# Halide and Tertiary Phosphine Derivatives of the Tungsten(IV) $\eta^2$ -Acetyl Complex CpW(NCMe)<sub>3</sub>( $\eta^2$ -COMe)<sup>2+</sup>. Reversible Ag<sup>+</sup>-Assisted Opening of an $\eta^2$ -Acetyl Group?

## Vidar Skagestad, Christian Rømming, and Mats Tilset\*,1

Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

Received November 17, 1994<sup>⊗</sup>

The dicationic W(IV)  $\eta^2$ -acetyl complex CpW(NCMe)<sub>3</sub>( $\eta^2$ -COMe)<sup>2+</sup> (1) serves as the precursor for new tungsten(IV)  $\eta^2$ -acetyl derivatives. Treatment of 1 with halides provided *trans*-CpW(NCMe)<sub>2</sub>(X)( $\eta^2$ -COMe)<sup>+</sup> (X = Cl, Br, I) in high yields. The reaction between CpW(NCMe)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup> and dppe yielded the 5-ring chelate CpW( $\eta^2$ -dppe)(Br)( $\eta^2$ -COMe)<sup>+</sup>, while reactions with monodentate tertiary phosphines led to *trans*-CpW-(PR<sub>3</sub>)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup> via the intermediate CpW(NCMe)(PR<sub>3</sub>)(Br)( $\eta^2$ -COMe)<sup>+</sup> (PR<sub>3</sub> = PMePh<sub>2</sub>, PPh<sub>3</sub>). Addition of acetonitrile to a nitromethane solution of CpW(PPh<sub>3</sub>)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup> set up an equilibrium between the substrate and CpW(NCMe)(PPh<sub>3</sub>)(Br)( $\eta^2$ -COMe)<sup>+</sup>. When AgBF<sub>4</sub> was added, this ligand substitution reaction was accelerated. Reversible attachment of Ag<sup>+</sup> at the  $\eta^2$ -acetyl oxygen, ring opening, and reversible BF<sub>4</sub><sup>-</sup> binding at the resulting vacant coordination site at W in *trans*-CpW(PMePh<sub>2</sub>)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup> is suggested on the basis of <sup>1</sup>H and <sup>19</sup>F NMR spectroscopic observations. Similar steps are thought to be involved in the Ag<sup>+</sup>-catalyzed ligand substitution reaction. A single-crystal X-ray structure determination of CpW(NCMe)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup> revealed a four-legged piano stool structure in which the Br and  $\eta^2$ -acetyl ligands are located in a trans relationship and the C-O bond vector points away from the Cp ligand. Crystal data for 4(BF<sub>4</sub><sup>-</sup>): space group  $P\overline{1}$ , a = 7.782(2) Å, b = 12.277(3) Å, c = 16.173(4) Å,  $\alpha = 89.48(2)^\circ$ ,  $\beta = 88.81(2)^\circ$ , and  $\gamma = 88.74(2)^\circ$ . Least-squares refinement based on 4849 reflections converged to R = 0.056 and  $R_w = 0.054$ .

#### Introduction

Ligand substitution and CO insertion reactions are pivotal to organometallic chemistry. The migratory insertion of CO into a metal-carbon bond is usually considered to occur by a movement of the migrating group to the CO ligand to generate a formally unsaturated metal-acyl intermediate which is subsequently captured by an incoming nucleophile.<sup>2</sup> It has been suggested that the  $\eta^2$ -coordination mode of the acyl group<sup>3</sup> can provide electronic stabilization of the unsaturated intermediate. The  $\eta^2$ -acyl coordination is particularly prevalent among early, especially group 4, transition elements and other relatively highoxidation state oxophilic metals. Recently, we reported that the relatively high-oxidation state tungsten(IV) dication CpW- $(NCMe)_2(CO)_2Me^{2+}$ , readily available from  $CpW(CO)_3Me$  by a two-electron oxidation in acetonitrile,<sup>4a</sup> underwent facile CO insertion and substitution resulting in high yields of CpW- $(NCMe)_{3}(\eta^{2}-COMe)^{2+}(1).^{4b}$ 

This work was followed by an account of nucleophilic catalysis of ligand substitution reactions in  $1.^{4c}$  The substitution of acetonitrile ligands in 1 by other nitriles or tertiary phosphines was catalyzed by tertiary phosphines. Evidence was presented that the catalysis occurred by initial phosphine attack at the  $\eta^2$ -acetyl carbon atom to give  $\eta^2$ -acetylphosphonium complexes as intermediates. The acetylphosphonium group exerted a predominantly cis-labilizing effect which led to the generation of a vacant cis coordination site and subsequent binding of the

\* Abstract published in Advance ACS Abstracts, May 15, 1995.

- (2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. Principles and Applications of Organotransition Metal Chemistry; University Science Books: Mill Valley, CA, 1987.
- (3) Durfee, L. D.; Rothwell, I. P. Chem. Rev. 1988, 88, 1059.
- (4) (a) Skagestad, V.; Tilset, M. Organometallics 1991, 10, 2110. (b) Skagestad, V.; Tilset, M. Organometallics 1992, 11, 3293. (c) Skagestad, V.; Tilset, M. Organometallics 1994, 13, 3134.

incoming ligand. Reactions between 1 and monodentate phosphines led to new tungsten(IV)  $\eta^2$ -acetyl species, *cis*- and *trans*-CpW(NCMe)<sub>2</sub>(PR<sub>3</sub>)( $\eta^2$ -COMe)<sup>2+</sup> (2a, R = PMePh<sub>2</sub>; 2b, R = PPh<sub>3</sub>). With dppm,<sup>5</sup> the chelating acetylphosphonium complex CpW(NCMe)<sub>2</sub>( $\eta^3$ -Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>COMe)<sup>2+</sup> was isolated; with dppe,<sup>5</sup> the chelating diphosphine substitution product CpW-(NCMe)( $\eta^2$ -dppe)( $\eta^2$ -COMe)<sup>2+</sup> was produced with the analogous acetylphosphonium complex CpW(NCMe)<sub>2</sub>( $\eta^3$ -Ph<sub>2</sub>PCH<sub>2</sub>-CH<sub>2</sub>PPh<sub>2</sub>COMe)<sup>2+</sup> as an observed intermediate. A temperature-dependent equilibrium that was established by the rapid and reversible attack of PMePh<sub>2</sub> at *trans*-2a was furthermore seen by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy.



In this paper, we describe new findings from our ongoing exploration of the ligand-substitution chemistry of **1**. The synthesis of new, monocationic halide complexes CpW(NCMe)<sub>2</sub>- $(X)(\eta^2$ -COMe)<sup>+</sup> and phosphine-substituted derivatives will be discussed. A novel, *electrophile*-assisted ligand substitution reaction of a cationic  $\eta^2$ -acetyl complex will also be presented.

#### **Results and Discussion**

Synthesis of CpW(NCMe)<sub>2</sub>(X)( $\eta^2$ -COMe)<sup>+</sup> (X = I, Br, Cl). Treatment of CpW(NCMe)<sub>3</sub>( $\eta^2$ -COMe)<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (1(BF<sub>4</sub><sup>-</sup>)<sub>2</sub>)

<sup>\*</sup> Corresponding author: FAX +47 2285 5507 or +47 2285 5441.

<sup>(1)</sup> E-mail: mats.tilset@kjemi.uio.no.

<sup>(5)</sup> Abbreviations: dppm = bis(diphenylphosphino)methane: dppe = 1,3bis(diphenylphosphino)ethane; AcFc = acetylferrocene, (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>-COMe)CpFe.

Table 1. Key <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR Spectroscopic Data for W(IV) Complexes<sup>a</sup>

	<sup>1</sup> H NMR <sup>b</sup>			<sup>13</sup> C NMR <sup>b</sup>			
compound	Ср	COMe	MeCN	COMe	Ср	COMe	<sup>31</sup> P NMR <sup>c</sup>
$\overline{\mathrm{CpW}(\mathrm{NCMe})_3(\eta^2 - \mathrm{COMe})^{2+}(1)^d}$	5.82 (s)	3.42 (s)	2.43 (s, 6H), 2.69 (s, 3H)	30.4	100.0	276.1	
$trans$ -CpW(NCMe) <sub>2</sub> (PMePh <sub>2</sub> )( $\eta^2$ -COMe) <sup>2+</sup> ( $trans$ - <b>2a</b> )	5.79 (s)	3.53 (s)	2.58 (d, 6H)	е	94.7	е	-1.0(s)
$cis$ -CpW(NCMe) <sub>2</sub> (PMePh <sub>2</sub> )( $\eta^2$ -COMe) <sup>2+</sup> ( $cis$ - <b>2a</b> )	5.69 (d)	3.12 (d)	2.38 (s, 3H), 2.71 (d, 3H)	28.9	93.9	267.2 (d)	9.5 (s)
trans-CpW(NCMe) <sub>2</sub> ( $\eta^2$ -COMe)(I) <sup>+</sup> (3)	5.65 (s)	3.32 (s)	2.42 (s, 6H)	26.5	94.1	266.1	
trans-CpW(NCMe) <sub>2</sub> ( $\eta^2$ -COMe)(Br) <sup>+</sup> (4)	5.63 (s)	3.29 (s)	2.40 (s, 6H)	27.5	94.6	269.0	
trans-CpW(NCMe) <sub>2</sub> ( $\eta^2$ -COMe)(Cl) <sup>+</sup> (5)	5.62 (s)	3.29 (s)	2.42 (s, 6H)			266.1	
$CpW(\eta^2-dppe)(\eta^2-COMe)(Br)^+(6)$	5.21 (d)	2.68 (d)		28.6	92.2	262.0 (d)	23.0 (d), 35.0 (d)
$CpW(NCMe)(\eta^2-dppe)(\eta^2-COMe)^{2+}$ (7)	5.58 (d)	2.51 (d)	1.86 (d)	28.8	96.4	274.2 (d)	30.6 (d), 35.7 (d)
trans-CpW(PMePh <sub>2</sub> ) <sub>2</sub> (Br)( $\eta^2$ -COMe) <sup>+</sup> (8a)	5.15 (t)	2.29 (t)		26.3	90.5	271.6	4.7 (s)
trans-CpW(PPh <sub>3</sub> ) <sub>2</sub> (Br)( $\eta^2$ -COMe) <sup>+</sup> ( <b>8b</b> )	5.39 (t)	2.38 (t)		24.8	94.5	282.0	14.2(s)
$CpW(NCMe)(PMePh_2)(Br)(\eta^2-COMe)^+$ (9a)	5.44 (d)	2.91 (d)	2.43 (s)				12.0 (s)
$CpW(NCMe)(PPh_3)(Br)(\eta^2-COMe)^+$ (9b) <sup>e</sup>	5.54 (d)	3.10 (d)	2.52 (s)				22.2(s)
$\dot{CpW}(PMePh_2)_2(Br)(\eta^2-COMe)^+ AgBF_4^e$	5.50	3.00					

<sup>a</sup> In acetonitrile-d<sub>3</sub>. <sup>b</sup>  $\delta$  (ppm) relative to TMS. <sup>c</sup>  $\delta$  (ppm) relative to 85% H<sub>3</sub>PO<sub>4</sub>. <sup>d</sup> Reference 7a. <sup>e</sup> In nitromethane-d<sub>3</sub>.

with KI or NaBr in acetonitrile provided high yields of the mono-substituted products *trans*-CpW(NCMe)<sub>2</sub>(X)( $\eta^2$ -COMe)<sup>+</sup> (**3**, X = I, 90%; **4**, X = Br, 94%) as their BF<sub>4</sub><sup>-</sup> salts. No intermediates were detected by <sup>1</sup>H NMR spectroscopy during the reaction between 1(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> and NaBr at 20 °C. The kinetics of the reactions have not been examined, but we have noted that the rate of formation of **4** increases with increasing concentration of NaBr. These ligand-substitution reactions were *not* catalyzed<sup>4c</sup> by PPh<sub>3</sub>.



