Halide and Tertiary Phosphine Derivatives of the Tungsten(IV) η^2-Acetyl Complex $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}$. Reversible Ag^+-Assisted Opening of an η^2-Acetyl Group?

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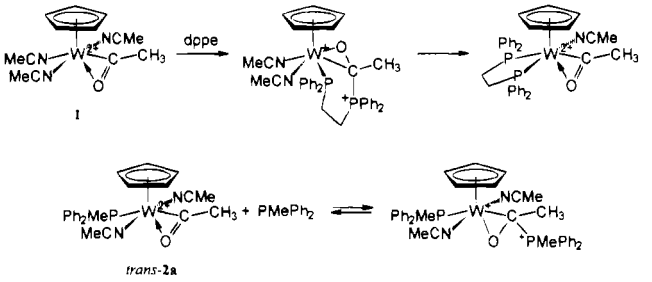
The dicationic W(IV) η^2-acetyl complex $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}$ (**1**) serves as the precursor for new tungsten(IV) η^2-acetyl derivatives. Treatment of **1** with halides provided *trans*-$CpW(NCMe)_2(X)(\eta^2\text{-}COMe)^+$ (X = Cl, Br, I) in high yields. The reaction between $CpW(NCMe)_2(Br)(\eta^2\text{-}COMe)^+$ and dppe yielded the 5-ring chelate $CpW(\eta^2\text{-}dppe)(Br)(\eta^2\text{-}COMe)^+$, while reactions with monodentate tertiary phosphines led to *trans*-$CpW(PR_3)_2(Br)(\eta^2\text{-}COMe)^+$ via the intermediate $CpW(NCMe)(PR_3)(Br)(\eta^2\text{-}COMe)^+$ (PR_3 = $PMePh_2$, PPh_3). Addition of acetonitrile to a nitromethane solution of $CpW(PPh_3)_2(Br)(\eta^2\text{-}COMe)^+$ set up an equilibrium between the substrate and $CpW(NCMe)(PPh_3)(Br)(\eta^2\text{-}COMe)^+$. When $AgBF_4$ was added, this ligand substitution reaction was accelerated. Reversible attachment of Ag^+ at the η^2-acetyl oxygen, ring opening, and reversible BF_4^- binding at the resulting vacant coordination site at W in *trans*-$CpW(PMePh_2)_2(Br)(\eta^2\text{-}COMe)^+$ is suggested on the basis of ^1H and ^{19}F NMR spectroscopic observations. Similar steps are thought to be involved in the Ag^+-catalyzed ligand substitution reaction. A single-crystal X-ray structure determination of $CpW(NCMe)_2(Br)(\eta^2\text{-}COMe)^+$ revealed a four-legged piano stool structure in which the Br and η^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_4^-): space group $P\bar{1}$, a = 7.782(2) Å, b = 12.277(3) Å, c = 16.173(4) Å, α = 89.48(2)°, β = 88.81(2)°, and γ = 88.74(2)°. 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.[2] It has been suggested that the η^2-coordination mode of the acyl group[3] can provide electronic stabilization of the unsaturated intermediate. The η^2-acyl coordination is particularly prevalent among early, especially group 4, transition elements and other relatively high-oxidation 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,[4a] underwent facile CO insertion and substitution resulting in high yields of $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}$ (**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 η^2-acetyl carbon atom to give η^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 incoming ligand. Reactions between **1** and monodentate phosphines led to new tungsten(IV) η^2-acetyl species, *cis*- and *trans*-$CpW(NCMe)_2(PR_3)(\eta^2\text{-}COMe)^{2+}$ (**2a**, R = $PMePh_2$; **2b**, R = PPh_3). With dppm,[5] the chelating acetylphosphonium complex $CpW(NCMe)_2(\eta^3\text{-}Ph_2PCH_2PPh_2COMe)^{2+}$ was isolated; with dppe,[5] the chelating diphosphine substitution product $CpW(NCMe)(\eta^2\text{-}dppe)(\eta^2\text{-}COMe)^{2+}$ was produced with the analogous acetylphosphonium complex $CpW(NCMe)_2(\eta^3\text{-}Ph_2PCH_2CH_2PPh_2COMe)^{2+}$ as an observed intermediate. A temperature-dependent equilibrium that was established by the rapid and reversible attack of $PMePh_2$ at *trans*-**2a** was furthermore seen by ^1H and $^{31}P\{^1H\}$ 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 $CpW(NCMe)_2(X)(\eta^2\text{-}COMe)^+$ and phosphine-substituted derivatives will be discussed. A novel, *electrophile*-assisted ligand substitution reaction of a cationic η^2-acetyl complex will also be presented.

Results and Discussion

Synthesis of $CpW(NCMe)_2(X)(\eta^2\text{-}COMe)^+$ (X = I, Br, Cl). Treatment of $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}(BF_4^-)_2$ (**1**(BF_4^-)$_2$)

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(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.
(5) Abbreviations: dppm = bis(diphenylphosphino)methane; dppe = 1,3-bis(diphenylphosphino)ethane; AcFc = acetylferrocene, (η^5-C_5H_4-COMe)CpFe.

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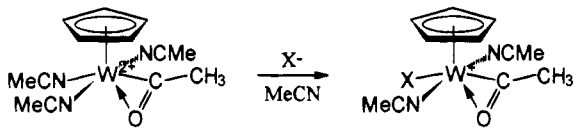
Table 1. Key ^{1}H, ^{13}C, and ^{31}P NMR Spectroscopic Data for W(IV) Complexes[a]

