Reaction of a Tungsten(II) Methylene Complex with Excess Base To Form a C₃H₅-Bridged Dimer

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Reaction of $[Tp'(CO)(PhC_2Me)W=CH_2][PF_6]$ (**1**) with excess base (NaOH/H₂O or KH) in methylene chloride yields the C_3H_5-bridged dimer $[Tp'(CO)(PhC_2Me)WCH_2C(H)CH_2W(PhC_2Me)(CO)Tp'][PF_6]$ (**2**). Dimer **2** is reproducibly formed in yields of 10−15%; it is inert toward a variety of nucleophiles. Structural and spectroscopic features of **2** form the basis for a discussion of the bonding in this unusual complex. Bonding extremes for the hydrocarbon bridge include an allylic C_3H_5 fragment bound to the two tungsten centers through opposite faces of the allyl ligand, a linkage which is σ-bonded at each metal with a carbocationic central carbon, and a σ,π-bridging system. Metric parameters in the solid state and ¹H, ¹³C NMR and infrared spectroscopies suggest that the dominant resonance contribution derives from the allylic formalism. A surrogate solvent (1,2-dichloroethane) results in no observable change in the reaction, and thus, the methide source needed to link the two monomeric fragments is believed to originate from the carbene complex.

Introduction

Polymetallic transition metal complexes bridged by hydrocarbons are important in a variety of chemical processes.[1] A wide array of bi- and trimetallic complexes with σ,π-bridging ligands have been synthesized.[2] Of particular importance here are $C_3H_{5-n}R_n$-bridged dimers (R = H, alkyl, or halogen) such as the dicarbonylcyclopentadienyliron dimer reported in 1967 by King and Bisnette.[3]

One methodology for the preparation of $C_3H_{5-n}R_n$-bridged dimers is net hydride removal from a saturated hydrocarbon linkage. Thus, treatment of $Fp(CH_2CH_2CH_2)Fp$ (Fp = CpFe(CO)₂) (**I**) with triphenylcarbenium hexafluorophosphate (trityl cation) yields the cationic complex $[Fp(\mu-C_3H_5)Fp][PF_6]$ (**II**) (Scheme 1).[3] Similarly, addition of the trityl cation to the 1,3-propanediyl-bridged heterobimetallic complex $[Fp(CH_2)_3Mo(CO)_3Cp]$ (**III**) results in net hydride abstraction from the hydrocarbon bridge (Scheme 1).[4] The iron−ruthenium analog of **I** combined with trityl cation yields a cationic complex displaying spectral features resembling those of the Fp dimer **II**.[4]

Other routes to $C_3H_{5-n}R_n$-bridged dimers have been developed. For example, the reaction of $[CpMo(CO)(NO)(\eta^3\text{-allyl})][PF_6]$ with $[Na][Re(CO)_5]$ yields the C_3H_5-bridged complex $Cp(CO)(NO)Mo(\mu-C_3H_5)Re(CO)_5$ (Scheme 1).[5] Decomposition of the ethylidene carbene complex $[Cp(L)(CO)Fe=C(H)CH_3]^+$ (L = CO, P(OPh)₃) forms, among other products, the monocationic dimer $[Cp(L)-$ $(CO)Fe[\mu-CH_2C(H)C(Me)(H)]Fe(CO)(L)Cp]^+$ (**IV**) (Scheme 2).[6] Mechanistic speculation involves electrophilic attack of the ethylidene carbene on the β-carbon of the vinyl ligand of $Cp(L)(CO)Fe−C(H)=CH_2$ followed by rearrangement to **IV**.

We have previously communicated the synthesis and reactivity of the persistent methylene complex $[Tp'(CO)(PhC_2Me)W=CH_2][PF_6]$ (**1**).[7] Carbene **1** reacts with excess NaOH/H₂O or KH in methylene chloride to produce the C_3H_5-bridged dimer $[Tp'(CO)(PhC_2Me)W-(\mu-C_3H_5)W(PhC_2Me)(CO)Tp'][PF_6]$ (**2**) in low yields. The spectral and structural characteristics of **2** are discussed here along with mechanistic investigations.

Experimental Section

General Considerations. All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Infrared spectra were recorded on a Mattson Polaris FT-IR spectrometer. All NMR experiments and spectra were recorded on a Varian XL-400 spectrometer. ¹H and ¹³C NMR chemical shifts were referenced to residual ¹H signals and to the ¹³C signals of the deuterated methylene chloride.

$Tp'(CO)(PhC_2Me)WMe^8$ and $[Tp'(CO)(PhC_2Me)W=CH_2][PF_6]^7$ (**1**) were prepared according to literature methods. Methylene chloride and hexanes were purified under a dry argon atmosphere by passage through a column packed with activated alumina.[9] THF was distilled under a dry nitrogen atmosphere from sodium benzophenone ketyl. The solvent 1,2-dichloroethane was stirred over basic alumina (∼1 g/L), cannula-filtered into a flask containing P₂O₅, and distilled. Deuterated methylene chloride was deoxygenated by several freeze−

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(1) For a recent review of hydrocarbon-bridged metal complexes, see: Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 923.