Although 1, 3, and 4 have the same formal oxidation state, the reduced overall charge of the complexes leads to less electron-deficient metal centers for 3 and 4. This interpretation is corroborated by <sup>1</sup>H NMR spectroscopy, where the Cp and  $\eta^2$ -acetyl resonances were seen to move upfield relative to those reported for 1. Key spectroscopic data for new and some relevant old complexes are summarized in Table 1. The <sup>1</sup>H NMR spectra of 3 and 4 displayed Cp signals at  $\delta$  5.65 and 5.63, respectively, compared to 5.82 in 1. The  $\eta^2$ -acetyl singlets were observed at  $\delta$  3.32 and 3.29, compared to 3.42 in 1. Direct support for the presence of  $\eta^2$ -acetyl groups in 3 and 4 was provided by resonances at  $\delta$  266.1 and 269.0, respectively, in the  ${}^{13}C{}^{1}H$  NMR spectra. The chloro complex CpW(NCMe)<sub>2</sub>- $(Cl)(\eta^2$ -COMe)<sup>+</sup> (5) was obtained by treatment of  $1(BF_4^{-})_2$  with NaCl but unfortunately, 5 was contaminated by small amounts of other, unidentified Cp-containing species. The spectroscopic data, however, resembled those described for 3 and 4. The two coordinated acetonitrile ligands in 3-5 are mutually trans disposed and are identical by symmetry, as demonstrated by the presence of only one acetonitrile signal in the <sup>1</sup>H NMR spectra.

A simple experiment was performed to check whether the halide ligand could dissociate from the new complexes. A ca. 1:1 mixture of  $4(BF_4^-)$  and  $1(BF_4^-)_2$  was dissolved in acetonitrile- $d_3$ . It was reasoned that if  $Br^-$  dissociated from 4, a coordinatively unsaturated intermediate should form and immediately capture a molecule acetonitrile- $d_3$ , generating  $1-d_3$ . The dissociated  $Br^-$  would regenerate 4 by reaction with 1 or  $1-d_3$ . The overall hypothetical reaction is depicted below. The net observable effect—irregardless of reaction mechanism—would be a dilution of the trans acetonitrile label of 1 in the <sup>1</sup>H NMR spectrum. It was found that the rate of exchange of acetonitriled<sub>3</sub> for the trans acetonitrile ligand in 1 was unaffected, and this suggests that little or no  $Br^-$  dissociation takes place from 4 during a 1-h period. In support of this conclusion, no reaction took place when AgBF<sub>4</sub> was added to an acetonitrile-d<sub>3</sub> solution of 4(BF<sub>4</sub><sup>-</sup>).



Organometallic fluoro compounds are relatively rare, presumably due to the unfavorable combination of usually relatively soft low-valent metal centers and the hard fluoride ion.<sup>6</sup> With high-valent metal complexes, organometallic fluoro compounds are more frequently encountered.<sup>6,7</sup> Attempts to generate a fluoro complex by the reaction of  $1(BF_4^-)_2$  with NaF or anhydrous Bu<sub>4</sub>NF were unsuccessful (no consumption of 4 after heating at reflux for several days in acetonitrile). This reation also was not catalyzed<sup>4c</sup> by PPh<sub>3</sub>. It is at present not clear if the ineffectiveness of F<sup>-</sup> to cause substitution is caused by a high kinetic barrier, or by a thermodynamic instability of the particular product relative to the reactants. We have recently prepared a W-F derivative by a different route,<sup>8</sup> and this at least establishes that W-F complexes of this type are not necessarily inherently unstable.

X-ray Crystal Structure Determination of *trans*-CpW-(NCMe)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup>BF<sub>4</sub><sup>-</sup> (4(BF<sub>4</sub><sup>-</sup>)). The key spectroscopic data presented for 3 and 4 are consistent with their formulation as tungsten(IV)  $\eta^2$ -acetyl species. A number of group 6 metal  $\eta^2$ -acetyl complexes containing the Cp supporting ligand have been previously described,<sup>9</sup> and a few have been structurally characterized.<sup>9c-e,i-k</sup> A neutral W(IV) complex closely related to our systems, CpW(CO)(Cl)<sub>2</sub>( $\eta^2$ -COMe), was reported by Kreissl et al.<sup>9c,d</sup> The X-ray crystallographic analysis of this complex revealed a "four-legged piano stool" structure

(8) Skagestad, V.; Tilset, M. Manuscript under preparation.

<sup>(6)</sup> Doherty, N. M.; Hoffman, N. W. Chem. Rev. 1991, 91, 553 and references cited.

<sup>(7)</sup> O'Donell, T. A.; Philiphs, K. Inorg. Chem. 1973, 12, 1437.

**Table 2.** Crystallographic Data for  $4(BF_4^-)$ 

chem formula: $C_{11}H_{14}BBrF_4N_2OW$	$Q_{calcd} = 2.326 \text{ g/cm}^3$
fw = 540.80	Z = 4
space group: $P\overline{1}$	$V = 1544.2(6) \text{ Å}^3$
a = 7.782(2) Å	$T = -135 ^{\circ}\mathrm{C}$
b = 12.277(3)  Å	$\lambda = 0.710  69  \text{\AA}$
c = 16.173(4)  Å	$\mu = 102.3 \text{ cm}^{-1}$
$\alpha = 89.48(2)^{\circ}$	transm coeff = $0.65 - 1.41$
$\beta = 88.81(2)^{\circ}$	$R^a = 0.056$
$\gamma = 88.74(2)^{\circ}$	$R_{w}^{b} = 0.054$
${}^{a}R = \sum   F_{\sigma}  -  F_{c}   / \sum  F_{\sigma} . {}^{b}R_{w} = [$	$\sum w( F_{\sigma}  =  F_{c} )^{2} / \sum w F_{\sigma}^{2}]^{1/2}.$

in which the  $\eta^2$ -acetyl ligand occupied one coordination site and was orientated in such a way that the plane defined by W and the acetyl CO was essentially perpendicular to the basal plane of the molecule. The acetyl oxygen pointed away from the Cp ligand. It has been notoriously difficult to obtain X-ray diffraction quality crystals of the dicationic W(IV) complexes described by us previously.<sup>4</sup> However, the monocationic halide derivatives crystallized nicely, and we decided to subject  $4(BF_4^-)$  to a crystallographic analysis. Single crystals of  $4(BF_4^-)$  were grown from acetonitrile/ether. Crystallographic data are given in Table 2. Bond distances and angles are summarized in Table 3.

Figure 1 shows a PLUTO drawing of one of the two crystallographically independent molecules that were contained in the unit cell. In full agreement with the conclusions drawn from the spectroscopic data for 4, the X-ray diffraction analysis established that the acetyl ligand is bonded to the metal in an  $\eta^2$  fashion. As was found for the structure of CpW(CO)(Cl)<sub>2</sub>- $(\eta^2$ -COMe), <sup>9c,d</sup> the analysis reveals a "four-legged piano stool" structure. The two independent molecules were not significantly different and parameters for the average structure will be discussed. In the acetyl ligand, the W(1)-C(6) bond length (1.961(12) Å) and the W(1)-O(1) bond length (2.164(8) Å)are very similar to the corresponding bond lengths reported for  $CpW(CO)(Cl)_2(\eta^2-COMe)^+$  (1.999(8) and 2.167(6) Å, respectively<sup>9c,d</sup>). The acetyl C–O bond distance was 1.272(14) Å, to be compared with 1.246(9) Å in CpW(CO)(Cl)<sub>2</sub>( $\eta^2$ -COMe). The acetyl C-O bond vector points away from the Cp ligand; again this agrees with the structure of  $CpW(CO)(Cl)_2(\eta^2-COMe)$ . The coordinated bromide ligand is situated trans to the  $\eta^2$ -acetyl group, with a W-Br bond length of 2.601(2) Å. The difference between the W(1)-O(1) and W(1)-C(6) bond distances is 0.203 Å, which is in the range commonly observed for  $\eta^2$ -acyl complexes.<sup>3</sup> No F(anion) · · · H(cation) – C distances were shorter than the sum of the van der Waals radii (we were especially concerned about the possibility of a hydrogen-bonded interaction between  $BF_4^-$  and the acetyl group, considering that 1,8diazabicyclo[5.4.0]undecene (DBU) reversibly deprotonates the acyl group of CpW(CO)(CO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>( $\eta^2$ -COCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me)<sup>9g</sup> and that relatively high acidities ( $pK_a$  values in the range 9-18 exist

**Table 3.** Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations for Non-Hydrogen Atoms in One of the Crystallographically Independent Cations of  $CpW(NCMe)_2(Br)(\eta^2-COMe)^+BF_4^{-a}$ 