compound	^{1}H NMR[b] *Cp*	*COMe*	*MeCN*	^{13}C NMR[b] *COMe*	*Cp*	*COMe*	^{31}P NMR[c]
CpW(NCMe)$_3$(η^2-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)$_2$(PMePh$_2$)(η^2-COMe)$^{2+}$ (*trans*-**2a**)	5.79 (s)	3.53 (s)	2.58 (d, 6H)	*e*	94.7	*e*	−1.0 (s)
cis-CpW(NCMe)$_2$(PMePh$_2$)(η^2-COMe)$^{2+}$ (*cis*-**2a**)	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)$_2$(η^2-COMe)(I)$^+$ (**3**)	5.65 (s)	3.32 (s)	2.42 (s, 6H)	26.5	94.1	266.1	
trans-CpW(NCMe)$_2$(η^2-COMe)(Br)$^+$ (**4**)	5.63 (s)	3.29 (s)	2.40 (s, 6H)	27.5	94.6	269.0	
trans-CpW(NCMe)$_2$(η^2-COMe)(Cl)$^+$ (**5**)	5.62 (s)	3.29 (s)	2.42 (s, 6H)			266.1	
CpW(η^2-dppe)(η^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)(η^2-dppe)(η^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$_2$)$_2$(Br)(η^2-COMe)$^+$ (**8a**)	5.15 (t)	2.29 (t)		26.3	90.5	271.6	4.7 (s)
trans-CpW(PPh$_3$)$_2$(Br)(η^2-COMe)$^+$ (**8b**)	5.39 (t)	2.38 (t)		24.8	94.5	282.0	14.2 (s)
CpW(NCMe)(PMePh$_2$)(Br)(η^2-COMe)$^+$ (**9a**)	5.44 (d)	2.91 (d)	2.43 (s)				12.0 (s)
CpW(NCMe)(PPh$_3$)(Br)(η^2-COMe)$^+$ (**9b**)[e]	5.54 (d)	3.10 (d)	2.52 (s)				22.2 (s)
CpW(PMePh$_2$)$_2$(Br)(η^2-COMe)$^+$·AgBF$_4$[e]	5.50	3.00					

[a] In acetonitrile-d_3. [b] δ (ppm) relative to TMS. [c] δ (ppm) relative to 85% H_3PO_4. [d] Reference 7a. [e] In nitromethane-d_3.

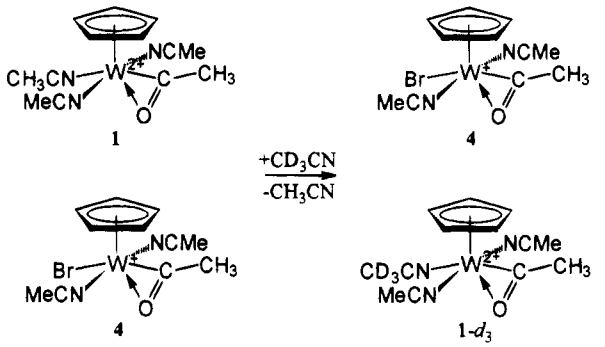
with KI or NaBr in acetonitrile provided high yields of the mono-substituted products *trans*-CpW(NCMe)$_2$(X)(η^2-COMe)$^+$ (**3**, X = I, 90%; **4**, X = Br, 94%) as their BF_4^- salts. No intermediates were detected by ^{1}H NMR spectroscopy during the reaction between **1**(BF_4^-)$_2$ and NaBr at 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[4c] by PPh_3.



1 **3**: X = I; **4**: X = Br; **5**: X = Cl

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 ^{1}H NMR spectroscopy, where the Cp and η^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 ^{1}H NMR spectra of **3** and **4** displayed Cp signals at δ 5.65 and 5.63, respectively, compared to 5.82 in **1**. The η^2-acetyl singlets were observed at δ 3.32 and 3.29, compared to 3.42 in **1**. Direct support for the presence of η^2-acetyl groups in **3** and **4** was provided by resonances at δ 266.1 and 269.0, respectively, in the ^{13}C{^{1}H} NMR spectra. The chloro complex CpW(NCMe)$_2$(Cl)(η^2-COMe)$^+$ (**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 ^{1}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 ^{1}H NMR spectrum. It was found that the rate of exchange of acetonitrile-d_3 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 $AgBF_4$ was added to an acetonitrile-d_3 solution of **4**(BF_4^-).



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.[6] With high-valent metal complexes, organometallic fluoro compounds are more frequently encountered.[6,7] Attempts to generate a fluoro complex by the reaction of **1**(BF_4^-)$_2$ with NaF or anhydrous Bu_4NF were unsuccessful (no consumption of **4** after heating at reflux for several days in acetonitrile). This reation also was not catalyzed[4c] by PPh_3. It is at present not clear if the ineffectiveness of F^- 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,[8] 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)$_2$(Br)(η^2-COMe)$^+$$BF_4^-$ (4(BF_4^-)). The key spectroscopic data presented for **3** and **4** are consistent with their formulation as tungsten(IV) η^2-acetyl species. A number of group 6 metal η^2-acetyl complexes containing the Cp supporting ligand have been previously described,[9] and a few have been structurally characterized.[9c-e,i-k] A neutral W(IV) complex closely related to our systems, CpW(CO)(Cl)$_2$(η^2-COMe), was reported by Kreissl et al.[9c,d] The X-ray crystallographic analysis of this complex revealed a "four-legged piano stool" structure

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(7) O'Donell, T. A.; Philiphs, K. *Inorg. Chem.* **1973**, *12*, 1437.
(8) Skagestad, V.; Tilset, M. Manuscript under preparation.

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

chem formula: $C_{11}H_{14}BBrF_4N_2OW$	ϱ_{calcd} = 2.326 g/cm^3
fw = 540.80	Z = 4
space group: $P\bar{1}$	V = 1544.2(6) Å^3
a = 7.782(2) Å	T = −135 °C
b = 12.277(3) Å	λ = 0.710 69 Å
c = 16.173(4) Å	μ = 102.3 cm^{-1}
α = 89.48(2)°	transm coeff = 0.65−1.41
β = 88.81(2)°	R^a = 0.056
γ = 88.74(2)°	$R_w{}^b$ = 0.054

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

in which the η^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.[4] 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 η^2 fashion. As was found for the structure of CpW(CO)(Cl)$_2$(η^2-COMe),[9c,d] 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)$_2$(η^2-COMe)$^+$ (1.999(8) and 2.167(6) Å, respectively[9c,d]). The acetyl C−O bond distance was 1.272(14) Å, to be compared with 1.246(9) Å in CpW(CO)(Cl)$_2$(η^2-COMe). The acetyl C−O bond vector points away from the Cp ligand; again this agrees with the structure of CpW(CO)(Cl)$_2$(η^2-COMe). The coordinated bromide ligand is situated trans to the η^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 η^2-acyl complexes.[3] 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 1,8-diazabicyclo[5.4.0]undecene (DBU) reversibly deprotonates the acyl group of CpW(CO)(CO_2CF_3)$_2$(η^2-$COCH_2C_6H_4Me$)[9g] and that relatively high acidities (pK_a values in the range 9−18 exist in acetonitrile) have recently been established for some cationic Nb(V) η^2-acyl complexes.[10]

