] cycloaddition involves half of the allylic ligand and the vinyl group and therefore should give a six-membered-ring product containing a CH_2 and a CD_2 group. In the ^1H NMR spectrum of **6** which is isolated from the cycloaddition reaction of TCNE with **5**-d_5, the pair of resonances at δ 3.22 and 3.78 disappear, indicating that the cycloaddition is [4 + 2] and involves the vinyl group and half of the allylic ligand.

Structure Description of $[Cp(CO)_2W(\eta^3\text{-}CH_2C(CMe_2)CH_2)]BF_4$ (3a) and $[Cp(CO)_2W(\eta^3\text{-}CH_2C(CPh_2)CH_2)]BF_4$ (3b). Although the spectroscopic data for **3a** and **3b** provided valuable structural information, the detailed bonding of the trimethylethylenemethane ligand to the metal center required an X-ray structure analysis. Therefore, both complexes **3a** and **3b** have also been characterized by single-crystal X-ray diffraction analysis and the results are illustrated in Figures 1 and 2, respectively. Figure 3 presents a perspective view of the cations of complexes **3a** and **3b**, down along the axis containing the center carbon of the trimethylenemethane and the metal center. The view reveals the "syn-staggered" conformation. Interatomic distances and angles for **3a** and **3b** are collected in Tables III and V, respectively.

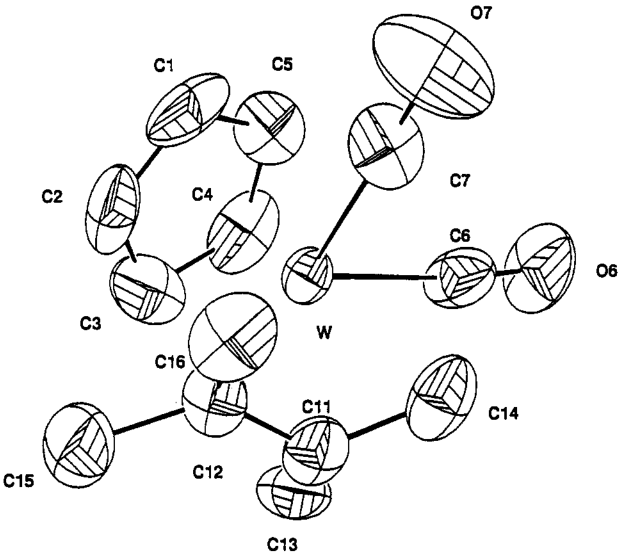

Figure 1. ORTEP drawing of complex **3a**.

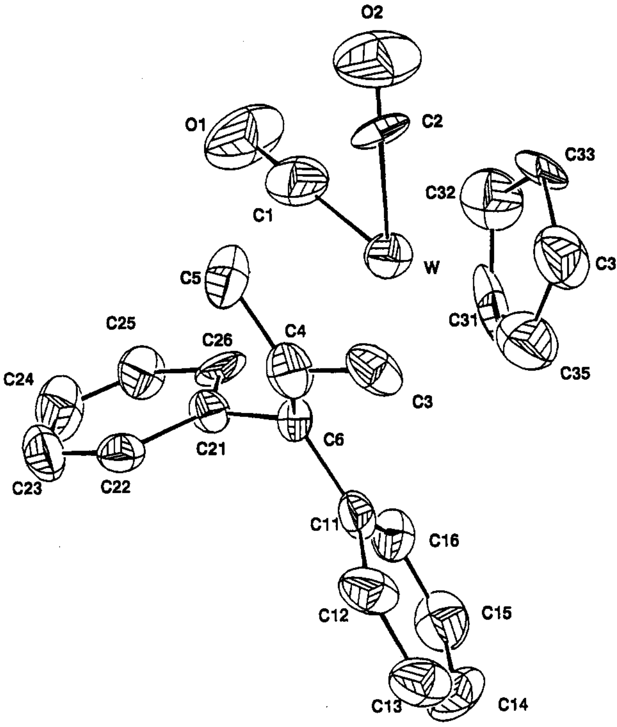

Figure 2. ORTEP drawing of complex **3b**.