	Bond I	Distances	
W(1) - Br(1)	2.601(2)	W(1) = O(1)	2.158(10)
W(1) - N(1)	2118(11)	W(1) - N(2)	2.149(11)
W(1) - C(1)	2.330(15)	W(1) - C(2)	2.170(11)
W(1) = C(2)	2.330(13)	W(1) = C(2) W(1) = C(4)	2.370(13)
W(1) = C(5) W(1) = C(5)	2.312(17)	W(1) = C(4)	2.209(19)
w(1) = C(3)	2.251(10)	W(1) = C(6)	1.960(17)
O(1) - C(6)	1.2/8(19)	N(1) = C(8)	1.137(17)
N(2) - C(10)	1.144(17)	C(1) - C(5)	1.38(3)
C(1) - C(2)	1.46(3)	C(3) - C(4)	1.44(2)
C(2) - C(3)	1.32(3)	C(6) - C(7)	1.46(3)
C(4) - C(5)	1.42(3)	C(10) - C(11)	1.443(18)
C(8)-C(9)	1.478(18)		
	Bond	Angles	
$B_{r}(1) - W(1) - O(1)$	80 7(3)	Br(1) = W = N(1)	82 1(4)
D(1) = W(1) = U(1)	82 0(4)	$B_{r}(1) = W(1) = C(1)$	150.0(5)
DI(1) = W(1) = IV(2) $P_{\pi}(1) = W(1) = C(2)$	05.9(4)	$B_1(1) = W(1) = C(1)$	130.0(3)
Dr(1) = W(1) = C(2)	115.5(4)	Br(1) = w(1) = C(3)	91.2(5)
Br(1) - W(1) - C(4)	99.0(5)	Br(1) = W(1) = C(5)	134.5(4)
Br(1) - W(1) - C(6)	125.4(5)	O(1) - W(1) - N(1)	78.5(5)
O(1) - W(1) - N(2)	79.0(5)	O(1) - W(1) - C(1)	118.9(5)
O(1) - W(1) - C(2)	139.4(5)	O(1) - W(1) - C(3)	169.8(4)
O(1) - W(1) - C(4)	152.8(5)	O(1) - W(1) - C(5)	125.2(5)
O(1) - W(1) - C(6)	35.7(6)	N(1) = W(1) = N(2)	153.4(5)
N(1) - W(1) - C(1)	110.8(5)	N(1) - W(1) - C(2)	133.4(5)
N(1) - W(1) - C(3)	111.7(5)	N(1) - W(1) - C(4)	77.3(6)
N(1) - W(1) - C(5)	78.2(5)	N(1) = W(1) = C(6)	84 0(5)
N(2) - W(1) - C(1)	92 4(6)	N(2) - W(1) - C(2)	73 1(5)
N(2) - W(1) - C(3)	91.0(5)	N(2) - W(1) - C(4)	127 3(6)
N(2) - W(1) - C(5)	126.9(5)	N(2) = W(1) = C(4)	86.0(6)
R(2) = W(1) = C(3)	120.9(3)	R(2) = W(1) = C(0)	50.0(0)
C(1) = W(1) = C(2)	50.5(0)	C(1) = W(1) = C(3)	39.0(0)
C(1) = W(1) = C(4)	00.0(0)	C(1) = W(1) = C(5)	35.0(6)
C(1) = W(1) = C(6)	83.8(7)	C(2) = W(1) = C(3)	32.8(6)
C(2) = W(1) = C(4)	58.1(6)	C(2) = W(1) = C(5)	58.4(5)
C(2) = W(1) = C(6)	112.2(6)	C(3) - W(1) - C(4)	36.7(6)
C(3) - W(1) - C(5)	59.8(6)	C(3) - W(1) - C(6)	142.5(7)
C(4) - W(1) - C(5)	36.6(7)	C(4) = W(1) = C(6)	128.5(7)
C(5) = W(1) = C(6)	92.9(7)	W(1) = O(1) = C(6)	63.6(9)
W(1) - N(1) - C(8)	179.0(12)	W(1) = N(2) = C(10)	177.8(13)
W(1) - C(1) - C(2)	73.4(9)	W(1) - C(1) - C(5)	69.4(9)
C(2) - C(1) - C(5)	104.9(13)	W(1) - C(2) - C(1)	70.3(9)
W(1) - C(2) - C(3)	71.2(10)	C(1) = C(2) = C(3)	110.1(13)
W(1) - C(3) - C(2)	76.0(10)	W(1) - C(3) - C(4)	70.0(10)
C(2) - C(3) - C(4)	109 2(15)	W(1) = C(4) = C(3)	73 3(10)
W(1) - C(4) - C(5)	710(10)	C(3) = C(4) = C(5)	105.3(10)
W(1) = C(5) = C(1)	75.6(0)	W(1) = C(5) = C(3)	72 2(10)
r(1) = C(3) = C(1)	110 4(12)	W(1) = C(3) = C(4) W(1) = C(4) = O(1)	72.3(10)
U(1) = U(3) = U(4)	110.4(13)	w(1) = C(0) = O(1)	80.0(9)
W(1) - C(0) - C(7)	151.6(14)	U(1) = C(6) = C(7)	127.7(16)
N(1) = C(8) = C(9)	179.2(17)	N(2) - C(10) - C(11)	177.4(17)

<sup>*a*</sup> Complete parameters, included those for the other crystallographically independent cation, are given in the supplementary material.

in acetonitrile) have recently been established for some cationic Nb(V)  $\eta^2$ -acyl complexes.<sup>10</sup>

**Preparation of CpW**( $\eta^2$ -**dppe**)(**Br**)( $\eta^2$ -**COMe**)<sup>+</sup>**BF**<sub>4</sub><sup>-</sup>. Treatment of 4(**B**F<sub>4</sub><sup>-</sup>) with 1 equiv of dppe<sup>5</sup> in acetonitrile proceeded smoothly to give CpW( $\eta^2$ -dppe)(**B**r)( $\eta^2$ -**COMe**)<sup>+</sup>**B**F<sub>4</sub><sup>-</sup>(6(**B**F<sub>4</sub><sup>-</sup>))) in high yield (85%). The <sup>1</sup>H NMR spectrum of **6** displayed a doublet for the Cp at  $\delta$  5.21 and a doublet for the acetyl methyl at  $\delta$  2.68. The  $\eta^2$ -acetyl group gave rise to a resonance at  $\delta$  262.0 in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum displayed two mutually coupled doublets (<sup>2</sup>*J*<sub>PP</sub> = 3.4 Hz) at  $\delta$  23.0 and 35.0, both with <sup>183</sup>W satellites, in agreement with the presence of two nonequivalent, W-bonded phosphorus nuclei because the phosphines are constrained to a cis geometry in **6** by chelation. As a consequence, the coordinated bromide is located cis to the  $\eta^2$ -acetyl group, differing from the trans orientation found in **4**. Quite conveniently, **6**(**B**F<sub>4</sub><sup>-</sup>) could be

<sup>(9) (</sup>a) Cotton, F. A.; French, B. A.; Shaver, A. Inorg. Chim. Acta 1973, 7, 161. (b) Alt, H. G. J. Organomet. Chem. 1977, 127, 349. (c) Kreissl, F. R.; Sieber, W. J.; Wolfgruber, M.; Riede, J. Angew. Chem., Int. Ed. Engl. 1984, 23, 640. (d) Kreissl, F. R.; Werner, J. S.; Keller, H.; Riede, J.; Wolfgruber, M. J. Organomet. Chem. 1987, 320, 83. (e) Bonnesen, P. V.; Yau, P. K. L.; Hersh, W. H. Organometallics 1987, 6, 1587. (f) Carter, J. D.; Schoch, T. K.; McElwee-White, L. Organometallics 1992, 11, 3571. (g) Kreissl, F. R.; Keller, H.; Schütt, W. J. Organomet. Chem. 1992, 441, 75. (h) Kingsbury, K. B.; Carter, J. D.; Wilde, A.; Park, H.; Takusagawa, F.; McElwee-White, L. J. Am. Chem. Soc. 1993, 115, 10056. (i) Dryden, N. H.; Legzdins, P.; Lundmark, P. J.; Riesen, A.; Einstein, F. W. B. Organometallics 1993, 12, 2094. (k) Debad, J. D.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. Organometallics 193, 12, 21714. (l) Mortimer, M. D.; Carter, J. D.; Kingsbury, K. B.; Abboud, K. A.; McElwee-White, L. J. Am. Chem. Soc. 19.; Nametallics 1993, 12, 2014. (k) Debad, J. D.; Carter, J. D.; Kingsbury, K. B.; Abboud, K. A.; McElwee-White, L. J. Am. Chem. M. D.; Carter, J. D.; Kingsbury, K. B.; Abboud, K. A.; McElwee-White, L. J. Am. Chem. Soc. 1994, 116, 8629.

<sup>(10)</sup> Fermin, M. C.; Thiyagarajan, B.; Bruno, J. W. J. Am. Chem. Soc. 1993, 115, 974.



Figure 1. PLUTO plot of one of the crystallographically independent cations of CpW(NCMe)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup>BF<sub>4</sub><sup>-</sup> (4(BF<sub>4</sub><sup>-</sup>)). The hydrogen atoms have been omitted for clarity.

prepared in a one-pot reaction, starting from CpW(CO)<sub>3</sub>Me, in 71% total yield with no intermittent workup. The reaction conditions involved oxidation of CpW(CO)<sub>3</sub>Me with AcFc<sup>+</sup>BF4<sup>-5</sup> in acetonitrile to give CpW(CO)<sub>2</sub>(NCMe)<sub>2</sub>Me<sup>2+</sup>,<sup>4a</sup> followed by a thermal reaction which yielded 1(BF4<sup>-</sup>)<sub>2</sub>.<sup>4b</sup> NaBr was added, and the mixture was heated before dppe was finally added. The generation of **6**(BF4<sup>-</sup>) was also accomplished by the reaction of CpW(NCMe)( $\eta^2$ -dppe)( $\eta^2$ -COMe)<sup>2+</sup>(BF4<sup>-</sup>)<sub>2</sub><sup>4c</sup> (7(BF4<sup>-</sup>)<sub>2</sub>) with NaBr in acetonitrile. The latter reaction was, however, rather slow in comparison (reflux, 16 h) and was therefore not used for the synthesis of **6**.



When the reaction between  $4(BF_4^-)$  and dppe was monitored by <sup>1</sup>H NMR spectroscopy, several species were observed before the reaction was complete. These have not been identified, and it is not clear if they are all true intermediates en route from 4 to 6 or if they arise from nonproductive side equilibria. It is therefore not possible to firmly establish the sequence of events that must be involved in the overall transformation.

The exchange of acetonitrile- $d_3$  for acetonitrile in 4 was considerably accelerated in the presence of dppe. In the presence of 4, a broad  ${}^{31}P{}^{1}H$  NMR resonance for free dppe was observed at  $\delta$  -12. In accord with our previous suggestions,<sup>4c</sup> this broadening is indicative of rapid and reversible phosphine attack at the carbonyl carbon in 4 to give an  $\eta^2$ -acetylphosphonium intermediate with labile acetonitrile ligands, thence the acceleration of the ligand exchange. The important consequence of this observation is that phosphine catalysis of ligand-exchange reactions is not confined to dicationic complexes. Catalyzed acetonitrile/acetonitrile-d3 exchange was also observed in the reaction to be described later between 4 and PMePh<sub>2</sub>, but not in the reaction between 4 and PPh<sub>3</sub>. In contrast, there was such a catalytic effect when 1 reacted with both PMePh<sub>2</sub> and PPh<sub>3</sub>,<sup>4c</sup> and the difference in the behavior of 1 and 4 can be caused by a combination of steric and electronic effects.