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)(η^2-COMe)$^+BF_4^-$ [a]

Bond Distances			
W(1)−Br(1)	2.601(2)	W(1)−O(1)	2.158(10)
W(1)−N(1)	2.118(11)	W(1)−N(2)	2.149(11)
W(1)−C(1)	2.330(15)	W(1)−C(2)	2.370(15)
W(1)−C(3)	2.312(17)	W(1)−C(4)	2.269(19)
W(1)−C(5)	2.251(16)	W(1)−C(6)	1.960(17)
O(1)−C(6)	1.278(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			
Br(1)−W(1)−O(1)	89.7(3)	Br(1)−W−N(1)	82.1(4)
Br(1)−W(1)−N(2)	83.9(4)	Br(1)−W(1)−C(1)	150.0(5)
Br(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(6)	86.0(6)
C(1)−W(1)−C(2)	36.3(6)	C(1)−W(1)−C(3)	59.0(6)
C(1)−W(1)−C(4)	60.0(6)	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)	71.0(10)	C(3)−C(4)−C(5)	105.3(14)
W(1)−C(5)−C(1)	75.6(9)	W(1)−C(5)−C(4)	72.3(10)
C(1)−C(5)−C(4)	110.4(13)	W(1)−C(6)−O(1)	80.6(9)
W(1)−C(6)−C(7)	151.6(14)	O(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)

[a] Complete parameters, included those for the other crystallographically independent cation, are given in the supplementary material.

Preparation of CpW(η^2-dppe)(Br)(η^2-COMe)$^+BF_4^-$. Treatment of **4**(BF_4^-) with 1 equiv of dppe[5] in acetonitrile proceeded smoothly to give CpW(η^2-dppe)(Br)(η^2-COMe)$^+BF_4^-$ (**6**(BF_4^-)) in high yield (85%). The ^{1}H NMR spectrum of **6** displayed a doublet for the Cp at δ 5.21 and a doublet for the acetyl methyl at δ 2.68. The η^2-acetyl group gave rise to a resonance at δ 262.0 in the ^{13}C{^{1}H} NMR spectrum. The ^{31}P{^{1}H} NMR spectrum displayed two mutually coupled doublets ($^2J_{PP}$ = 3.4 Hz) at δ 23.0 and 35.0, both with ^{183}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 η^2-acetyl group, differing from the trans orientation found in **4**. Quite conveniently, **6**(BF_4^-) could be

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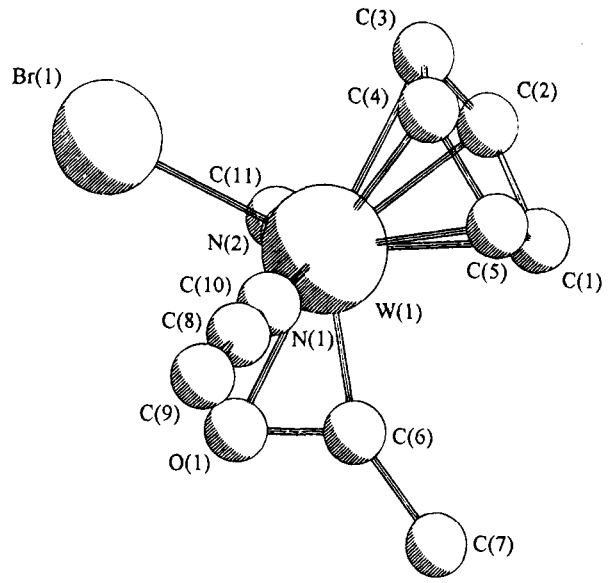
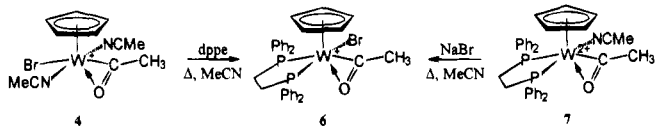


Figure 1. PLUTO plot of one of the crystallographically independent cations of $CpW(NCMe)_2(Br)(\eta^2\text{-}COMe)^+BF_4^-$ (**4**(BF_4^-)). The hydrogen atoms have been omitted for clarity.

prepared in a one-pot reaction, starting from $CpW(CO)_3Me$, in 71% total yield with no intermittent workup. The reaction conditions involved oxidation of $CpW(CO)_3Me$ with $AcFc^+BF_4^-$[5] in acetonitrile to give $CpW(CO)_2(NCMe)_2Me^{2+}$,[4a] followed by a thermal reaction which yielded **1**$(BF_4^-)_2$.[4b] NaBr was added, and the mixture was heated before dppe was finally added. The generation of **6**(BF_4^-) was also accomplished by the reaction of $CpW(NCMe)(\eta^2\text{-dppe})(\eta^2\text{-}COMe)^{2+}(BF_4^-)_2$[4c] (**7**$(BF_4^-)_2$) 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**.

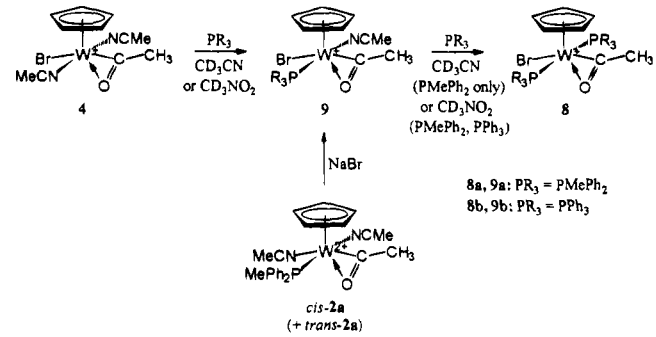


When the reaction between **4**(BF_4^-) and dppe was monitored by ^1H NMR spectroscopy, several species were observed before the reaction was complete. These have not been identified, and it is not clear if they are all true intermediates en route from **4** to **6** or if they arise from nonproductive 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 $^{31}P\{^1H\}$ NMR resonance for free dppe was observed at δ −12. In accord with our previous suggestions,[4c] this broadening is indicative of rapid and reversible phosphine attack at the carbonyl carbon in **4** to give an η^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-d_3 exchange was also observed in the reaction to be described later between **4** and $PMePh_2$, but not in the reaction between **4** and PPh_3. In contrast, there was such a catalytic effect when **1** reacted with both $PMePh_2$ and PPh_3,[4c] and the difference in the behavior of **1** and **4** can be caused by a combination of steric and electronic effects.