(2) Lotz, S.; Van Rooyen, P. H.; Meyer, R. *Adv. Organomet. Chem.* **1995,** *37,* 219.

(3) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967,** *7,* 311.

(4) Friedrich, H. B.; Moss, J. R. *J. Chem. Soc., Dalton Trans.* **1993,** 2863.

(5) Müller, H.; Nagel, U.; Beck, W. *Organometallics* **1987,** *6,* 193.

(6) Bodnar, T.; Cutler, A. R. *J. Organomet. Chem.* **1981,** *213,* C31.

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(8) Caldarelli, J. L.; Wagner, L. E.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1994,** *116,* 2878.

(9) For further information concerning the purification of solvents using activated alumina, see: Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996,** *15,* 1518.

Scheme 1. Representative Examples of the Formation of C_3H_5-Bridged Dimers
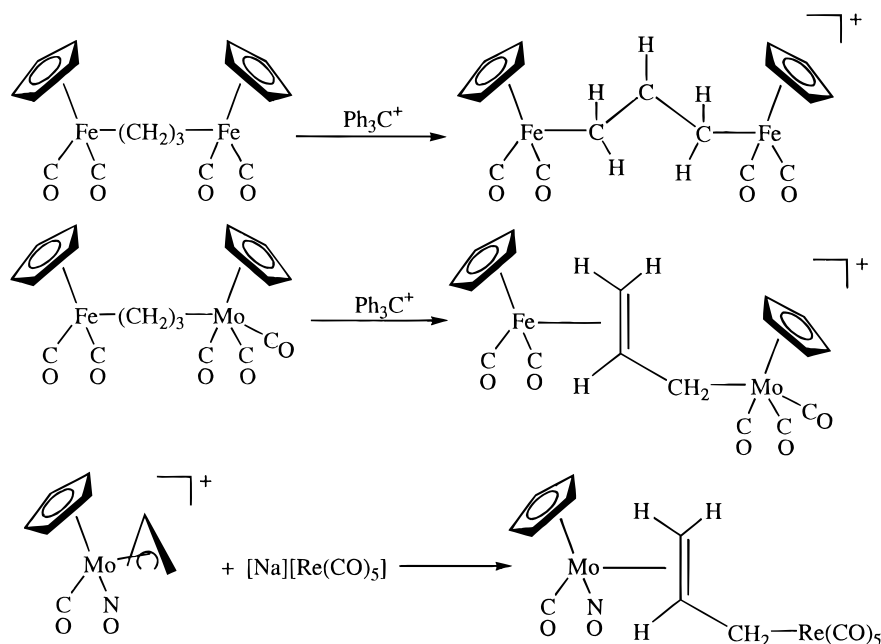
Scheme 2. Proposed Mechanism for the Formation of $[Cp(L)(CO)FeCH_2C(H)C(Me)Fe(CO)(L)Cp]^+$ (IV) via Decomposition of an Iron Ethylidene Carbene (L = CO, P(OPh)$_3$)

IV
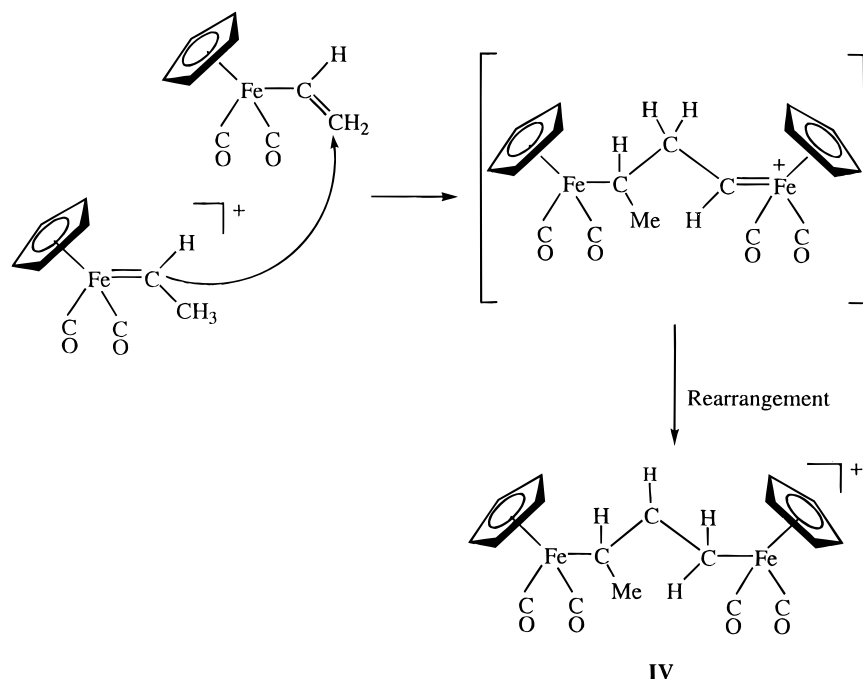
pump–thaw cycles and stored under a nitrogen atmosphere over 4 Å (8–12 mesh) molecular sieves. All solvents were purged with nitrogen prior to use. Triphenylcarbenium hexafluorophosphate, NaOH/H$_2$O, and potassium hydride were used as purchased from commercial sources.