Reaction of CpW(NCMe)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup> with PMePh<sub>2</sub>. Synthesis of *trans*-CpW(PMePh<sub>2</sub>)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup>BF<sub>4</sub><sup>-</sup>. When **4**(BF<sub>4</sub><sup>--</sup>) was stirred for 2 h with 3 equiv of PMePh<sub>2</sub> in acetonitrile at ambient temperature, a pale yellow product was obtained in high yields. The <sup>1</sup>H NMR resonances due to the Cp and acetyl ligands of **4** were replaced by triplets at considerably higher field,  $\delta$  5.15 (5 H) and 2.29 (3 H) in acetonitrile-*d*<sub>3</sub>. A resonance for two PMePh<sub>2</sub> ligands was seen as a virtual triplet at  $\delta$  2.02 (6 H). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum displayed an  $\eta^2$ -acetyl resonance at  $\delta$  271.6. The incorporation of two chemically identical, W-bonded phosphine ligands was established by the presence of a single <sup>31</sup>P{<sup>1</sup>H} NMR resonance with <sup>183</sup>W satellites at  $\delta$  4.7. The spectroscopic and elemental analysis data suggest that the compound is *trans*-CpW-(PMePh<sub>2</sub>)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup>BF<sub>4</sub><sup>--</sup> (**8a**(BF<sub>4</sub><sup>--</sup>)).

The intermediate  $CpW(NCCD_3)(PMePh_2)(Br)(\eta^2-COMe)^+$ (9a- $d_3$ ) was observed (<sup>1</sup>H NMR) when the reaction between  $4(BF_4^-)$  and PMePh<sub>2</sub> was done in acetonitrile- $d_3$ . In fact, all 4 was consumed, and  $9a \cdot d_3$  and 8a were present in a 4:1 ratio as the only detectable W-containing species after a 2-min reaction time. The <sup>1</sup>H NMR spectrum of **9a**- $d_3$  showed doublets at  $\delta$ 5.44 (Cp) and 2.91 ( $\eta^2$ -acetyl). In addition, a resonance for PMePh<sub>2</sub> was seen at  $\delta$  2.12 (d, 3 H). Compound **9a**(BF<sub>4</sub><sup>-</sup>) was obtained as the major product when a 4:1 mixture of cis- and trans-2a( $BF_4^-$ )<sub>2</sub> was treated with NaBr in actionitrile. The spectroscopic data for the isolated product, which rapidly underwent partial reaction in solution to give a mixture of mostly 4, 8a, and 9a, were identical with those of  $9a-d_3$ , except that the <sup>1</sup>H NMR spectrum (acetonitrile- $d_3$ ) of the isolated product also displayed a singlet due to coordinated acetonitrile at  $\delta$  2.43. As already discussed in our previous paper,<sup>4c</sup> the lack of coupling between the acetonitrile and phosphine ligands in these four-legged piano stool complexes is consistently seen when the two are mutually trans disposed. Similarly, a coupling between phosphine and an  $n^2$ -COMe ligand is seen when they are cis disposed.<sup>4c</sup> On the basis of these general observations, the most likely geometry for 9a is that shown below. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **9a** displayed a singlet at  $\delta$  12.0.



In nitromethane- $d_3$ , the rate of the reaction between  $4(BF_4^-)$  and PMePh<sub>2</sub> showed a dramatic increase. The reaction was done and yielded 8a in less than 5 min. The mono-substituted intermediate 9a, observed in acetonitrile- $d_3$ , was not detected in nitromethane- $d_3$ .

**Reaction of CpW(NCMe)**<sub>2</sub>(**Br**)( $\eta^2$ -**COMe**)<sup>+</sup> with **PPh**<sub>3</sub>. Experiments analogous to those described above were now performed with PPh<sub>3</sub> instead of PMePh<sub>2</sub>. In acetonitrile- $d_3$ , a slow reaction ensued with 2 equiv of PPh<sub>3</sub> present. During a 3-day period, partial consumption of starting material took place, and a new compound formed, along with unreacted 4, in a 2:1 ratio. Extended reaction times (5 d, 20 °C) led to no change in this ratio. The new complex exhibited <sup>1</sup>H NMR signals at  $\delta$  5.45 (d, 5 H) and 3.02 (d, 3 H) for the Cp and acetyl groups, respectively. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum exhibited a singlet at  $\delta$  24.3 accompanied by <sup>183</sup>W satellites. This product is identified as CpW(NCCD<sub>3</sub>)(PPh<sub>3</sub>)(Br)( $\eta^2$ -COMe)<sup>+</sup> (9b-d<sub>3</sub>), as will be discussed in the following. No disubstitution product was observed under these conditions.

With nitromethane as the solvent, the outcome of the reaction was altered. The reaction was much faster, with no starting material left after 2 h at ambient temperature, and yielded *trans*-CpW(PPh<sub>3</sub>)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup>BF<sub>4</sub><sup>-</sup> (**8b**(BF<sub>4</sub><sup>-</sup>)). The product showed two <sup>1</sup>H NMR triplets at  $\delta$  5.39 (5 H) and 2.38 (3 H). The <sup>13</sup>C{<sup>1</sup>H} spectrum revealed an  $\eta^2$ -acetyl resonance at  $\delta$ 282.2, and the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum displayed a singlet at  $\delta$ 14.2 with <sup>183</sup>W satellites. We assume that **9b** is an intermediate en route to **8b**. The intermediacy of **9b** was probed in a reaction of **4** with 1 equiv of PPh<sub>3</sub> in nitromethane-*d*<sub>3</sub>. A 1:1 mixture of **4** and **8b** was present after 3 h (<sup>1</sup>H NMR); minor amounts (ca. 10%) of **9b** were detected and its presence was also noted at earlier stages of the reaction.

Some Comments on the Substitution Reactions by PPh<sub>3</sub> and PMePh<sub>2</sub>. For the reactions of 4 to 8 via 9, the rate of incorporation of the second phosphine ligand was slower than of the first one in acetonitrile (10-15 min vs <1 min forPMePh<sub>2</sub>; no second incorporation was seen at all for PPh<sub>3</sub>). This may be interpreted as a combined effect of a lower phosphine concentration during the second substitution and a steric inhibition of the second substitution.



Primarily, the enhanced reaction rates in nitromethane relative to acetonitrile are most likely an effect of the acetonitrile substitution being reversible. The inhibiting back-reactions are less important in nitromethane, since no acetonitrile is present except that arising from the conversion of the substrate 4. Certain features of the reactions in nitromethane- $d_3$  are however unusual. First, with the second substitution being slower than the first, one would expect a significant buildup of the intermediate 9. However, for PMePh<sub>2</sub> the intermediate was not detectable in nitromethane; for PMePh<sub>2</sub>, the buildup was rather modest (ca. 10%). It therefore appears that in nitromethane, 9 is relatively unstable with respect to loss of phosphine (to give 4 after acetonitrile capture) or acetonitrile (to give 8 after phosphine capture). Second, as a closely related observation, we note that for PMePh<sub>2</sub> a 1:1 mixture of 4 and 8a is favored over 9a, still in nitromethane. This finding is quite surprising since, for steric reasons, 8a should be the most disfavored of the three. It may be that this destabilizing effect is offset by a somewhat greater stability of 4 relative to 9a so that a point of balance in favor of 4 and 8a is reached. It is also possible that the hard and soft acid and base principle comes into play here: the concentration of two relatively soft PMePh2 ligands in 8a and two harder acetonitrile ligands in 4 is favored over the combination of hard and soft ligands in 9a.<sup>11</sup>

**Reaction of CpW(PPh\_3)**<sub>2</sub>(**Br**)( $\eta^2$ -**COMe**)<sup>+</sup> (**8b**) with Acetonitrile. When **8b**(**B**F<sub>4</sub><sup>-</sup>) was dissolved *in acetonitrile-d*<sub>3</sub>, **9b***d*<sub>3</sub> was immediately formed (<1 min). Prolonged reaction times led to the appearance of **4**-*d*<sub>6</sub> (2:1 ratio of **4**-*d*<sub>6</sub> and **9b**-*d*<sub>3</sub> after 2 weeks). Over time, decomposition reactions that are not understood led to the production of cyclopentadiene.

The generation of **9b** from **8b** proceeded much slower when 14 equiv acetonitrile was added to a nitromethane- $d_3$  solution

of **8b**(BF<sub>4</sub><sup>-</sup>). After 10 min, a 2:1 mixture of **8b** and **9b** formed. The ratio did not change further over time (2 h), suggesting the attainment of an equilibrium. In addition to the Cp and acetyl resonances mentioned for **9b**- $d_3$  above, the <sup>1</sup>H NMR spectrum displayed a singlet due to coordinated acetonitrile in **9b** at  $\delta$  2.52, and an intense signal due to excess free acetonitrile at  $\delta$  2.00. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **9b** showed a singlet surrounded by <sup>183</sup>W satellites at  $\delta$  22.2.

Interaction between CpW(PMePh<sub>2</sub>)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup> (8a) and AgBF<sub>4</sub>. Silver Ion Coordination at the  $\eta^2$ -Acetyl Group? The dissociation of halide ions from organometallic compounds is frequently assisted by silver ions, often in the form of  $AgBF_4$  or  $AgPF_6$ . In an attempt to effect  $Br^$ abstraction from 8a, 2 equiv of AgBF<sub>4</sub> was added to a solution of  $8a(BF_4^-)$  in acetonitrile- $d_3$ , but no changes were observed in the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra. However, when the reaction was attempted in nitromethane- $d_3$ , a different result was obtained. The <sup>1</sup>H NMR Cp and  $\eta^2$ -acetyl resonances were shifted downfield compared to those of 8a. At high concentrations of  $AgBF_4$  (up to 32 equiv), the Cp resonance had moved downfield from  $\delta$  5.29 in 8a to a limiting value of 5.50. The observed change for the  $\eta^2$ -acetyl group was even greater, with a downfield shift from  $\delta$  2.34 in **8a** to a limiting value of 3.00. The magnitude of the Cp-phosphorus coupling was unaffected. For the  $\eta^2$ -acetyl, however, the  ${}^4J_{P-H}$  couplings were no longer resolved. The PMePh<sub>2</sub> resonances were unaffected. Unfortunately, extensive sample decomposition occurred during the acquisition of a <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, and no signal attributable to an acetyl group was observed. The <sup>19</sup>F NMR spectrum revealed a resonance shifted ca. 3 ppm downfield from that of Bu<sub>4</sub>NBF<sub>4</sub> when 32 equiv of AgBF<sub>4</sub> was employed. When the concentration of AgBF<sub>4</sub> was reduced, the <sup>19</sup>F NMR peak became broader and appeared even further downfield, and eventually merged with the baseline at the lowest concentrations employed (see Experimental Section for details). Assuming that the broadening was caused by a rapid exchange process, we examined a nitromethane- $d_3$  solution of  $8a(BF_4^-)$  and  $AgBF_4$ (1:8) at -30 °C. The only observable change was that the <sup>1</sup>H NMR Cp and  $\eta^2$ -acetyl resonances moved downfield from  $\delta$ 5.37 and 2.56 at 20 °C to 5.42 and 2.70 at -30 °C. No changes were seen in the <sup>1</sup>H NMR spectrum of  $8a(BF_4^-)$  in the presence of Bu<sub>4</sub>NBF<sub>4</sub>. This behavior must therefore be caused by a specific interaction between  $Ag^+$  and 8a. This conclusion is supported by the finding that when Bu<sub>4</sub>NBr was added to a nitromethane solution of  $8a(BF_4^-)$  and AgBF<sub>4</sub>, precipitation of AgBr was seen, and the BF<sub>4</sub><sup>-</sup>, Cp, and  $\eta^2$ -acetyl resonances in the NMR spectra again matched those of  $8a(BF_4^-)$ .