Reaction of $CpW(NCMe)_2(Br)(\eta^2\text{-}COMe)^+$ with $PMePh_2$. Synthesis of *trans*-$CpW(PMePh_2)_2(Br)(\eta^2\text{-}COMe)^+BF_4^-$. When **4**$(BF_4^-)$ was stirred for 2 h with 3 equiv of $PMePh_2$ in acetonitrile at ambient temperature, a pale yellow product was obtained in high yields. The ^1H NMR resonances due to the Cp and acetyl ligands of **4** were replaced by triplets at considerably higher field, δ 5.15 (5 H) and 2.29 (3 H) in acetonitrile-d_3. A resonance for two P*Me*Ph_2 ligands was seen as a virtual triplet at δ 2.02 (6 H). The $^{13}C\{^1H\}$ NMR spectrum displayed an η^2-acetyl resonance at δ 271.6. The incorporation of two chemically identical, W-bonded phosphine ligands was established by the presence of a single $^{31}P\{^1H\}$ NMR resonance with ^{183}W satellites at δ 4.7. The spectroscopic and elemental analysis data suggest that the compound is *trans*-$CpW(PMePh_2)_2(Br)(\eta^2\text{-}COMe)^+BF_4^-$ (**8a**(BF_4^-)).

The intermediate $CpW(NCCD_3)(PMePh_2)(Br)(\eta^2\text{-}COMe)^+$ (**9a**-d_3) was observed (^1H NMR) when the reaction between **4**(BF_4^-) and $PMePh_2$ was done in acetonitrile-d_3. In fact, all **4** was consumed, and **9a**-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 ^1H NMR spectrum of **9a**-d_3 showed doublets at δ 5.44 (Cp) and 2.91 (η^2-acetyl). In addition, a resonance for P*Me*Ph_2 was seen at δ 2.12 (d, 3 H). Compound **9a**(BF_4^-) was obtained as the major product when a 4:1 mixture of *cis*- and *trans*-**2a**$(BF_4^-)_2$ was treated with NaBr in acetonitrile. 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 ^1H NMR spectrum (acetonitrile-d_3) of the isolated product also displayed a singlet due to coordinated acetonitrile at δ 2.43. As already discussed in our previous paper,[4c] 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 η^2-CO*Me* ligand is seen when they are cis disposed.[4c] On the basis of these general observations, the most likely geometry for **9a** is that shown below. The $^{31}P\{^1H\}$ NMR spectrum of **9a** displayed a singlet at δ 12.0.



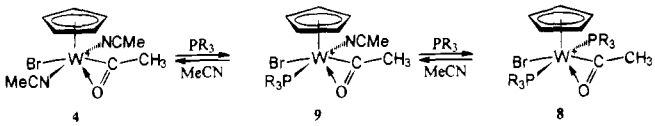
In nitromethane-d_3, the rate of the reaction between **4**(BF_4^-) and $PMePh_2$ showed a dramatic increase. The reaction was done and yielded **8a** in less than 5 min. The mono-substituted intermediate **9a**, observed in acetonitrile-d_3, was not detected in nitromethane-d_3.

Reaction of $CpW(NCMe)_2(Br)(\eta^2\text{-}COMe)^+$ with PPh_3. Experiments analogous to those described above were now performed with PPh_3 instead of $PMePh_2$. In acetonitrile-d_3, a slow reaction ensued with 2 equiv of PPh_3 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 ^{1}H NMR signals at δ 5.45 (d, 5 H) and 3.02 (d, 3 H) for the Cp and acetyl groups, respectively. The ^{31}P{^{1}H} NMR spectrum exhibited a singlet at δ 24.3 accompanied by ^{183}W satellites. This product is identified as CpW(NCCD$_3$)(PPh$_3$)(Br)(η^2-COMe)$^+$ (**9b**-d_3), 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$_3$)$_2$(Br)(η^2-COMe)$^+$BF$_4^-$ (**8b**(BF$_4^-$)). The product showed two ^{1}H NMR triplets at δ 5.39 (5 H) and 2.38 (3 H). The ^{13}C{^{1}H} spectrum revealed an η^2-acetyl resonance at δ 282.2, and the ^{31}P{^{1}H} NMR spectrum displayed a singlet at δ 14.2 with ^{183}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$_3$ in nitromethane-d_3. A 1:1 mixture of **4** and **8b** was present after 3 h (^{1}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$_3$ and PMePh$_2$. 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 for PMePh$_2$; no second incorporation was seen at all for PPh$_3$). 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$_2$ the intermediate was not detectable in nitromethane; for PMePh$_2$, 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$_2$ 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 PMePh$_2$ ligands in **8a** and two harder acetonitrile ligands in **4** is favored over the combination of hard and soft ligands in **9a**.[11]

Reaction of CpW(PPh$_3$)$_2$(Br)(η^2-COMe)$^+$ (8b) with Acetonitrile. When **8b**(BF$_4^-$) was dissolved *in acetonitrile-d_3*, **9b**-d_3 was immediately formed (<1 min). Prolonged reaction times led to the appearance of **4**-d_6 (2:1 ratio of **4**-d_6 and **9b**-d_3 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$_4^-$). 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 ^{1}H NMR spectrum displayed a singlet due to coordinated acetonitrile in **9b** at δ 2.52, and an intense signal due to excess free acetonitrile at δ 2.00. The ^{31}P{^{1}H} NMR spectrum of **9b** showed a singlet surrounded by ^{183}W satellites at δ 22.2.