[Tp′(CO)(PhC$_2$Me)WCH$_2$C(H)CH$_2$W(PhC$_2$Me)(CO)Tp′]-[PF$_6$] (2). Method A. In a solution of cold (−78 °C) methylene chloride, 1 equiv of triphenylcarbenium hexafluorophosphate was added to a known amount of Tp′(CO)(PhC$_2$Me)WCH$_3$. Upon addition of the trityl cation, the solution turned from deep blue to reddish-brown in color, indicating formation of [Tp′(CO)(PhC$_2$Me)W=CH$_2$][PF$_6$] (**1**). After 10 min, an excess of NaOH/H$_2$O was syringed into the solution. The resulting mixture was stirred overnight at room temperature, during which time a color change from reddish-brown to aqua-blue was noted. Solvent removal under reduced pressure followed by purification via alumina chromatography allowed isolation

of a blue-green oil. Dissolution of the oil in methylene chloride followed by layering with hexanes resulted in the formation of deep green crystals of dimer **2** (10–15% yield). IR (ν_{CO}) (KBr) 1905 cm^{-1}; (CH$_2$Cl$_2$) 1914 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, δ): 9.85 (1H, m {seven-line pattern}, $^3J_{HH}$ = 13, 6 Hz, [W]CH$_2$C-(H)CH$_2$[W]), 7.20, 6.40 (10 H, 3:2, phenyl Hs), 6.10, 5.97, 5.71 (6H, 1:1:1, Tp′CH), 3.16 (6H, PhC$_2$CH_3), 3.03, 2.61, 2.47, 2.44, 1.30, 1.20 (36 H,1:1:1:1:1:1, Tp′CCH_3), 1.90 (2H, d of d, $^3J_{HH}$ = 13, $^2J_{HH}$ = 6 Hz, [W]C(H)(H)CHC(H)(H)[W]), 1.62 (2H, t, $^3J_{HH}$ = $^2J_{HH}$ = 6 Hz, [W]C(H)(H)CHC(H)(H)[W]). ^{13}C NMR (CD$_2$-Cl$_2$, δ): 234.6 ($^1J_{WC}$ = 140 Hz, CO), 212.7, 211.1 (PhC$_2$Me), 157.8 (d, $^1J_{CH}$ = 160 Hz, [W]CH$_2$$C$(H)CH$_2$[W]), 153.4, 152.9, 150.5, 146.6, 146.2, 145.5 (Tp′CCH$_3$), 136.8, 129.9, 129.1, 128.3 (phenyl Cs), 109.4, 109.2 107.7 (Tp′ CH), 58.1 (t, $^1J_{CH}$ = 140 Hz, $^1J_{WC}$ = 42 Hz, ^{183}W (14% abundance), I = $^1/_2$, [W]CH$_2$C-(H)CH$_2$[W]), 21.4, 16.2, 16.1, 15.5, 13.1, 13.0, 12.8 (Tp′ CCH_3 and alkyne CH$_3$). Anal. Calcd for [Tp′(CO)(PhC$_2$Me)WCH$_2$-

C(H)CH₂W(PhC₂Me)(CO)Tp′][PF₆]; C₅₃H₆₅N₁₂B₂F₆O₂P₁W₂: C, 44.32; H, 4.56; N 11.70. Found: C, 44.41; H, 4.61; N, 11.64.

Method B. The procedure from Method A is followed, except KH is used in place of NaOH/H₂O (10% yield).

Method C. The procedure from Method A is followed, except 1,2-dichloroethane is used as the solvent (14% yield).

X-ray Structure Determination of 2. Slow diffusion of hexanes into a methylene chloride solution of **2** yielded deep green crystals. A suitable crystal (dimensions 0.35 × 0.35 × 0.40 mm) was selected for a single-crystal X-ray diffraction study. The selected crystal was monoclinic ($P2_1/n$) with the unit cell dimensions determined from 36 reflections: $a = 11.392(3)$ Å, $b = 19.359(7)$ Å, $c = 27.559(6)$ Å; $\beta = 99.987(22)°$; $V = 5986(3)$ Å³; $Z = 4$; fw = 1521.38; density(calcd) = 1.688 g/cm³. Data were collected at -100 °C on a Rigaku diffractometer using Mo Kα radiation ($\lambda = 0.717\,03$ Å). The total number of reflections measured was 8258 (max $h, k, l = 12, 21, 30$) resulting in 5851 unique reflections with $I > 2.5\sigma(I)$.