The molecular structures of both **3a** and **3b** consist of a mononuclear cation and a BF_4 anion. In both complexes, the bond distances and angles within the anion, as well as the Cp groups of the cation, are typical and require no further comment. The coordination around the W atom involves the cyclopentadienyl ligand, two CO ligands, and four carbon atoms of the substituted trimethylenemethane group. From the ORTEP drawing, it is clear that the trimethylenemethane ligand is bonded to the metal in an η^4 fashion in both **3a** and **3b**. As shown in Figure 3, the $Cp(CO)_2W$ group occupies a staggered conformation relative to the peripheral carbon atoms of the trimethylenemethane ligand, and the more substituted carbon atom of the trimethylenemethane ligand is in a syn configuration with respect to the centroid of the Cp ligand, marked as "X" in Figure 3. While the gross features of **3a**

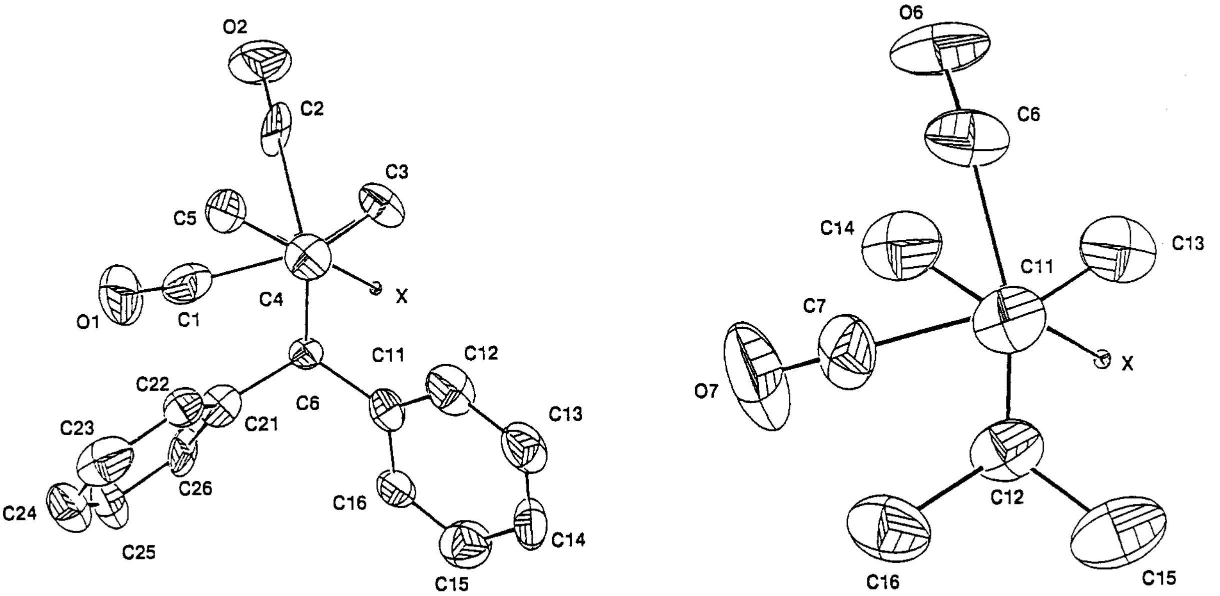

Figure 3. ORTEP drawings of complexes **3a** (right) and **3b** (left), with views down the axis containing the center C of the trimethylenemethane and the metal.

Table VI. Comparison of Structural Data for Metal Trimethylenemethane Complexes

	3a	3b	MoTMM[8c]	FeTMMPh[17a]	FeTMMCy[17b]	FeTMM[8a]	IrTMM[8b]
M–C(t),[a] Å	2.50(1) 2.34(1) 2.32(1)	2.51(1) 2.34(2) 2.34(1)	2.392(11) 2.358(9) 2.324(9)	2.162(9) 2.118(10) 2.098(11)	2.192(3) 2.175(3) 2.120(3)	2.123(5)	2.288(15) 2.201(12) 2.173(15)
M–C(c),[b] Å	2.19(1)	2.18(2)	2.213(10)	1.932(10)	1.946(2)	1.938(5)	2.053(12)
C(c)–C(t), Å	1.44(2) 1.43(2) 1.38(2)	1.45(2) 1.45(2) 1.41(2)	1.46(2) 1.40(2) 1.39(1)	1.44(1) 1.41(1) 1.41(1)	1.428(5) 1.412(4) 1.405(4)	1.437(3)	
C(t)–C(s),[a] Å	1.50(2) 1.52(2)	1.51(2) 1.52(2)		1.47(1)	1.408(6) 1.456(5)		
θ,[d] deg	13.3(7) 12.7(7) 4.3(8)	13.4(9) 12.0(9) 5.0(9)	14.6(5) 12.0(6) 10.6(6)	13.9(6) 13.0(6) 11.7(5)	13.9(2) 11.0(1) 10.1(2)	13.6(2)	14.0(8)
C(t)–C(c)–C(t), deg	120(1) 120(1) 111(1)	123(1) 116(1) 113(1)	119(1) 115(1) 112(1)	116.2(9) 115.0(8) 114.4(8)	119.9(2) 114.9(3) 113.4(3)	114.6(2)	
d	0.245(16)	0.242(19)		0.315	0.285		

[a] C(t) is the outer carbon atom of the trimethylenemethane ligand. [b] C(c) is the central carbon atom of the trimethylenemethane ligand. [c] C(s) is the α-carbon atom of the substituted group on the trimethylenemethane ligand. [d] θ is defined as 90 − ∠(M–C(c)–C(t)).