Interaction between CpW(PMePh$_2$)$_2$(Br)(η^2-COMe)$^+$ (8a) and AgBF$_4$. Silver Ion Coordination at the η^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$_4$ was added to a solution of **8a**(BF$_4^-$) in acetonitrile-d_3, but no changes were observed in the ^{1}H and ^{31}P{^{1}H} NMR spectra. However, when the reaction was attempted in nitromethane-d_3, a different result was obtained. The ^{1}H NMR Cp and η^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 δ 5.29 in **8a** to a limiting value of 5.50. The observed change for the η^2-acetyl group was even greater, with a downfield shift from δ 2.34 in **8a** to a limiting value of 3.00. The magnitude of the Cp−phosphorus coupling was unaffected. For the η^2-acetyl, however, the $^4J_{P-H}$ couplings were no longer resolved. The P*Me*Ph$_2$ resonances were unaffected. Unfortunately, extensive sample decomposition occurred during the acquisition of a ^{13}C{^{1}H} NMR spectrum, and no signal attributable to an acetyl group was observed. The ^{19}F NMR spectrum revealed a resonance shifted ca. 3 ppm downfield from that of Bu$_4$NBF$_4$ when 32 equiv of AgBF$_4$ was employed. When the concentration of AgBF$_4$ was reduced, the ^{19}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 ^{1}H NMR Cp and η^2-acetyl resonances moved downfield from δ 5.37 and 2.56 at 20 °C to 5.42 and 2.70 at −30 °C. No changes were seen in the ^{1}H NMR spectrum of **8a**(BF$_4^-$) in the presence of Bu$_4$NBF$_4$. This behavior must therefore be caused by a specific interaction between Ag$^+$ and **8a**. This conclusion is supported by the finding that when Bu$_4$NBr was added to a nitromethane solution of **8a**(BF$_4^-$) and AgBF$_4$, precipitation of AgBr was seen, and the BF$_4^-$, Cp, and η^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$_4^-$) and 4 equiv of AgBF$_4$. The ^{1}H NMR spectrum changed in such a way that the Cp and η^2-acetyl resonances moved upfield again (in the direction of **8a** alone). A signal due to coordinated acetonitrile was seen at δ 2.40. This signal was also seen in a solution of AgBF$_4$ and 4 equiv of acetonitrile in nitromethane-d_3 and presumably arises from Ag(NCMe)$_4^+$.[12] 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$^+$-bonded) acetonitrile signal grew in intensity and the chemical shift approached that of acetonitrile in nitromethane-d_3 (δ 2.00). Simultaneously, the initially broadened and downfield-shifted ^{19}F NMR spectrum sharpened and moved upfield, approaching the appearance of the spectrum of Bu$_4$NBF$_4$.

Attempts were made to look at the spectroscopic behavior in

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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 $AgBF_4$, 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 ^{19}F NMR chemical shift of $AgBF_4$ equaled that of Bu_4NBF_4 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 $AgBF_4$ concentrations, as well as the finding that addition of acetonitrile or Bu_4NBr 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^+, and BF_4^-. A Lewis acid/base interaction between Ag^+ and **8a** conceivably can occur at the acetyl oxygen atom, at the metal,[13a-c] or at the halide.[13d-f] The spectroscopic data do not allow a definitive conclusion to be drawn regarding the nature of the interaction between **8a** and $AgBF_4$. Metal binding appears unlikely for steric reasons. Coordination at Br presumably could lead to expulsion of AgBr when acetonitrile is added.[13a] We suggest, with some support from the rather large chemical shift perturbation of the acetyl ^1H NMR resonance from δ 2.29 to 3.00 (even the *dicationic* $CpW(NCMe)(\eta^2\text{-dppe})(\eta^2\text{-COMe})^+$ gives rise to a signal at only δ 2.51), that Ag^+ coordinates at the acetyl oxygen atom. The coordination of Lewis acids at acyl ligands is precedented.[14] In order to rationalize the broadening of the BF_4^- resonance in the ^{19}F spectrum, we propose that the Ag^+ coordination leads to a change of the acetyl coordination mode[15] at W from η^2 to η^1. This generates a vacant coordination site at W which is reversibly occupied by the BF_4^- counterion. A possible formulation of the complex between **8a** and $AgBF_4$, **10**, is depicted.

8a **10**

The reversible formation of a species like **10** accounts for the described spectroscopic behavior. The broadening in the ^{19}F NMR spectra is caused by rapidly exchanging free and coordinated BF_4^-; the coordinated BF_4^- furthermore may exhibit fluxional behavior.[16] 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_4NBr removes Ag^+ and serves to re-form **8a**; likewise, the addition of acetonitrile removes Ag^+ by coordination and consequently regenerates **8a**.

Despite the fact that nitromethane and acetonitrile have quite similar dielectric constants (ϵ = 38.0 and 38.6, respectively[17]), 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[17]). 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 (^1H, ^{19}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 $LiBF_4$ in nitromethane-d_3, suggesting that the Lewis acid/base interaction is somehow specific to Ag^+ (the lack of effect by $LiBF_4$ could, however, also be caused by the poor solubility of $LiBF_4$ in this solvent).

Ag^+-Assisted Substitution of Acetonitrile for PPh_3 in $CpW(PPh_3)_2(Br)(\eta^2\text{-}COMe)^+$ (8b). Unlike the situation for **8a**, the addition of $AgBF_4$ led to no discernible changes in the ^1H spectrum of **8b**(BF_4^-) in nitromethane-d_3. The difference may be due to the poorer donor strength and/or greater steric bulk of the PPh_3 ligand relative to $PMePh_2$. 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 $AgBF_4$ to this mixture caused a faster reaction to take place. Coordinated acetonitrile was observed at δ 2.52, and the ^1H NMR spectrum revealed that **9b** was the *only* W-containing compound present! $AgBF_4$ apparently catalyzed the substitution of acetonitrile for PPh_3. In view of the observed reactivity of **8a** in the presence of $AgBF_4$, we propose that the reaction involves a change of the

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(15) Despite the common notion that η^2-acetyl bonding may stabilize the otherwise unsaturated intermediate in CO insertion reactions, direct η^2-to-η^1 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.