Results and Discussion

Synthesis and Spectral Characterization. Addition of trityl cation to a methylene chloride solution of Tp′(CO)(PhC₂Me)WCH₃ yields the methylene carbene [Tp′(CO)(PhC₂Me)W=CH₂][PF₆] (**1**).[7] Carbene **1** slowly reacts with excess NaOH/H₂O or KH to give a blue-green solution. The tungsten dimer [Tp′(CO)(PhC₂-Me)W(μ-C₃H₅)W(PhC₂Me)(CO)Tp′][PF₆] (**2**) is formed in low yields, along with intractable products (eq 1).
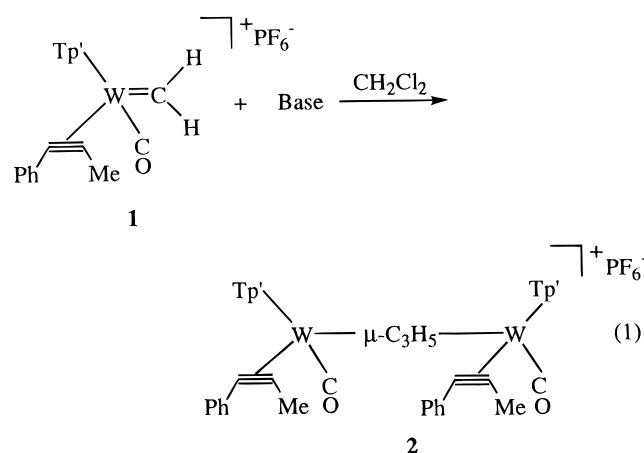
Purification by chromatography on alumina, followed by layering of a CH₂Cl₂ solution of **2** with hexanes, reproducibly forms green, air-stable crystals in 10−15% yield.

The IR spectrum of **2** displays a single CO stretching frequency at 1905 cm⁻¹, and any bonding description will need to be consistent with the apparent electronic equivalence of the two metal centers. The ¹H NMR of **2** in CD₂Cl₂ reveals characteristic features for the Tp′ and alkyne moieties along with a seven-line pattern at low-field (9.8 ppm) and resonances at 1.9 and 1.6 ppm (a doublet of doublets and a triplet, respectively), which integrate for a ratio of 1:2:2. The downfield multiplet (9.8 ppm) is not a true septet, but rather a seven-line pattern with intensities expected from coupling to two inequivalent sets of two protons with approximately a 2:1 ratio of coupling constants (Figure 1).

Homonuclear decoupling experiments were useful in assigning the proton coupling constants. Irradiation of the resonance at 1.9 ppm resulted in a triplet ($J_{HH} = 6$ Hz) at 9.8 ppm and a doublet ($J_{HH} = 6$ Hz) at 1.6 ppm.
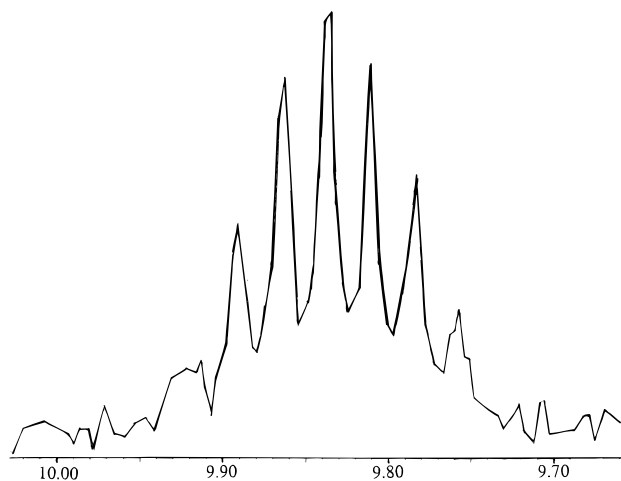
Figure 1. Proton NMR of [Tp′(CO)(PhC₂Me)W(μ-C₃H₅)-W(PhC₂Me)(CO)Tp′][PF₆] (**2**) between 9.70 and 10.00 ppm, illustrating the seven-line pattern due to the central proton of the bridging unit.

Degradation of the signal at 1.6 ppm produced a triplet ($J_{HH} = 13$ Hz) at 9.8 ppm and a doublet ($J_{HH} = 6$ Hz) at 1.9 ppm. Irradiation of the downfield multiplet at 9.8 ppm collapsed both upfield signals into doublets ($J_{HH} = 6$ Hz). Therefore, three coupling constants (one of 13 Hz and two of 6 Hz) are inferred.

The ¹³C NMR spectrum of **2** reveals a doublet which resonates at 157.8 ppm ($^1J_{CH} = 160$ Hz) and a triplet at 58.1 ppm with tungsten satellites observed in the proton decoupled spectrum ($^1J_{CH} = 140$ Hz; $^1J_{WC} = 42$ Hz; ¹⁸³W, 14% abundance, $I = \frac{1}{2}$).

On the basis of the spectroscopic and structural (*vide infra*) information, we formulate the product as a C₃H₅-bridged dimer ([W]−(CH₂−C(H)−CH₂)−[W]). The low-field doublet (157.8 ppm) in the ¹³C spectrum is assigned to the central carbon of the bridge, while the triplet at 58.1 ppm is attributed to the two equivalent terminal methylene carbons. The three sets of proton resonances mentioned above (9.8, 1.9, and 1.6 ppm) are assigned to the μ-C₃H₅ unit. Due to the chiral metal center, each set of methylene protons is diastereotopic. However, on the basis of the chemical shifts and coupling patterns, protons on opposite methylene groups are pairwise equivalent. In other words, there is either a C_2 axis or a mirror plane through the central carbon of the bridging unit. The observation of only a single diastereomer in ¹H and ¹³C NMR spectra and an X-ray crystal structure of **2** (*vide infra*) with approximate C_2 molecular symmetry demonstrate the two metal centers' predilection for coupling metal stereocenters of the same configuration, either R,R or S,S.