Interesting observations were made when small amounts of acetonitrile was added to a nitromethane solution of **8a**(BF<sub>4</sub><sup>-</sup>) and 4 equiv of AgBF<sub>4</sub>. The <sup>1</sup>H NMR spectrum changed in such a way that the Cp and  $\eta^2$ -acetyl resonances moved upfield again (in the direction of **8a** alone). A signal due to coordinated acetonitrile was seen at  $\delta$  2.40. This signal was also seen in a solution of AgBF<sub>4</sub> and 4 equiv of acetonitrile in nitromethaned<sub>3</sub> and presumably arises from Ag(NCMe)<sub>4</sub><sup>+</sup>.<sup>12</sup> When more acetonitrile (up to 100 equiv) was added, the Cp and acetyl resonances approached those of **8a** alone; the averaged (of free and Ag<sup>+</sup>-bonded) acetonitrile signal grew in intensity and the chemical shift approached that of acetonitrile in nitromethaned<sub>3</sub> ( $\delta$  2.00). Simultaneously, the initially broadened and downfield-shifted <sup>19</sup>F NMR spectrum sharpened and moved upfield, approaching the appearance of the spectrum of Bu<sub>4</sub>NBF<sub>4</sub>.

Attempts were made to look at the spectroscopic behavior in

<sup>(11)</sup> Davies, J. A.; Hartley, F. R. Chem. Rev. 1981, 81, 79.

<sup>(12)</sup> Cotton, F. A.; Kim, Y.; Ren, T. Inorg. Chem. 1992, 31, 2608.

dichloromethane- $d_2$  which offers the benefit of being less polar as well as giving access to much lower temperatures. Unfortunately, when a solution of  $8a(BF_4^-)$  in dichloromethane- $d_2$ was treated with AgBF<sub>4</sub>, instant decomposition occurred with the generation of a black solution from which no useful NMR data could be obtained.

There are several conceivable sources of the broadening effects. It should be emphasized that in the absence of 8a, the <sup>19</sup>F NMR chemical shift of AgBF<sub>4</sub> equaled that of Bu<sub>4</sub>NBF<sub>4</sub> in nitromethane- $d_3$ . This rules out that the broadening is caused by purely electrostatic ion-pairing effects. The fact that the broadening was greatest at low AgBF<sub>4</sub> concentrations, as well as the finding that addition of acetonitrile or Bu<sub>4</sub>NBr suppressed the broadening, argue against trace decomposition being the cause. The observations are in our view best explained by assuming that a complex is reversibly (hence the broadening effects due to dynamic behavior) formed between 8a, Ag<sup>+</sup>, and  $BF_4^-$ . A Lewis acid/base interaction between  $Ag^+$  and 8aconceivably can occur at the acetyl oxygen atom, at the metal,<sup>13a-c</sup> or at the halide.<sup>13d-f</sup> The spectroscopic data do not allow a definitive conclusion to be drawn regarding the nature of the interaction between 8a and AgBF<sub>4</sub>. Metal binding appears unlikely for steric reasons. Coordination at Br presumably could lead to expulsion of AgBr when acetonitrile is added.<sup>13a</sup> We suggest, with some support from the rather large chemical shift perturbation of the acetyl 'H NMR resonance from  $\delta$  2.29 to 3.00 (even the *dicationic* CpW(NCMe)( $\eta^2$ -dppe)- $(\eta^2$ -COMe)<sup>+</sup> gives rise to a signal at only  $\delta$  2.51), that Ag<sup>+</sup> coordinates at the acetyl oxygen atom. The coordination of Lewis acids at acyl ligands is precedented.<sup>14</sup> In order to rationalize the broadening of the BF4<sup>-</sup> resonance in the <sup>19</sup>F spectrum, we propose that the Ag<sup>+</sup> coordination leads to a change of the acetyl coordination mode<sup>15</sup> at W from  $\eta^2$  to  $\eta^1$ . This generates a vacant coordination site at W which is reversibly occupied by the BF4<sup>-</sup> counterion. A possible formulation of the complex between 8a and AgBF4, 10, is depicted.



The reversible formation of a species like **10** accounts for the described spectroscopic behavior. The broadening in the <sup>19</sup>F NMR spectra is caused by rapidly exchanging free and coordinated  $BF_4^-$ ; the coordinated  $BF_4^-$  furthermore may exhibit fluxional behavior.<sup>16</sup> The temperature dependence of the spectra indicates a shift of the equilibrium to the right at lower temperatures, as expected for entropy reasons. The addition of Bu<sub>4</sub>NBr removes Ag<sup>+</sup> and serves to re-form **8a**; likewise, the addition of acetonitrile removes Ag<sup>+</sup> by coordination and consequently regenerates **8a**.

Despite the fact that nitromethane and acetonitrile have quite similar dielectric constants ( $\epsilon = 38.0$  and 38.6, respectively<sup>17</sup>), the two solvents have caused important differences in the progress of many reactions that have been described thus far. The key to the differences lies in the poor coordinating ability of nitromethane relative to acetonitrile (donor numbers 2.7 and 14.1, respectively<sup>17</sup>). Nitromethane is much less frequently used in organometallic chemistry than dichloromethane, which is often employed as a "noncoordinating" solvent. Nitromethane nicely combines the noncoordinating capability of dichloromethane with the polar properties of acetonitrile or acetone. This enables the investigation of dicationic species (often essentially insoluble in dichloromethane) under nonnucleophilic conditions.

In the absence of  $Br^-$  abstraction, the observed interaction between the cationic complex **8a** and  $Ag^+$  was rather unexpected, and suggests that the metal, although formally W(IV) and cationic, is not terribly electron deficient. The spectroscopic data in Table 1 indicate that **1** is considerably more electron deficient than **8a**. In accord with this, there was no spectroscopic evidence (<sup>1</sup>H, <sup>19</sup>F NMR) for a similar interaction between  $1(BF_4^-)_2$  and  $AgBF_4$  in nitromethane- $d_3$ . There was also no evidence for an interaction between **8a** and LiBF<sub>4</sub> in nitromethane- $d_3$ , suggesting that the Lewis acid/base interaction is somehow specific to  $Ag^+$  (the lack of effect by LiBF<sub>4</sub> could, however, also be caused by the poor solubility of LiBF<sub>4</sub> in this solvent).

Ag<sup>+</sup>-Assisted Substitution of Acetonitrile for PPh<sub>3</sub> in  $CpW(PPh_3)_2(Br)(\eta^2-COMe)^+$  (8b). Unlike the situation for **8a**, the addition of  $AgBF_4$  led to no discernible changes in the <sup>1</sup>H spectrum of **8b**(BF<sub>4</sub><sup>-</sup>) in nitromethane- $d_3$ . The difference may be due to the poorer donor strength and/or greater steric bulk of the PPh<sub>3</sub> ligand relative to PMePh<sub>2</sub>. When 14 equiv of acetonitrile was added to a nitromethane- $d_3$  solution of  $8b(BF_4^-)$ , a ca. 2:1 equilibrium ratio of 8b and 9b was reached within 5-10 min. (The equilibrium was further displaced toward **9b** when the amount of acetonitrile was increased.) Contrasting this behavior, the addition of 2 equiv of AgBF<sub>4</sub> to this mixture caused a faster reaction to take place. Coordinated acetonitrile was observed at  $\delta$  2.52, and the <sup>1</sup>H NMR spectrum revealed that 9b was the only W-containing compound present! AgBF4 apparently catalyzed the substitution of acetonitrile for PPh3. In view of the observed reactivity of 8a in the presence of AgBF<sub>4</sub>, we propose that the reaction involves a change of the

<sup>(13) (</sup>a) Liston, D. J.; Reed, C. A.; Eigenbrot, C. W.; Scheidt, W. R. Inorg. Chem. 1989, 26, 2739. (b) Usón, R.; Forniés, J.; Tomás, M.; Casas, J. M.; Cotton, F. A.; Falvello, L. R. J. Am. Chem. Soc. 1985, 107, 2556. (c) Smith, G.; Cole-Hamilton, D. J.; Gregory, A. C.; Gooden, N. G. Polyhedron 1982, I, 97. (d) Usón, R.; Forniés, J.; Menjon, B.; Cotton, F. A.; Falvello, L. R.; Tomás, M. Inorg. Chem. 1985, 24, 4651. (e) Mattson, B. M.; Graham, W. A. G. Inorg. Chem. 1981, 20, 3186. (f) Salnikova, T. N.; Adrianov, V. G.; Struchkov, Y. T. Koord. Khim. 1976, 2, 707.

<sup>(14) (</sup>a) Butts, S. B.; Strauss, S. H.; Holt, E. M.; Stimson, R. E.; Alcock, N. W.; Shriver, D. F. J. Am. Chem. Soc. 1980, 102, 5093. (b) Labinger, J. A.; Bonfiglio, J. N.; Grimmett, D. L.; Masuo, S. T.; Shearin, E.; Miller, J. S. Organometallics 1983, 2, 733.

<sup>(15)</sup> Despite the common notion that η<sup>2</sup>-acetyl bonding may stabilize the otherwise unsaturated intermediate in CO insertion reactions, direct η<sup>2</sup>-to-η<sup>1</sup> interconversions are quite rare. For examples, see: (a) Carmona, E.; Sánchez, L.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Priester, R. D.; Rogers, R. D. J. Am. Chem. Soc. 1984, 106, 3214. (b) Birk, R.; Berke, H.; Huttner, G.; Zsolnai, L. Chem. Ber. 1988, 121, 1557. (c) Jablonski, C.; Bellachioma, G.; Cardaci, G.; Reichenbach, G. J. Am. Chem. Soc. 1990, 112, 1632. (d) Kölbener, P.; Hund, H.-U.; Bosch, H. W.; Sontag, C.; Berke, H. Helv. Chim. Acta 1990, 73, 2251. (e) Carmona, E.; Contreras, L.; Poveda, M. L.; Sánchez, L. J. J. Am. Chem. Soc. 1991, 113, 4322. (f) Contreras, L.; Monge, A.; Pizzano, A.; Ruiz, C.; Sánchez, L.; Carmona, E. Organometallics 1992, 11, 3971. (g) Debad, J. D.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. Organometallics 1994, 12, 2714.