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acetyl bonding from η^2 to η^1 induced by Ag^+ coordination at the acetyl oxygen. The opened coordination site at W (maybe shielded by weakly bonded BF_4^-) is captured by acetonitrile, and phosphine loss and η^1 to η^2 acetyl conversion eventually generate the product. This reaction involves an electrophile-assisted 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 $AgBF_4$ 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_3 that is liberated is subsequently scavenged by Ag^+ to give the known[18] $Ag(PPh_3)_4^+$ cation. The removal of free PPh_3 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 $AgBF_4$ 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 $AgBF_4$.

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,[19a] and by thermodynamic data for a variety of ligand substitution reactions.[19b] 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.[4c] 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,[4c] we have now discovered that ligand-substitution reactions at η^2-acetyl complexes can also be assisted by the electrophile Ag^+. These findings supplement early reports of amphoteric behavior of η^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_2O_5, and acetonitrile-d_3 was distilled from CaH_2. Nitromethane and nitromethane-d_3 were distilled from $CaCl_2$. ^1H NMR spectra were recorded on Varian Gemini-200 (unless otherwise indicated) or Varian XL-300 instruments. $^{13}C\{^1H\}$ NMR spectra were recorded on the Varian Gemini-200 or Varian XL-300 instruments operating at 50 and 75 MHz. $^{31}P\{^1H\}$ and ^{19}F NMR spectra were recorded on the Varian XL-300 instrument operating at 120 and 280 MHz, respectively. ^1H and ^{13}C NMR chemical shifts are reported downfield from tetramethylsilane using the residual solvent resonances as internal standards (for acetonitrile-d_3: ^1H NMR δ 1.93, ^{13}C NMR δ 1.3; for nitromethane-d_3: ^1H NMR δ 4.33, ^{13}C NMR δ 62.8). $^{31}P\{^1H\}$ NMR chemical shifts are reported downfield from H_3PO_4. A capillary tube containing PPh_3 in the solvent of choice was placed in the NMR tube and used as an external reference (in acetonitrile-d_3, δ −4.7; in nitromethane-d_3, δ −5.4). ^{19}F NMR chemical shifts are reported downfield from $CFCl_3$. A capillary tube containing Bu_4NBF_4 in the solvent of choice was placed in the NMR tube and used as an external reference (in acetonitrile-d_3, δ −151.8; nitromethane-d_3, δ −153.2). Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

The compounds $CpW(CO)_2(NCMe)_2Me^{2+}(BF_4^-)_2$,[4a] $\mathbf{1}(BF_4^-)_2$,[4b] $\mathbf{2a}(BF_4^-)_2$,[4c] $\mathbf{2b}(BF_4^-)_2$,[4c] 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)$_2$(I)(η^2-COMe)$^+$BF$_4^-$ (3(BF$_4^-$)).** An acetonitrile solution (20 mL) of $\mathbf{1}(BF_4^-)_2$ (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 $\mathbf{3}(BF_4^-)$ as a red powder (89 mg, 90%). ^1H NMR (acetonitrile-d_3): δ 2.42 (s, 6 H, NC*Me*), 3.32 (s, 3 H, CO*Me*), 5.65 (s, 5 H, *Cp*); $^{13}C\{^1H\}$ NMR (50 MHz, acetonitrile-d_3): δ 4.6 (s, NC*Me*), 26.5 (s, CO*Me*), 94.1 (s, *Cp*), 125.5 (N*C*Me), 266.1 (s, *C*OMe).

***trans*-CpW(NCMe)$_2$(Br)(η^2-COMe)$^+$BF$_4^-$ (4(BF$_4^-$)).** An acetonitrile solution (25 mL) of $\mathbf{1}(BF_4^-)_2$ (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 $\mathbf{3}(BF_4^-)$ yielded $\mathbf{4}(BF_4^-)$ as an orange powder (130 mg, 94%). ^1H NMR (acetonitrile-d_3): δ 2.40 (s, 6 H, NC*Me*), 3.29 (s, 3 H, CO*Me*), 5.63 (s, 5 H, *Cp*). $^{13}C\{^1H\}$ NMR (50 MHz, acetonitrile-d_3): δ 4.6 (s, NC*Me*), 27.5 (s, CO*Me*), 94.6 (s, *Cp*), 125.1 (N*C*Me), 269.0 (s, *C*OMe). Anal. Calcd for $C_{11}H_{14}BBrF_4N_2OW$: 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)$_2$(Br)(η^2-COMe)$^+$BF$_4^-$ (4(BF$_4^-$)). Crystals of $\mathbf{4}(BF_4^-)$ were obtained by diffusion of ether vapors into an acetonitrile solution of $\mathbf{4}(BF_4^-)$ at ambient temperature. A crystal was mounted on a glass fiber and placed in a cold N_2 stream. Intensity data were obtained with graphite-monochromated Mo Kα 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.[20a] The structure was determined using direct methods (MITHRIL[20b]), and refinements were carried out using the GX Crystallographic Program System.[20c] 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)$_2$(Cl)(η^2-COMe)$^+$BF$_4^-$ (5(BF$_4^-$)).** An acetonitrile solution (20 mL) of $\mathbf{1}(BF_4^-)_2$ (100 mg, 0.17 mmol) and NaCl (11.0 mg, 0.19 mmol) was heated at reflux for 3 h. Workup as described for $\mathbf{3}(BF_4^-)$ yielded impure (ca. 90% by ^1H NMR) $\mathbf{5}(BF_4^-)$ as a red powder (61 mg, 73%). ^1H NMR (acetonitrile-d_3): δ 2.41 (s, 6 H, NC*Me*), 3.29 (s, 3 H, CO*Me*), 5.62 (s, 5 H, *Cp*). Other Cp-containing species were seen at δ 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_3. Compounds $\mathbf{4}(BF_4^-)$ (5 mg, 0.009 mmol) and $\mathbf{1}(BF_4^-)_2$ (4 mg, 0.007 mmol) were dissolved in acetonitrile-d_3 (1.0 mL). The ^1H 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$_4$NF in Acetonitrile-d_3. An NMR tube was filled with an acetonitrile-d_3 solution (0.5 mL) of $\mathbf{1}(BF_4^-)_2$ (20 mg, 0.03 mmol) and anhydrous Bu_4NF (13 mg, 0.05 mmol), and the tube was sealed under vacuum. The tube was held for several days at 80 °C, but the ^1H NMR spectrum displayed $\mathbf{1}(BF_4^-)_2$ as the only observable tungsten containing complex. The tube was

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opened, and PPh_3 (1.5 mg, 0.006 mmol) was added before the tube was closed again. The ^1H NMR spectrum revealed exclusively **1**$(BF_4^-)_2$ after 2 days at ambient temperature.