X-ray Crystal Structure of 2. Crystallographic data and selected bond distances and angles for **2** are summarized in Tables 1 and 2, and labeled ORTEP diagrams are shown in Figures 2 and 3. As mentioned above, the two tungsten centers are related by a C_2 axis of rotation which bisects the central carbon of the hydrocarbon bridge. The X-ray structure confirms the proclivity of two metal centers with identical absolute configurations to combine; i.e., only the R,R or S,S confirmations are observed. What are the geometric features of the [W]−CH₂C(H)CH₂−[W] moiety? Bond distances of 2.240(10) and 2.232(9) Å for the W(1)−C(91) and W(2)−C(93) bonds, respectively, are typical for tungsten−carbon single bonds.[10] The bond distances
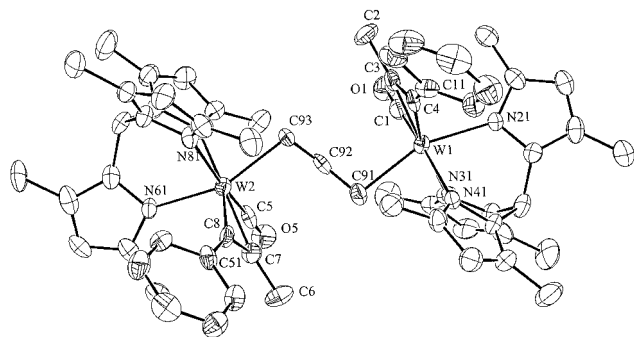
Figure 2. ORTEP diagram for [Tp′(CO)(PhC₂Me)W(μ-C₃H₅)W(PhC₂Me)(CO)Tp′][PF₆] (**2**), counterion and solvent have been omitted for clarity.

**Table 1. Crystallographic Data for
[Tp′(CO)(PhC₂Me)W(μ-C₃H₅)W(PhC₂Me)(CO)Tp′]-
[PF₆] (2)**

formula	$C_{54}H_{67}B_2Cl_2F_6N_{12}O_2PW_2$
mol wt	1521.38
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	11.392(3)
b, Å	19.359(7)
c, Å	27.559(6)
β, deg	99.987(22)
V, Å³	5986(3)
Z	4
D_{calcd}, g cm⁻³	1.688
$F(000)$	3001.68
cryst dimens, mm	0.35 × 0.35 × 0.40
temp, °C	−100
radiation (λ, Å)	Mo Kα (0.710 73)
2θ range, deg	5.00 < θ < 45.00
μ, mm⁻¹	4.11
scan mode	ω
total no. of data	8258
total no. of unique data	8245
no. of obsd data ($I > 2.5\sigma(I)$)	5851
R_F	0.041
R_w	0.045
GOF	1.35

between each tungsten atom and the central carbon of the hydrocarbon bridge (2.846(10), 2.857(10) Å) imply little direct electronic participation between the two metal centers and the central carbon. The C(91)−C(92)−C(93) bond angle is 126.4(9)°, while the W−C−C angles are 100.2(6)° and 99.7(6)°.

Discussion of Bonding for 2. Three possible resonance structures corresponding to two σ,π conformations and a β-carbocation bridge were proposed for the Fp dimer analog (**II**) (Scheme 3).[4,11] Detailed variable-temperature NMR studies of **II** and related complexes suggested that carbocation structure **IIB** may contribute significantly.[11] Subsequently, a single-crystal X-ray structural study of **II** supported this conclusion, while showing that the carbocation center could be stabilized via interaction with the two nearby metal centers.[12] In addition, the iron−ruthenium analog of **II** displays spectral features consistent with the Fp dimer **II**.[5]

(10) See, for example: (a) Schrock, R. R.; Kolodziej, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338. (b) O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331. (c) Schrock, R. R.; Glassman, T. E.; Vale, M. G.; Kol, M. *J. Am. Chem. Soc.* **1993**, *115*, 1760. (d) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282.

(11) Kerber, R. C.; Giering, W. P.; Bauch, T.; Waterman, P.; Chou, E. *J. Organomet. Chem.* **1976**, *120*, C31.