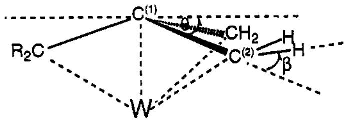

Figure 4.

and **3b** are similar, the details of the trimethylenemethane ligand on the metal coordination spheres are not.

The complexed trimethylenemethane ligands in **3** are both pyramidal, not planar as observed in other trimethylenemethane complexes.[8] The reasons for pyramidalization have been well-documented, and they may be quantified by the two angular parameters θ and β shown in Figure 4, where β is the angle between the line C(1)–C(2) and the plane C(2)H_2. The trigonal-pyramidal conformation of the trimethylenemethane residue in **3a** is emphasized by the angles W–C(11)–C(12), W–C(11)–C(13), and W–C(11)–C(14), which are 85.7(8), 77.7(7) and 76.7(7)°, (in θ scale 4.3, 12.3, and 13.3°), respectively, with the more substituted carbon C(12) lying farther away from the metal center and thus having a much smaller θ value. The corresponding angles are 85.0(9), 78.0(9), and 77.6(9)° for **3b**; again, the more substituted carbon gives much a smaller θ values. The central carbon atom is displaced 0.25(2) and 0.24(2) Å for **3a** and **3b**, respectively, away from the metal atom relative to a plane which passes through the three peripheral carbon atoms of the trimethylenemethane ligand. The pyramidalization of the trimethylenemethane fragment is insufficient to cause the distal carbon atoms to approach closer to the metal than does the central one. It is interesting to note that the trimethylenemethane ligand is not symmetrically bound to the tungsten metal center, with the W–C bond lengths apparently reflecting the differing steric influences of the substituents. The substituents cause a considerable increase of the M–C distance, as shown in Table VI. Disubstitution has a more pronounced effect than monosubstitution, as can be seen in the Fe(CO)$_3$ group, where monosubstitution causes only slight elongation of the M–C distance.[17] Carbon–carbon distances within the trimethylenemethane moiety are C(11)–C(12) = 1.38(2), C(11)–C(13) = 1.43(2), and C(11)–C(14) = 1.44(2) Å in **3a** and

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(17) (a) Churchill, M. R.; Gold, K. *Inorg. Chem.* **1969**, *8*, 401. (b) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1973**, *12*, 525.

C(3)–C(4) = 1.41(2), C(4)–C(5) = 1.45(2), and C(4)–C(6) = 1.45(2) Å in **3b**. Interatomic angles for **3a** are C(12)–C(11)–C(13) = 120.2(11), C(12)–C(11)–C(14) = 120.0(12), and C(13)–C(11)–C(14) = 111.0(10)°. The comparable angles in **3b** are 122.7(14), 115.8(13), and 113.1(13)°. Also in **3b**, the phenyl groups are not fully conjugated with the trimethylenemethane ligand, as can be seen from the following measurements: the C(6)–C(11) or C(6)–C(21) bond distance of 1.52(2) or 1.51(2) Å is not distinguishable from the C(sp^2)–C(sp^2) single-bond distance of 1.51 Å.[18] The structural parameters of several metal trimethylenemethane complexes are listed in Table VI for comparison.

The C–W–C bond angles between carbonyl groups are 88.3(5) and 88.7(6)° for **3a** and **3b**, respectively, which is comparable to 88.9(4)° found in Mo–trimethylenemethane complexes.[8b] The W–C–O angles range from 173.8(12) to 179.5(10)° for **3a** and 174.5(15) to 178.5(16)° for **3b** with W–CO = 2.01(1)–2.02(1) Å for **3a**, 2.01(2)–2.02(2) Å for **3b**, and C–O = 1.12(2)–1.14(2) Å.

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Supplementary Material Available: Tables of H atom positional parameters, all bond distances and angles, and anisotropic thermal parameters for both **3a** and **3b** (8 pages). Ordering information is given on any current masthead page.

OM920713T

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(18) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; Special Publication No. 18; The Chemical Society: London, 1965; Supplement 1956–1959, p S15s.