<sup>(16) (</sup>a) For a review of the coordination chemistry of BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>, see: Beck, W.; Sünkel, K. Chem. Rev. 1988, 88, 1405. For other, interesting examples of BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> coordination, see: (b) Honeychuck, R. V.; Hersh, W. H. J. Am. Chem. Soc. 1989, 111, 6056. (c) Honeychuck, R. V.; Hersh, W. H. Inorg. Chem. 1989, 28, 2869. (d) Yang, C. S.; Horng, H. C.; Liao, F. L.; Cheng, C. P. J. Chem. Soc., Chem. Commun. 1994, 1637. (e) Krämer, R.; Lippmann, E.; Noisternig, K.; Steimann, M.; Nagel, U.; Beck, W. Chem. Ber. 1993, 126, 927. (f) Lundquist, E. G.; Folting, K.; Huffman, J. C.; Caulton, K. G. Organometallics 1990, 9, 2254.

<sup>(17)</sup> Lowry, T. H.; Richardson, K. S. Mechanism and Theory in Organic Chemistry, 3rd ed.; Harper & Row: New York, 1987.

acetyl bonding from  $\eta^2$  to  $\eta^1$  induced by Ag<sup>+</sup> coordination at the acetyl oxygen. The opened coordination site at W (maybe shielded by weakly bonded BF<sub>4</sub><sup>-</sup>) is captured by acetonitrile, and phosphine loss and  $\eta^1$  to  $\eta^2$  acetyl conversion eventually generate the product. This reaction involves an electrophileassisted ligand substitution in **8b**.

The outcome of the reaction of 8b with 14 equiv of acetonitrile in nitromethane- $d_3$  showed that **8b** is thermodynamically favored over 9b in the presence of acetonitrile at low concentrations. The rapid appearance of 9b from 8b in the presence of AgBF<sub>4</sub> apparently represents a perturbation past the equilibrium situation. This apparent contradiction is most readily accounted for if one assumes that the rapid formation of 9b is catalyzed by  $Ag^+$  (as evidenced by the dramatic rate enhancement) and that the PPh<sub>3</sub> that is liberated is subsequently scavenged by  $Ag^+$  to give the known<sup>18</sup>  $Ag(PPh_3)_4^+$  cation. The removal of free PPh<sub>3</sub> perturbs the position of the equilibrium when compared with the unassisted reaction. In accord with these observations, we found that when only 0.1-0.2 equiv of AgBF<sub>4</sub> was used, the reaction was still accelerated (equilibrium within 1 min), but-as our interpretation requires-the 8b:9b equilibrium was essentially the same as in the total absence of AgBF<sub>4</sub>.

It is also interesting to note that  $Ag^+$  did not appear to catalyze a further reaction of **9b** to give **4**; we attribute this difference to a greater electron deficiency of **9b** relative to **8b**.

The substitution of acetonitrile for phosphine in **8** is somewhat unusual in that the thermodynamics of such reactions is usually the opposite, i.e. the phosphine complexes are often the thermodynamically favored ones. This has been established, for example, through the electron-transfer-catalyzed substitution reactions by Kochi and co-workers,<sup>19a</sup> and by thermodynamic data for a variety of ligand substitution reactions.<sup>19b</sup> Steric effects are likely to significantly contribute to this reversal.

**Concluding Remarks.** We have extended the scope of substitution reactions of the tungsten(IV) acetyl complexes that were described previously.<sup>4c</sup> The substitution of tertiary phosphine for acetonitrile in these complexes are reversible reactions, the positions of which are highly sensitive to the nature of the phosphine and of the solvent. Complementing the nucleophile-catalyzed ligand substitution reactions described in our previous paper,<sup>4c</sup> we have now discovered that ligand-substitution reactions at  $\eta^2$ -acetyl complexes can also be assisted by the electrophile Ag<sup>+</sup>. These findings supplement early reports of amphoteric behavior of  $\eta^2$ -acyl ligands.

### **Experimental Section**

General Procedures. Organometallic complexes were handled under inert atmosphere by use of standard vacuum line, Schlenk, syringe, and drybox techniques. Acetonitrile was distilled from P<sub>2</sub>O<sub>5</sub>, and acetonitrile-d<sub>3</sub> was distilled from CaH<sub>2</sub>. Nitromethane and nitromethane-d<sub>3</sub> were distilled from CaCl<sub>2</sub>. <sup>1</sup>H NMR spectra were recorded on Varian Gemini-200 (unless otherwise indicated) or Varian XL-300 instruments. <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on the Varian Gemini-200 or Varian XL-300 instruments operating at 50 and 75 MHz. <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F NMR spectra were recorded on the Varian XL-300 instrument operating at 120 and 280 MHz, respectively. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported downfield from tetramethylsilane using the residual solvent resonances as internal standards (for acetonitrile-d<sub>3</sub>: <sup>1</sup>H NMR  $\delta$  1.93, <sup>13</sup>C NMR  $\delta$  1.3; for nitromethane-d<sub>3</sub>: <sup>1</sup>H NMR  $\delta$  4.33, <sup>13</sup>C NMR  $\delta$  62.8). <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts are reported downfield from H<sub>3</sub>PO<sub>4</sub>. A capillary tube containing PPh<sub>3</sub> in the solvent of choice was placed in the NMR tube and used as an external reference (in acetonitrile- $d_3$ ,  $\delta -4.7$ ; in nitromethane- $d_3$ ,  $\delta -5.4$ ). <sup>19</sup>F NMR chemical shifts are reported downfield from CFCl<sub>3</sub>. A capillary tube containing Bu<sub>4</sub>NBF<sub>4</sub> in the solvent of choice was placed in the NMR tube and used as an external reference (in acetonitrile- $d_3$ ,  $\delta -151.8$ ; nitromethane- $d_3$ ,  $\delta -153.2$ ). Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

The compounds  $CpW(CO)_2(NCMe)_2Me^{2+}(BF_4^{-})_2$ ,<sup>4a</sup>  $1(BF_4^{-})_2$ ,<sup>4b</sup>  $2a(BF_4^{-})_2$ ,<sup>4c</sup>  $2b(BF_4^{-})_2$ ,<sup>4c</sup> and  $AcFc^+BF_4^{-5,19}$  were prepared according to published procedures. All other chemicals were obtained from commercial suppliers and were used as received.

trans-CpW(NCMe)<sub>2</sub>(I)( $\eta^2$ -COMe)<sup>+</sup>BF<sub>4</sub><sup>-</sup> (3(BF<sub>4</sub><sup>-</sup>)). An acetonitrile solution (20 mL) of 1(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (100 mg, 0.17 mmol) and KI (23.8 mg, 0.19 mmol) was heated at reflux for 3 h. The solution was cooled and filtered through Celite. The product was precipitated by addition of ether at -20 °C, washed with ether (5 × 10 mL), and dried under vacuum to yield 3(BF<sub>4</sub><sup>-</sup>) as a red powder (89 mg, 90%). <sup>1</sup>H NMR (acetonitrile-d<sub>3</sub>):  $\delta$  2.42 (s, 6 H, NCMe), 3.32 (s, 3 H, COMe), 5.65 (s, 5 H, Cp); <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, acetonitrile-d<sub>3</sub>):  $\delta$  4.6 (s, NCMe), 26.5 (s, COMe), 94.1 (s, Cp), 125.5 (NCMe), 266.1 (s, COMe).

*trans*-CpW(NCMe)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup>BF<sub>4</sub><sup>-</sup> (4(BF<sub>4</sub><sup>-</sup>)). An acetonitrile solution (25 mL) of 1(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (150 mg, 0.25 mmol) and NaBr (29.1 mg, 0.28 mmol) was heated at reflux for 70 min. Workup analogous to that described for 3(BF<sub>4</sub><sup>-</sup>) yielded 4(BF<sub>4</sub><sup>-</sup>) as an orange powder (130 mg, 94%). <sup>1</sup>H NMR (acetonitrile- $d_3$ ):  $\delta$  2.40 (s, 6 H, NCMe), 3.29 (s, 3 H, COMe), 5.63 (s, 5 H, Cp). <sup>13</sup>C{<sup>1</sup>H} NMR (50 MHz, acetonitrile- $d_3$ ):  $\delta$  4.6 (s, NCMe), 27.5 (s, COMe), 94.6 (s, Cp), 125.1 (NCMe), 269.0 (s, COMe). Anal. Calcd for C<sub>11</sub>H<sub>14</sub>-BBrF<sub>4</sub>N<sub>2</sub>OW: C, 24.43; H, 2.61; N, 5.18. Found: C, 24.95; H, 2.97; N, 5.27.

X-ray Crystallographic Determination and Refinement of trans-CpW(NCMe)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup>BF<sub>4</sub><sup>-</sup> (4(BF<sub>4</sub><sup>-</sup>)). Crystals of 4(BF<sub>4</sub><sup>-</sup>) were obtained by diffusion of ether vapors into an acetonitrile solution of 4(BF<sub>4</sub><sup>-</sup>) at ambient temperature. A crystal was mounted on a glass fiber and placed in a cold N<sub>2</sub> stream. Intensity data were obtained with graphite-monochromated Mo K $\alpha$  radiation on a Nicolet P3/F diffractometer. Unit cell dimensions were based upon 25 well-centered reflections (26° < 2 $\theta$  < 35°). Empirical absorption corrections were applied to the data set.<sup>20a</sup> The structure was determined using direct methods (MITHRIL<sup>20b</sup>), and refinements were carried out using the GX Crystallographic Program System.<sup>20c</sup> Some of the light atoms did not yield physically meaningful anisotropic thermal parameters. These were refined isotropically and therefore, the structure in Figure 1 is presented as a PLUTO, rather than ORTEP, plot. A summary of crystal structure data is given in Table 2.

trans-CpW(NCMe)<sub>2</sub>(Cl)( $\eta^2$ -COMe)<sup>+</sup>BF<sub>4</sub><sup>-</sup> (5(BF<sub>4</sub><sup>-</sup>)). An acetonitrile solution (20 mL) of 1(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (100 mg, 0.17 mmol) and NaCl (11.0 mg, 0.19 mmol) was heated at reflux for 3 h. Workup as described for 3(BF<sub>4</sub><sup>-</sup>) yielded impure (ca. 90% by <sup>1</sup>H NMR) 5(BF<sub>4</sub><sup>-</sup>) as a red powder (61 mg, 73%). <sup>1</sup>H NMR (acetonitrile-d<sub>3</sub>):  $\delta$  2.41 (s, 6 H, NCMe), 3.29 (s, 3 H, COMe), 5.62 (s, 5 H, Cp). Other Cp-containing species were seen at  $\delta$  5.64 and 5.59.

Attempted Detection of Bromide Dissociation from  $4(BF_4^-)$ through Mixing  $1(BF_4^-)_2$  and  $4(BF_4^-)$  in Acetonitrile-d<sub>3</sub>. Compounds  $4(BF_4^-)$  (5 mg, 0.009 mmol) and  $1(BF_4^-)_2$  (4 mg, 0.007 mmol) were dissolved in acetonitrile-d<sub>3</sub> (1.0 mL). The <sup>1</sup>H NMR spectrum showed the resonances due to 1 and 4. The rate of exchange of the trans acetonitrile in 1 was essentially the same as in the absence of 4 for 1 h; i.e., bromide dissociation from 4 does not appear to take place to a significant extent on this time scale.