$CpW(\eta^2\text{-dppe})(Br)(\eta^2\text{-}COMe)^+BF_4^-$ (6(BF_4^-)). (a) From 4(BF_4^-) in Acetonitrile. An acetonitrile solution (15 mL) of **4**(BF_4^-) (50 mg, 0.092 mmol) and dppe[5] (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 × 15 mL) and drying under vacuum left **6**(BF_4^-) as an orange powder (63 mg, 81%). ^1H NMR (acetonitrile-d_3): δ 2.68 (d, J = 1.3 Hz, 3 H, CO*Me*), 2.8 (m, 4 H, dppe-CH_2), 5.21 (d, J = 2.6 Hz, 5 H, *Cp*), 7.2−8.0 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, acetonitrile-d_3): δ 25.8 (dd, J = 7.1, 30.6 Hz, dppe-*C*H_2), 27.7 (dd, J = 9.3, 32.1 Hz, dppe-*C*H_2), 28.6 (s, CO*Me*), 92.2 (s, *Cp*), 124−130 (*Ph*), 262.0 (d, J = 5.9 Hz, *C*OMe). $^{31}P\{^1H\}$ NMR (acetonitrile-d_3): δ 23.0 (d, J_{PP} = 3.4 Hz, J_{PW} = 120 Hz), 35.0 (d, J_{PP} = 3.4 Hz, J_{PW} = 120 Hz). Anal. Calcd for $C_{33}H_{32}BBrF_4OP_2W$: C, 46.24; H, 3.76; Found: C, 46.00; H, 4.04.

(b) One-Pot Reaction from $CpW(CO)_3Me$ in Acetonitrile. An acetonitrile solution (40 mL) of **1**$(BF_4^-)_2$ was prepared from $CpW(CO)_3Me$ (100 mg, 0.287 mmol) and $AcFc^+BF_4^-$ (180 mg, 0.572 mmol).[4b] 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 $CpW(CO)_3Me$).

(c) From $CpW(NCMe)(\eta^2\text{-dppe})(\eta^2\text{-}COMe)^{2+}(BF_4^-)_2$ (7(BF_4^-)$_2$) in Acetonitrile. An acetonitrile solution (20 mL) of **7**$(BF_4^-)_2$ (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_4^-) gave **6**(BF_4^-) (32 mg, 73%).

***trans*-$CpW(PMePh_2)_2(Br)(\eta^2\text{-}COMe)^+(BF_4^-)$ (8a(BF_4^-)). (a) from 4(BF_4^-) in Acetonitrile.** An acetonitrile solution (20 mL) of **4**(BF_4^-) (40 mg, 0.074 mmol) and $PMePh_2$ (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%). ^1H NMR (acetonitrile-d_3): δ 2.02 (vt, "J" = 4.8 Hz, 6 H, P*Me*Ph_2), 2.29 (t, J = 1.0 Hz, 3 H, CO*Me*), 5.15 (t, J = 2.6 Hz, 5 H, *Cp*), 7.2−8.0 (m, 20 H). $^{13}C\{^1H\}$ NMR (75 MHz, acetonitrile-d_3): δ 11.3 (vt, "J" = 11 Hz, P*Me*Ph_2), 26.3 (s, CO*Me*), 90.5 (s, *Cp*), 125−133 (*Ph*), 271.6 (t, J = 6 Hz, *C*OMe). $^{31}P\{^1H\}$ NMR (acetonitrile-d_3): δ 4.7 (s, J_{PW} = 102 Hz). ^{19}F NMR (acetonitrile-d_3): δ −151.8. Anal. Calcd for $C_{33}H_{34}BBrF_4P_2OW$: 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. $PMePh_2$ (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_4^-) in Nitromethane. A nitromethane solution (10 mL) of **4**(BF_4^-) (40 mg, 0.074 mmol) and $PMePh_2$ (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_4^-) (45 mg, 72%) as a yellow powder. ^1H NMR (nitromethane-d_3): δ 2.15 (vt, "J" = 4.8 Hz, 6 H, P*Me*Ph_2), 2.34 (dd, J = 1.0 Hz, 3 H, CO*Me*), 5.29 (t, J = 2.6 Hz, 5 H, *Cp*), 7.2−8.0 (m, 20 H, *Ph*). $^{31}P\{^1H\}$ NMR (nitromethane-d_3): δ 3.5 (s, J_{PW} = 102 Hz). ^{19}F NMR (nitromethane-d_3): δ -153.2, sharp.

***trans*-$CpW(PPh_3)_2(Br)(\eta^2\text{-}COMe)^+(BF_4^-)$ (8b(BF_4^-)).** A nitromethane solution (4 mL) of **4**(BF_4^-) (50 mg, 0.093 mmol) and PPh_3 (97 mg, 0.37 mmol) was stirred at ambient temperature for 5 h. Workup as described for **8a**(BF_4^-) (when prepared in nitromethane) left **8b**(BF_4^-) as a yellow powder (71 mg, 78%). ^1H NMR (nitromethane-d_3): δ 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*). $^{13}C\{^1H\}$ NMR (75 MHz, nitromethane-d_3): δ 24.8 (s, CO*Me*), 94.5 (s, *Cp*), 115−125 (*Ph*), 282.2 (t, J = 6 Hz, *C*OMe). $^{31}P\{^1H\}$ NMR (nitromethane-d_3): δ 14.2 (s, J_{PW} = 102 Hz). ^{19}F NMR (nitromethane-d_3): δ −153.2, sharp. Anal. Calcd for $C_{43}H_{38}BBrF_4OP_2W$: C, 52.53; H, 3.87. Found: C, 51.78; H, 3.97.