(12) Laing, M.; Moss, J. R.; Johnson, J. *J. Chem. Soc., Chem. Commun.* **1977**, 656.
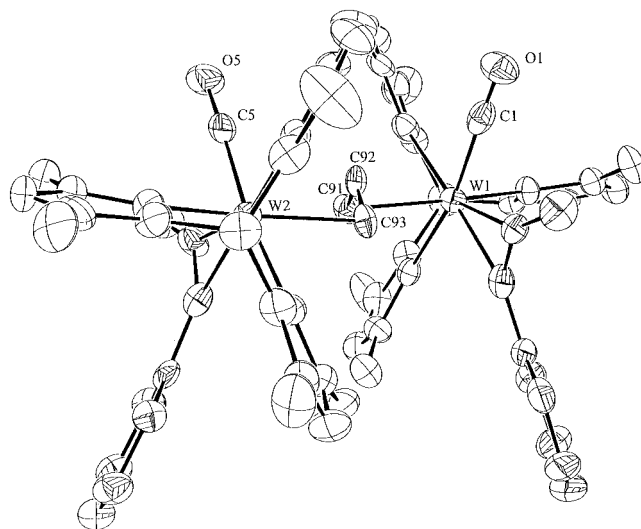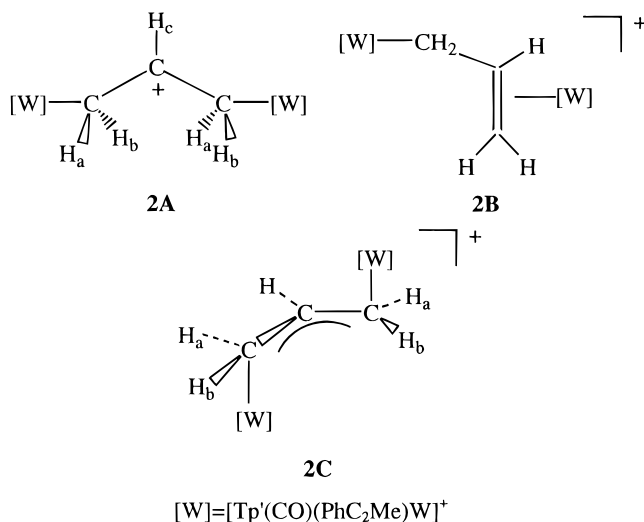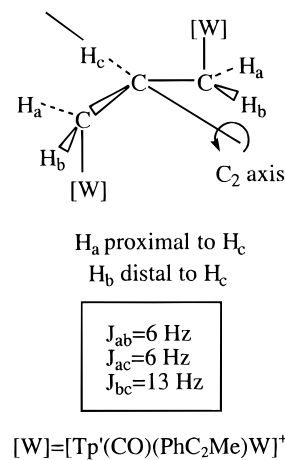

Figure 3. ORTEP diagram for [Tp′(CO)(PhC₂Me)W(μ-C₃H₅)W(PhC₂Me)(CO)Tp′][PF₆] (**2**), counterion and solvent have been omitted for clarity.

**Table 2. Selected Bond Distances and Bond Angles for
[Tp′(CO)(PhC₂Me)W(μ-C₃H₅)W(PhC₂Me)(CO)Tp′]-
[PF₆] (2)**[a]

W(1)−C(1)	1.966(12)	W(2)−N(81)	2.253(8)
W(1)−C(3)	2.036(10)	W(2)−C(92)	2.857(10)
W(1)−C(4)	2.023(11)	W(2)−C(93)	2.232(9)
W(1)−N(21)	2.171(7)	C(1)−O(1)	1.158(14)
W(1)−N(31)	2.262(8)	C(2)−C(3)	1.494(15)
W(1)−N(41)	2.247(8)	C(3)−C(4)	1.302(15)
W(1)−C(91)	2.240(10)	C(4)−C(11)	1.471(15)
W(1)−C(92)	2.846(10)	C(5)−O(5)	1.165(14)
W(2)−C(5)	1.940(11)	C(6)−C(7)	1.467(15)
W(2)−C(7)	2.042(10)	C(7)−C(8)	1.302(14)
W(2)−C(8)	2.007(10)	C(8)−C(51)	1.460(14)
W(2)−N(61)	2.171(8)	C(91)−C(92)	1.419(15)
W(2)−N(71)	2.246(8)	C(92)−C(93)	1.433(14)