Attempted Reaction of  $1(BF_4^-)_2$  with Bu<sub>4</sub>NF in Acetonitrile-d<sub>3</sub>. An NMR tube was filled with an acetonitrile-d<sub>3</sub> solution (0.5 mL) of  $1(BF_4^-)_2$  (20 mg, 0.03 mmol) and anhydrous Bu<sub>4</sub>NF (13 mg, 0.05 mmol), and the tube was sealed under vacuum. The tube was held for several days at 80 °C, but the <sup>1</sup>H NMR spectrum displayed  $1(BF_4^-)_2$  as the only observable tungsten containing complex. The tube was

 (21) (a) Walker, N.; Stuart, D. Acta Crystallogr., Sect. A 1983, A39, 158.
(b) Gilmore, C. J. J. Appl. Crystallogr. 1984, 17, 42. (c) Mallinson, P. R.; Muir, K. W. J. Appl. Crystallogr. 1985, 18, 51.

<sup>(18)</sup> Cotton, F. A.; Goodgame, D. M. L. J. Chem. Soc. 1960, 5267.

<sup>(19) (</sup>a) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. J. Am. Chem. Soc. 1983, 105, 61. (b) Hoff, C. D. Progr. Inorg. Chem. 1992, 40, 503.

<sup>(20)</sup> Carty, P.; Dove, M. F. A. J. Organomet. Chem. 1971, 28, 125.

opened, and PPh<sub>3</sub> (1.5 mg, 0.006 mmol) was added before the tube was closed again. The <sup>1</sup>H NMR spectrum revealed exclusively  $1(BF_4^{-})_2$  after 2 days at ambient temperature.

 $CpW(\eta^2-dppe)(Br)(\eta^2-COMe)^+BF_4^-$  (6(BF<sub>4</sub><sup>-</sup>)). (a) From 4(BF<sub>4</sub><sup>-</sup>) in Acetonitrile. An acetonitrile solution (15 mL) of  $4(BF_4^{-1})$  (50 mg, 0.092 mmol) and dppe<sup>5</sup> (44 mg, 0.1 mmol) was heated at reflux for 1 h. The solution was filtered, and acetonitrile was removed under vacuum. The residue was taken up in dichloromethane, and the product was precipitated by addition of ether. Washing of the precipitate with ether (5  $\times$  15 mL) and drying under vacuum left 6(BF<sub>4</sub><sup>-</sup>) as an orange powder (63 mg, 81%). <sup>1</sup>H NMR (acetonitrile- $d_3$ ):  $\delta$  2.68 (d, J = 1.3Hz, 3 H, COMe), 2.8 (m, 4 H, dppe-CH<sub>2</sub>), 5.21 (d, J = 2.6 Hz, 5 H, Cp), 7.2-8.0 (m, 20 H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, acetonitrile $d_3$ ):  $\delta$  25.8 (dd, J = 7.1, 30.6 Hz, dppe-CH<sub>2</sub>), 27.7 (dd, J = 9.3, 32.1 Hz, dppe-CH<sub>2</sub>), 28.6 (s, COMe), 92.2 (s, Cp), 124-130 (Ph), 262.0 (d, J = 5.9 Hz, COMe). <sup>31</sup>P{<sup>1</sup>H} NMR (acetonitrile- $d_3$ ):  $\delta$  23.0 (d,  $J_{PP} = 3.4 \text{ Hz}, J_{PW} = 120 \text{ Hz}), 35.0 \text{ (d}, J_{PP} = 3.4 \text{ Hz}, J_{PW} = 120 \text{ Hz}).$ Anal. Calcd for C<sub>33</sub>H<sub>32</sub>BBrF<sub>4</sub>OP<sub>2</sub>W: C, 46.24; H, 3.76; Found: C, 46.00; H, 4.04.

(b) One-Pot Reaction from CpW(CO)<sub>3</sub>Me in Acetonitrile. An acetonitrile solution (40 mL) of  $1(BF_4^{-})_2$  was prepared from CpW(CO)<sub>3</sub>Me (100 mg, 0.287 mmol) and AcFc<sup>+</sup>BF<sub>4</sub><sup>-</sup> (180 mg, 0.572 mmol).<sup>4b</sup> NaBr (31.2 mg, 0.300 mmol) was added and the mixture was heated for 1 h at reflux before dppe (115 mg, 0.3 mmol) was added. After 1 h at reflux, the solution was filtered through Celite, and acetonitrile was removed under vacuum. Workup as described above left  $6(BF_4^{-})$  (171 mg, 71% based on CpW(CO)<sub>3</sub>Me).

(c) From CpW(NCMe)( $\eta^2$ -dppe)( $\eta^2$ -COMe)<sup>2+</sup>(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (7(BF<sub>4</sub><sup>-</sup>)<sub>2</sub>) in Acetonitrile. An acetonitrile solution (20 mL) of 7(BF<sub>4</sub><sup>-</sup>)<sub>2</sub> (40 mg, 0.048 mmol) and NaBr (6.2 mg, 0.06 mmol) was heated at reflux for 13 h. Workup as described for 3(BF<sub>4</sub><sup>-</sup>) gave 6(BF<sub>4</sub><sup>-</sup>) (32 mg, 73%).

trans-CpW(PMePh<sub>2</sub>)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup>(BF<sub>4</sub><sup>-</sup>) (8a(BF<sub>4</sub><sup>-</sup>)). (a) from  $4(BF_4^-)$  in Acetonitrile. An acetonitrile solution (20 mL) of  $4(BF_4^-)$ (40 mg, 0.074 mmol) and PMePh<sub>2</sub> (44 mg, 0.22 mmol) was stirred at room temperature for 2 h. The solution was filtered. Ether (10 mL) was added, and the sample was held at -20 °C for 5 h. During this time, some precipitation took place. The precipitate was removed by filtration, and the desired product was precipitated by addition of more ether (40 mL). This procedure left  $8a(BF_4^-)$  as a pale yellow powder (42 mg, 67%). <sup>1</sup>H NMR (acetonitrile- $d_3$ ):  $\delta$  2.02 (vt, "J" = 4.8 Hz, 6 H, PMePh<sub>2</sub>), 2.29 (t, J = 1.0 Hz, 3 H, COMe), 5.15 (t, J = 2.6 Hz, 5 H, Cp), 7.2-8.0 (m, 20 H). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, acetonitrile $d_3$ ):  $\delta$  11.3 (vt, "J" = 11 Hz, PMePh<sub>2</sub>), 26.3 (s, COMe), 90.5 (s, Cp), 125-133 (Ph), 271.6 (t, J = 6 Hz, COMe). <sup>31</sup>P{<sup>1</sup>H} NMR (acetonitrile*d*<sub>3</sub>):  $\delta$  4.7 (s,  $J_{PW} = 102$  Hz). <sup>19</sup>F NMR (acetonitrile-*d*<sub>3</sub>):  $\delta$  -151.8. Anal. Calcd for C<sub>33</sub>H<sub>34</sub>BBrF<sub>4</sub>P<sub>2</sub>OW: C, 46.14; H, 3.99. Found: C, 45.77; H, 4.28.

(b) From  $1(BF_4^{-})_2$  in Acetonitrile. An acetonitrile solution (60 mL) of  $1(BF_4^{-})_2$  (270 mg, 0.46 mmol) and NaBr (53 mg, 0.52 mmol) was heated at reflux for 1 h. The solution was cooled at -20 °C, and precipitated NaBr was removed by filtration. PMePh<sub>2</sub> (350 mg, 1.75 mmol) was added to the solution, and the mixture was stirred at 20 °C for 5 h. The solution was concentrated to ca. 5 mL under vacuum. Filtration through Celite into vigorously stirred ether (100 mL) caused the product to precipitate. The product (311 mg, 78%) was washed with ether (3 × 50 mL) and dried under vacuum.

(c) From 4(BF<sub>4</sub><sup>-</sup>) in Nitromethane. A nitromethane solution (10 mL) of 4(BF<sub>4</sub><sup>-</sup>) (40 mg, 0.074 mmol) and PMePh<sub>2</sub> (44 mg, 0.22 mmol, 3 equiv) was stirred at ambient temperature for 5 min. Ether was added (100 mL), and a yellow crystalline precipitate formed. The solvent was decanted, and the precipitate was washed with ether (8 × 20 mL). (It is crucial to use a large amounts of ether in this process. If the nitromethane is not completely removed with the ether, an oil will result when the material is dried under vacuum.) Drying under vacuum left 9(BF<sub>4</sub><sup>-</sup>) (45 mg, 72%) as a yellow powder. <sup>1</sup>H NMR (nitromethane-d<sub>3</sub>):  $\delta$  2.15 (vt, "J" = 4.8 Hz, 6 H, PMePh<sub>2</sub>), 2.34 (dd, J = 1.0 Hz, 3 H, COMe), 5.29 (t, J = 2.6 Hz, 5 H, Cp), 7.2–8.0 (m, 20 H, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (nitromethane-d<sub>3</sub>):  $\delta$  3.5 (s, J<sub>PW</sub> = 102 Hz). <sup>19</sup>F NMR (nitromethane-d<sub>3</sub>):  $\delta$  -153.2, sharp.

*trans*-CpW(PPh<sub>3</sub>)<sub>2</sub>(Br)( $\eta^2$ -COMe)<sup>+</sup>(BF<sub>4</sub><sup>-</sup>) (8b(BF<sub>4</sub><sup>-</sup>)). A nitromethane solution (4 mL) of 4(BF<sub>4</sub><sup>-</sup>) (50 mg, 0.093 mmol) and PPh<sub>3</sub> (97 mg, 0.37 mmol) was stirred at ambient temperature for 5 h. Workup

**Table 4.** NMR Data for  $8a(BF_4^-)$  (0.01 mmol) in Nitromethane- $d_3$  (0.5 mL) in the Presence of AgBF<sub>4</sub>

amt of AgBF <sub>4</sub> ,	'H NMR, δ				
mmol	mol <u>Cp COMe</u>		<sup>19</sup> F NMR, $\delta$		
0.0	5.29	2.34	-153.2 (sharp)		
0.006	5.30	2.38	too broad to observe		
0.012	5.32	2.48	too broad to observe		
0.024	5.33	2.48	-145.0 (half-width 400 Hz)		
0.048	5.37	2.56	-148.0 (half-width 280 Hz)		
0.096	5.44	2.74	-150.0 (half-width 140 Hz)		
0.384	5.50	3.00	-152.5 (half-width 80 Hz)		

as described for **8a**(BF<sub>4</sub><sup>-</sup>) (when prepared in nitromethane) left **8b**(BF<sub>4</sub><sup>-</sup>) as a yellow powder (71 mg, 78%). <sup>1</sup>H NMR (nitromethane*d*<sub>3</sub>):  $\delta$  2.38 (t, *J* = 1.0 Hz, 3 H, CO*Me*), 5.39 (t, *J* = 2.6 Hz, 5 H, *Cp*), 7.4–7.8 (m, 30 H, *Ph*). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, nitromethane-*d*<sub>3</sub>):  $\delta$ 24.8 (s, CO*Me*), 94.5 (s, *Cp*), 115–125 (*Ph*), 282.2 (t, *J* = 6 Hz, *C*OMe). <sup>31</sup>P{<sup>1</sup>H} NMR (nitromethane-*d*<sub>3</sub>):  $\delta$  14.2 (s, *J*<sub>PW</sub> = 102 Hz). <sup>19</sup>F NMR (nitromethane-*d*<sub>3</sub>):  $\delta$  –153.2, sharp. Anal. Calcd for C<sub>43</sub>H<sub>38</sub>-BBrF<sub>4</sub>OP<sub>2</sub>W: C, 52.53; H, 3.87. Found: C, 51.78; H, 3.97.