$CpW(NCMe)(PPh_2Me)(Br)(\eta^2\text{-}COMe)^+(BF_4^-)$ (9a(BF_4^-)). An acetonitrile solution (10 mL) of a mixture of *cis*- and *trans*-**2a**$(BF_4^-)_2$ (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**(BF_4^-) yielded **9a**(BF_4^-) as a light orange powder (35 mg, 83%, ca. 80−90% pure by ^1H NMR). ^1H NMR (acetonitrile-d_3) δ 2.12 (d, J = 10 Hz, 3 H, P*Me*Ph_2), 2.43 (s, 3 H, NC*Me*), 2.91 (d, J = 1.2 Hz, 3 H, CO*Me*), 5.44 (d, J = 2.6 Hz, 5 H, *Cp*), 7.2−7.8 (m, 10 H, *Ph*); $^{31}P\{^1H\}$ NMR (acetonitrile-d_3) δ 12.0 (s, J_{PW} = 102 Hz). In addition, the ^1H NMR spectrum revealed contamination from **4** and **8a** (<20% combined). An acetonitrile-d_3 solution of **9a**(BF_4^-) reacted within 30 min in the absence of added $PMePh_2$ to a mixture of **4**, **8a**, and an unknown species with a Cp ^1H NMR resonance at δ 5.20 (ca. 30%). In nitromethane-d_3, **9a** underwent rapid disproportionation to give **4** and **8a**.

Interaction between 8a(BF_4^-) and $AgBF_4$. The compound **8a**(BF_4^-) (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, $AgBF_4$ was added in quantities according to Table 4, and ^1H and ^{19}F NMR spectra were recorded. The ^1H NMR resonances for the $PMePh_2$ ligand underwent no discernible changes when $AgBF_4$ was added. The Cp−P couplings were unaffected by the presence of $AgBF_4$, whereas the η^2-acetyl couplings to P were lost.

When **8a**(BF_4^-) (10 mg, 0.012 mmol) and $AgBF_4$ (4.0 mg, 0.020 mmol) were dissolved in acetonitrile-d_3 (0.5 mL), the ^1H NMR spectrum displayed the ordinary, sharp resonances of **8a**. The ^{19}F NMR spectrum displayed the normal "free" BF_4^- resonance at δ −151.8. There was no evidence for specific interactions between **8a**, Ag^+, and BF_4^- in this solvent.

Interaction between Acetonitrile and $AgBF_4$ in Nitromethane-d_3. The ^1H NMR spectrum of a solution of $AgBF_4$ (9.3 mg, 0.048 mmol) and acetonitrile (2.0 μL, 0.038 mmol) in nitromethane-d_3 (ca. 0.5 mL) showed a singlet at δ 2.40 which is tentatively attributed to $Ag(NCMe)_4^+$.[10] An averaged signal of bonded and free acetonitrile resulted when large amounts of acetonitrile were added.

Reaction between the 8a/$AgBF_4$ Complex and Acetonitrile in Nitromethane-d_3. $AgBF_4$ (9.3 mg, 0.048 mmol) was added to a solution of **8a**(BF_4^-) (10 mg, 0.012 mmol) in nitromethane-d_3 (ca. 0.5 mL). The ^1H and ^{19}F NMR spectra showed the broadened resonances due to the **8a**/$AgBF_4$ complex as described above. Successive additions of acetonitrile caused the ^1H and ^{19}F NMR spectra to gradually approach those of **8a**(BF_4^-) alone. The averaged acetonitrile signal appeared at first at δ 2.40 and then moved toward the 2.00 value of free acetonitrile.

Reaction of 8b(BF_4^-) with Acetonitrile in Nitromethane-d_3. (a) In the Absence of $AgBF_4$. Acetonitrile (3.5 μL, 0.07 mmol) was added to a solution of **8b**(BF_4^-) (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_4^-): ^1H NMR (nitromethane-d_3) δ 2.52 (s, 3 H, NC*Me*), 3.10 (d, J = 0.8 Hz, 3 H, CO*Me*), 5.54 (d, J = 2.6 Hz, 5 H, *Cp*), 7.2−8.0 (m, 15 H); $^{31}P\{^1H\}$ NMR (nitromethane-

Table 4. NMR Data for **8a**(BF_4^-) (0.01 mmol) in Nitromethane-d_3 (0.5 mL) in the Presence of $AgBF_4$

amt of $AgBF_4$, mmol	^1H NMR, δ		^{19}F NMR, δ
	Cp	CO*Me*	
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)

d_3) δ 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 $AgBF_4$. Acetonitrile (3.5 μL, 0.07 mmol) was added to a solution of **8b**(BF_4^-) (5 mg, 0.005 mmol) and $AgBF_4$ (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 ^{1}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 $AgBF_4$, the same equilibrium ratio between **9b** and **8b** as in (a) was established within 2 min.

Reaction of 4(BF_4^-) with PPh_3 in Acetonitrile-d_3. An acetonitrile-d_3 solution (0.4 mL) of **4**(BF_4^-) (8 mg, 0.015 mmol) and PPh_3 (7.8 mg, 0.03 mmol) was stirred at 20 °C. The ^{1}H NMR spectrum showed a 2:1 mixture of **9b**-d_3 and **4** after 60 h. Spectroscopic data for **9b**-d_3: ^{1}H NMR (acetonitrile-d_3) δ 3.02 (d, J = 0.8 Hz, 3 H, CO*Me*), 5.45 (d, J = 2.6 Hz, 5 H, *Cp*), 7.2−8.0 (m, 15 H); ^{31}P{^{1}H} NMR (acetonitrile-d_3) δ 24.2 (s, J_{PW} = 102 Hz).

Reaction of 8b(BF_4^-) in Acetonitrile-d_3. When **8b**(BF_4^-) was dissolved in acetonitrile-d_3, the ^{1}H NMR spectrum displayed **9b**-d_3 as the only detectable species present after 1 min.

Reaction of 4(BF_4^-) with 1 Equiv of PPh_3 or $PMePh_2$ in Nitromethane-d_3. Nitromethane-d_3 solutions (0.5 mL) of **4**(BF_4^-) (8 mg, 0.015 mmol) and PR_3 (PR_3 = $PMePh_2$, 3 μL, 0.015 mmol; PPh_3, 3.9 mg, 0.015 mmol) were inspected by ^{1}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 $PMePh_2$; with PPh_3, ca. 10% of **9b** was present. Prolonged reaction times led to unselective decomposition reactions. Cyclopentadiene was one of the decomposition products.

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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.

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