C(1)−W(1)−C(4)	106.9(4)	C(8)−W(2)−N(61)	90.0(3)
C(1)−W(1)−N(21)	95.2(4)	C(8)−W(2)−N(71)	162.1(3)
C(1)−W(1)−N(31)	85.1(4)	C(8)−W(2)−N(81)	83.4(4)
C(1)−W(1)−N(41)	167.8(4)	C(8)−W(2)−C(93)	104.3(4)
C(1)−W(1)−C(91)	97.1(4)	N(61)−W(2)−N(71)	78.0(3)
C(1)−W(1)−C(92)	71.7(4)	N(61)−W(2)−N(81)	85.0(3)
C(3)−W(1)−N(21)	99.0(3)	N(61)−W(2)−C(93)	158.9(3)
C(3)−W(1)−N(31)	154.5(4)	N(71)−W(2)−N(81)	82.4(3)
C(3)−W(1)−N(41)	122.3(3)	N(71)−W(2)−C(93)	84.2(3)
C(3)−W(1)−C(91)	101.9(4)	N(81)−W(2)−C(93)	81.5(3)
C(4)−W(1)−N(21)	91.5(3)	W(1)−C(1)−O(1)	177.6(9)
C(4)−W(1)−N(31)	165.3(4)	W(1)−C(3)−C(2)	150.0(8)
C(4)−W(1)−N(41)	85.3(4)	C(2)−C(3)−C(4)	139.2(10)
C(4)−W(1)−C(91)	101.8(4)	W(1)−C(4)−C(11)	147.8(8)
N(21)−W(1)−N(31)	78.8(3)	C(3)−C(4)−C(11)	139.4(10)
N(21)−W(1)−N(41)	84.7(3)	W(2)−C(5)−O(5)	176.4(9)
N(21)−W(1)−C(91)	158.4(3)	W(2)−C(7)−C(6)	151.0(8)
N(31)−W(1)−N(41)	82.9(3)	C(6)−C(7)−C(8)	139.2(10)
N(31)−W(1)−C(91)	84.6(3)	W(2)−C(8)−C(51)	149.9(7)
N(41)−W(1)−C(91)	79.5(3)	C(7)−C(8)−C(51)	136.0(10)
C(5)−W(2)−C(8)	106.2(4)	W(1)−C(91)−C(92)	99.7(6)
C(5)−W(2)−N(61)	95.1(3)	W(1)−C(92)−W(2)	160.0(4)
C(5)−W(2)−N(71)	88.2(4)	W(1)−C(92)−C(91)	50.9(5)
C(5)−W(2)−N(81)	170.4(4)	W(1)−C(92)−C(93)	118.5(6)
C(5)−W(2)−C(93)	95.5(4)	W(2)−C(92)−C(91)	118.6(6)
C(7)−W(2)−N(61)	99.2(4)	W(2)−C(92)−C(93)	50.3(5)
C(7)−W(2)−N(71)	157.1(3)	C(91)−C(92)−C(93)	126.4(9)
C(7)−W(2)−N(81)	120.3(3)	W(2)−C(93)−C(92)	100.2(6)
C(7)−W(2)−C(93)	101.6(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

The dimer [Fp(μ-CH₂C(H)CH₂)Mo(CO)₃Cp][PF₆] displays spectral and structural features more consistent with a hybrid of the three previously described struc-

Scheme 3. Three Possible Resonance Structures for [Fp(μ-C₃H₅)Fp][PF₆] (II)

IIA   **IIC**

IIB
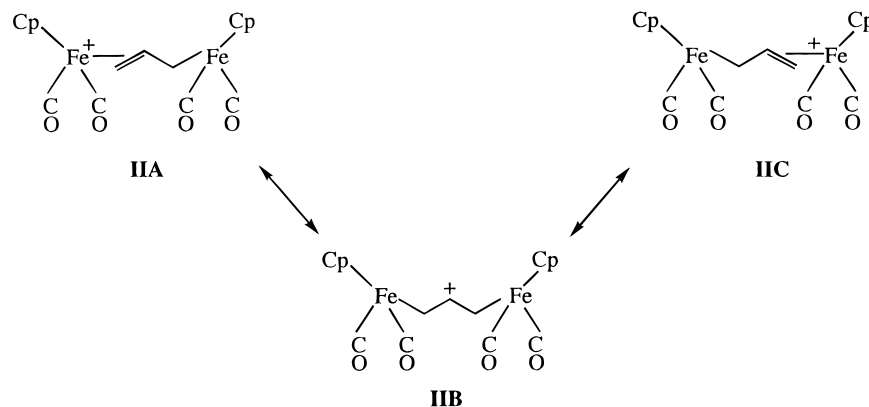
Scheme 4. Three Proposed Structures for Dimer 2

2A   **2B**

2C

[W]=[Tp'(CO)(PhC₂Me)W]⁺

Scheme 5. Hydrogen Coupling Constants for the C₃H₅ Bridge for Dimer 2

H_a proximal to H_c
H_b distal to H_c

$J_{ab}=6$ Hz
$J_{ac}=6$ Hz
$J_{bc}=13$ Hz

[W]=[Tp'(CO)(PhC₂Me)W]⁺

tural forms with more π character for the carbons positioned next to iron (**IIA** and **IIC** in Scheme 3).[5] Similarly, the C_3H_5 bridge of the complex Cp(CO)(NO)-Mo(μ-C_3H_5)Re(CO)₅ is clearly bound to the metals through a σ bond at rhenium and a π bond at molybdenum.[6] Apparently, metal differentiation results in more σ,π character for these complexes than is observed for the cation **II**.

Examination of the bonding in dimer **2** presents some ambiguities. Three extreme bonding situations are proposed in Scheme 4. Structures **2A** and **2B** have been discussed for the dimer **II** (*vide supra*) and correspond to a C_3 bridge with a carbocation at the central carbon and a σ,π bridge, respectively. The third possibility (**2C**) is an allyl species bound to each metal through opposite faces of the allyl moiety. In this case, bonding presumably occurs primarily through the terminal carbons, which are canted toward each respective metal center in the solid state structure of **2** (*vide supra*).