**CpW(NCMe)(PPh<sub>2</sub>Me)(Br)(\eta^2-COMe)<sup>+</sup>(<b>BF**\_4<sup>-</sup>) (9a(**BF**\_4<sup>-</sup>)). An acetonitrile solution (10 mL) of a mixture of *cis*- and *trans*-2a(**B**F\_4<sup>-</sup>)<sub>2</sub> (40 mg, 0.052 mmol) and NaBr (6 mg, 0.06 mmol) was heated at reflux for 1 h. The solution was cooled at -20 °C and filtered to remove precipitated material. Workup as described for 4(**B**F\_4<sup>-</sup>) yielded 9a(**B**F\_4<sup>-</sup>) as a light orange powder (35 mg, 83%, ca. 80-90% pure by <sup>1</sup>H NMR). <sup>1</sup>H NMR (acetonitrile-*d*<sub>3</sub>)  $\delta$  2.12 (d, J = 10 Hz, 3 H, PMePh<sub>2</sub>), 2.43 (s, 3 H, NCMe), 2.91 (d, J = 1.2 Hz, 3 H, COMe), 5.44 (d, J = 2.6 Hz, 5 H, *Cp*), 7.2–7.8 (m, 10 H, *Ph*); <sup>31</sup>P{<sup>1</sup>H} NMR (acetonitrile-*d*<sub>3</sub>)  $\delta$  12.0 (s,  $J_{\text{FW}} = 102$  Hz). In addition, the <sup>1</sup>H NMR spectrum revealed contamination from 4 and 8a (<20% combined). An acetonitrile-*d*<sub>3</sub> solution of 9a(**B**F\_4<sup>-</sup>) reacted within 30 min in the absence of added PMePh<sub>2</sub> to a mixture of 4, 8a, and an unknown species with a Cp <sup>1</sup>H NMR resonance at  $\delta$  5.20 (ca. 30%). In nitromethane-*d*<sub>3</sub>, 9a underwent rapid disproportionation to give 4 and 8a.

Interaction between 8a(BF<sub>4</sub><sup>-</sup>) and AgBF<sub>4</sub>. The compound 8a(BF<sub>4</sub><sup>-</sup>) (50 mg, 0.06 mmol) was dissolved in nitromethane- $d_3$  (3.0 mL) and distributed in roughly equal portions into six NMR tubes. Into each tube, AgBF<sub>4</sub> was added in quantities according to Table 4, and <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded. The <sup>1</sup>H NMR resonances for the PMePh<sub>2</sub> ligand underwent no discernible changes when AgBF<sub>4</sub> was added. The Cp-P couplings were unaffected by the presence of AgBF<sub>4</sub>, whereas the  $\eta^2$ -acetyl couplings to P were lost.

When  $8a(BF_4^-)$  (10 mg, 0.012 mmol) and AgBF<sub>4</sub> (4.0 mg, 0.020 mmol) were dissolved in acetonitrile- $d_3$  (0.5 mL), the <sup>1</sup>H NMR spectrum displayed the ordinary, sharp resonances of 8a. The <sup>19</sup>F NMR spectrum displayed the normal "free" BF<sub>4</sub><sup>-</sup> resonance at  $\delta$  –151.8. There was no evidence for specific interactions between 8a, Ag<sup>+</sup>, and BF<sub>4</sub><sup>-</sup> in this solvent.

Interaction between Acetonitrile and AgBF<sub>4</sub> in Nitromethaned<sub>3</sub>. The <sup>1</sup>H NMR spectrum of a solution of AgBF<sub>4</sub> (9.3 mg, 0.048 mmol) and acetonitrile (2.0  $\mu$ L, 0.038 mmol) in nitromethane-d<sub>3</sub> (ca. 0.5 mL) showed a singlet at  $\delta$  2.40 which is tentatively attributed to Ag(NCMe)<sub>4</sub><sup>+</sup>.<sup>10</sup> An averaged signal of bonded and free acetonitrile resulted when large amounts of acetonitrile were added.

Reaction between the 8a/AgBF<sub>4</sub> Complex and Acetonitrile in Nitromethane-d<sub>3</sub>. AgBF<sub>4</sub> (9.3 mg, 0.048 mmol) was added to a solution of 8a(BF<sub>4</sub><sup>-</sup>) (10 mg, 0.012 mmol) in nitromethane-d<sub>3</sub> (ca. 0.5 mL). The <sup>1</sup>H and <sup>19</sup>F NMR spectra showed the broadened resonances due to the 8a/AgBF<sub>4</sub> complex as described above. Successive additions of acetonitrile caused the <sup>1</sup>H and <sup>19</sup>F NMR spectra to gradually approach those of 8a(BF<sub>4</sub><sup>-</sup>) alone. The averaged acetonitrile signal appeared at first at  $\delta$  2.40 and then moved toward the 2.00 value of free acetonitrile.

Reaction of 8b(BF<sub>4</sub><sup>-</sup>) with Acetonitrile in Nitromethane- $d_3$ . (a) In the Absence of AgBF<sub>4</sub>. Acetonitrile (3.5  $\mu$ L, 0.07 mmol) was added to a solution of 8b(BF<sub>4</sub><sup>-</sup>) (5 mg, 0.005 mmol) in nitromethane- $d_3$  (ca. 0.5 mL). After 10 min, a 2:1 ratio of 8b to 9b was observed. This ratio did not change during the next 2 h, although partial reaction to yield some 4 and several unidentified decomposition products occurred. Spectroscopic data for 9b(BF<sub>4</sub><sup>-</sup>): <sup>1</sup>H NMR (nitromethane- $d_3$ )  $\delta$  2.52 (s, 3 H, NCMe), 3.10 (d, J = 0.8 Hz, 3 H, COMe), 5.54 (d, J = 2.6 Hz, 5 H, Cp), 7.2–8.0 (m, 15 H); <sup>31</sup>P{<sup>1</sup>H} NMR (nitromethane $d_3$ )  $\delta$  22.2 (s,  $J_{PW} = 106$  Hz). In separate experiments it was found that, qualitatively, the pseudoequilibrium ratio between **9b** and **8b** increased when more than 14 equiv of acetonitrile was used.

(b) In the Presence of AgBF<sub>4</sub>. Acetonitrile (3.5  $\mu$ L, 0.07 mmol) was added to a solution of **8b**(BF<sub>4</sub><sup>-</sup>) (5 mg, 0.005 mmol) and AgBF<sub>4</sub> (2.0 mg, 0.01 mmol) in nitromethane- $d_3$  (ca. 0.5 mL). In comparison with the above experiment, the rate with which **9b** formed increased. Within 2 min, the <sup>1</sup>H NMR spectrum showed no evidence for **8b** at all, and **9b** as the only tungsten-containing product.

When an analogous experiment was performed with 0.1-0.2 equiv of AgBF<sub>4</sub>, the same equilibrium ratio between **9b** and **8b** as in (a) was established within 2 min.

**Reaction of 4(BF**<sub>4</sub><sup>-</sup>) with **PPh**<sub>3</sub> in Acetonitrile-*d*<sub>3</sub>. An acetonitrile*d*<sub>3</sub> solution (0.4 mL) of 4(BF<sub>4</sub><sup>-</sup>) (8 mg, 0.015 mmol) and PPh<sub>3</sub> (7.8 mg, 0.03 mmol) was stirred at 20 °C. The <sup>1</sup>H NMR spectrum showed a 2:1 mixture of **9b**-*d*<sub>3</sub> and **4** after 60 h. Spectroscopic data for **9b**-*d*<sub>3</sub>: <sup>1</sup>H NMR (acetonitrile-*d*<sub>3</sub>)  $\delta$  3.02 (d, J = 0.8 Hz, 3 H, COMe), 5.45 (d, J = 2.6 Hz, 5 H, *Cp*), 7.2–8.0 (m, 15 H); <sup>31</sup>P{<sup>1</sup>H} NMR (acetonitrile*d*<sub>3</sub>)  $\delta$  24.2 (s,  $J_{PW} = 102$  Hz).

**Reaction of 8b(BF\_4^-) in Acetonitrile-d<sub>3</sub>.** When  $8b(BF_4^-)$  was dissolved in acetonitrile-d<sub>3</sub>, the <sup>1</sup>H NMR spectrum displayed 9b-d<sub>3</sub> as the only detectable species present after 1 min.

**Reaction of 4(BF<sub>4</sub><sup>-</sup>) with 1 Equiv of PPh<sub>3</sub> or PMePh<sub>2</sub> in Nitromethane-d<sub>3</sub>. Nitromethane-d<sub>3</sub> solutions (0.5 mL) of 4(BF<sub>4</sub><sup>-</sup>) (8 mg, 0.015 mmol) and PR<sub>3</sub> (PR<sub>3</sub> = PMePh<sub>2</sub>, 3 \muL, 0.015 mmol; PPh<sub>3</sub>, 3.9 mg, 0.015 mmol) were inspected by <sup>1</sup>H NMR spectroscopy. The spectra revealed 1:1 mixtures of 4 and 8a, and of 4 and 8b, respectively. There was no evidence for the monophosphine-substituted complex 9a in the reaction with PMePh<sub>2</sub>; with PPh<sub>3</sub>, ca. 10% of 9b was present. Prolonged reaction times led to unselective decomposition reactions. Cyclopentadiene was one of the decomposition products.** 

Acknowledgment. We gratefully acknowledge generous support from Statoil under the VISTA program, administered by the Norwegian Academy of Science and Letters. C.R. is grateful for financial support from the Norwegian Research Council (NFR).

Supplementary Material Available: PLUTO plot of both crystallographically independent molecules and tables of crystallographic data, positional and thermal parameters, bond lengths, and bond angles for  $4(BF_4^{-})$  (9 pages). Ordering information is given on any current masthead page.

IC941329M