The existence of a carbocation seems unlikely given the reluctant reactivity of **2**. Complex **2** is relatively inert, as exhibited by its stability in air and on an alumina column, lack of decomposition in solution for indefinite periods of time, and failure to react with nucleophiles such as MeLi, LiEt₃BH, n-BuLi, NaOMe, and NaOH. Degradation of dimer **2** occurs upon reaction with [Et₄N][CN] or Cp₂Co; however, isolation of products proved difficult. The tungsten−carbon−carbon bond angles of the bridging unit (100.2(6)° and 99.7-(6)°, *vide supra*) are smaller than would be expected for

sp³-hybridized carbon atoms. While the chemical shift of the central carbon and the carbon−hydrogen coupling constants are similar to previously reported values for carbocations, the divergent coupling constants between the central proton and each inequivalent methylene proton provide additional evidence that a significant contribution from structure **2A** is unlikely (*vide infra*).

The three proton coupling constants observed for the C_3H_5 linkage provide some insight into the structure of **2**. If a three-coordinate carbocation were present in the bridge, nearly equivalent hydrogen coupling constants would be expected ($J_{ac} \cong J_{bc}$ for Scheme 4, **2A**). However, structure **2C** can easily account for the discrepancies in J_{ac} and J_{bc} (Scheme 5). In this bonding description, both H_a protons are proximal to H_c while both H_b protons are distal to H_c, resulting in distinct coupling constants of 13 and 6 Hz. Also, increased sp² character for the terminal carbons would explain the small geminal coupling constant (6 Hz) and large carbon−hydrogen coupling constant (140 Hz). The low-field chemical shifts of the proton and carbon (9.8, 157.8 ppm, respectively) of the central carbon decrease the likelihood of any significant contribution from structure **2B**. Therefore, we propose that structure **2C** contributes significantly to the overall bonding for **2**.

Discussion of Mechanism. Rationalizing the formation of dimer **2** from methylene carbene **1** and base is difficult. A source of "CH⁻" is needed to link the two [Tp'(CO)(PhC₂Me)W=CH₂]⁺ fragments: the two most likely sources are either solvent or the metal methylene fragment.

In order to probe the question of methide source, we initially used deuterated solvents. Substitution of deuterated (d_2) methylene chloride as the solvent in eq 1 results in no observable deuterium incorporation in the final product, and dimer **2** does not exhibit H/D exchange upon treatment with D_2O. However, H/D exchange during column chromatography is a possibility. Low yields make observation of the proton resonances for the bridging fragment difficult prior to workup.

In order to further investigate the involvement of methylene chloride in the production of dimer **2**, the reaction was carried out in 1,2-dichloroethane. If methylene chloride is the source of the methide fragment, the use of another solvent would be expected to eliminate dimer production. However, when 1,2-dichloroethane is the solvent, no differences in the reaction are observed. Therefore, we believe that the methide fragment originates from another source.

Dimer formation via an electrophilic carbene and a vinyl ligand has been described (Scheme 2, *vide supra*).[6] Evidence exists for the decomposition of a less-stable methylene complex $[Tp(CO)(PhC_2Ph)W=CH_2][PF_6]$ through formation an ethylene complex $[Tp(CO)(PhC_2Ph)W(H_2C=CH_2)][PF_6]$ (Tp = hydridotris(pyrazolyl)-borate).[13] It is conceivable that carbene **1** decomposes to form an intermediate ethylene complex. In the presence of base, this might be deprotonated to form the vinyl complex $Tp'(CO)(PhC_2Me)W-C(H)=CH_2$ (**3**), and attack of **1** at the β-carbon of **3** followed by rearrangement would yield **2**. Thus, the slow decom-

position of carbene **1** may be a prerequisite for formation of **2** and, hence, for low yields of **2**.

Another possibility is an initial interaction of base with carbene **1** to form the terminal carbyne $Tp'(CO)(PhC_2Me)W\equiv CH$. Decomposition of the carbyne could provide a source of CH^-. Attempts to independently synthesize and observe the terminal carbyne complex have been unsuccessful.

Summary

A new, low-yield route to a C_3H_5-bridged dimer has been discovered. The reaction involves addition of base to a methylene chloride solution of the methylene complex $[Tp'(CO)(PhC_2Me)W=CH_2][PF_6]$ (**1**). Although the ultimate source of the central methide moiety remains unknown, it seems that a metal-based source is more likely than solvent activation. Dimer **2** is surprisingly inert as it fails to react with a variety of nucleophiles. Steric inaccessibility likely contributes to the lack of reactivity at the allyl bridge here. Spectroscopic data in solution and solid state structural data point to a species with significant π-allyl character for the C_3H_5 bridge.

Supporting Information Available: A figure giving the ORTEP diagram and tables of the atomic positional parameters, complete bond lengths and angles, and anisotropic temperature factors (9 pages). Ordering information is given on any current masthead page.

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(13) Unpublished results. Literature precedence exists for the decomposition of methylene carbenes to bound ethylene complexes; see, for example: (a) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760. (b) Merrifield, J. H.; Lin, G.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.