Nucleophilic Catalysis of Ligand Substitution Reactions in Tungsten(IV) η^2-Acetyl Complexes

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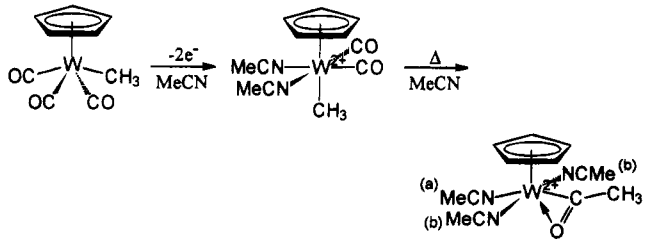
Received January 12, 1994®

The substitution chemistry of the tungsten(IV) η^2-acetyl complex $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}$ (**3a**) has been investigated and a number of derivatives of **3a** containing other nitriles or tertiary phosphine ligands have been synthesized. Ligand substitutions at **3a** are catalyzed by tertiary phosphines. The catalytic effect is due to reversible attack of the phosphine at the carbonyl carbon atom of the η^2-acetyl group in **3a** to yield η^2-acetylphosphonium complexes with labile acetonitrile ligands. The η^2-acetyl/η^2-acetylphosphonium equilibrium was directly observed in the reaction between *trans*-$CpW(NCMe)_2(PMePh_2)(\eta^2\text{-}COMe)^{2+}$ and $PMePh_2$, which reversibly produced $CpW(NCMe)_2(PMePh_2)(\eta^2\text{-}COMe(PMePh_2))^{2+}$. The acetylphosphonium ligands exert a strong cis labilizing effect on coordinated acetonitrile in the four-legged piano-stool complexes. As a result, the reaction of **3a** with PPh_3 produces *cis*-$CpW(NCMe)_2(PPh_3)(\eta^2\text{-}COMe)^{2+}$ as the kinetically favored substitution product. The trans isomer, which is produced at a slower rate, is formed in part by reversion of the cis product to **3a** and a slow trans substitution and in part by a cis/trans interconversion without the involvement of **3a**. Reactions between **3a** and dppe or dppp led to the diphosphine products $CpW(NCMe)(\eta^2\text{-dppe})(\eta^2\text{-}COMe)^{2+}$ and $CpW(NCMe)(\eta^2\text{-dppp})(\eta^2\text{-}COMe)^{2+}$, respectively. The acetylphosphonium complex $CpW(NCMe)_2(\eta^3\text{-}Ph_2PCH_2CH_2PPh_2COMe)^{2+}$ was an observed intermediate in the former reaction. The reaction of **3a** with dppm yielded the acetylphosphonium complex $CpW(NCMe)_2(\eta^3\text{-}Ph_2PCH_2PPh_2COMe)^{2+}$ without observable intermediates. Ring-strain effects probably favor this product over the alternative four-ring chelate $CpW(NCMe)(\eta^2\text{-dppm})(\eta^2\text{-}COMe)^{2+}$.

Introduction

The insertion of carbon monoxide into metal–carbon bonds is one of the most important and well-studied reactions in organotransition-metal chemistry. The CO insertion is a key step in numerous processes that are of great practical and commercial importance.[2,3] The reaction is usually considered to occur by a two-step mechanism in which initial migration of the alkyl group to the CO leaves an open coordination site which is subsequently captured by an incoming ligand.[2b] The formally unsaturated intermediate may be stabilized by interactions with the solvent,[4] agostic interactions,[5] and η^2-acyl coordination.[2b,6] Oxophilic early transition metals and high-oxidation-state complexes of later metals show a tendency to promote η^2-coordination of acyl groups.[6]

We recently reported[7a] that the pseudooctahedral tungsten(IV) alkyl complex $CpW(CO)_2(NCMe)_2Me^{2+}$, available in good yields from the two-electron chemical oxidation of $CpW(CO)_3Me$ in acetonitrile,[7b] undergoes CO insertion and ligand substitution to yield $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}$. Steric factors significantly contributed to the driving force for the CO insertion. Interestingly, the unique trans acetonitrile ligand[8a] in **3**, labeled (a), underwent exchange with acetonitrile-d_3 much faster than the two identical cis acetonitriles (b):[8a]



Furthermore, the exchange of the cis acetonitriles

® Abstract published in *Advance ACS Abstracts,* June 15, 1994.

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0276-7333/94/2313-3134$04.50/0

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

compd	^{1}H NMR[b] *Cp*	^{1}H NMR[b] COMe	^{1}H NMR[b] *Me*CN	^{13}C NMR[b] COMe	^{31}P NMR[c]
$CpW(CO)_2(NCMe)_2Me^{2+}$ (**2a**)[d]	6.40 (s)	1.49 (s) (W—*Me*)	2.58 (s)		
$CpW(CO)_2(NCEt)_2Me^{2+}$ (**2b**)	6.39 (s)	1.49 (s) (W—*Me*)			
$CpW(CO)_2(NCCH_2Ph)_2Me^{2+}$ (**2c**)	6.43 (s)	1.43 (s) (W—*Me*)			
$CpW(NCMe)_3(\eta^2\text{-COMe})^{2+}$ (**3a**)[d]	5.82 (s)	3.42 (s)	2.43 (s, 6H), 2.69 (s, 3H)	276.1	
$CpW(NCEt)_3(\eta^2\text{-COMe})^{2+}$ (**3b**)	5.82 (s)	3.41 (s)			
$CpW(NCCH_2Ph)_3(\eta^2\text{-COMe})^{2+}$ (**3c**)	5.90 (s)	3.42 (s)			
cis-$CpW(NCMe)_2(PMePh_2)(\eta^2\text{-COMe})^{2+}$ (*cis*-**4**)	5.69 (d)	3.12 (d)	2.38 (s, 3H), 2.71 (d, 3H)	267.2 (d)	9.5 (s)
trans-$CpW(NCMe)_2(PMePh_2)(\eta^2\text{-COMe})^{2+}$ (*trans*-**4**)	5.79 (s)	3.53 (s)	2.58 (d, 6H)	*e*	−1.0 (s)
cis-$CpW(NCMe)_2(PPh_3)(\eta^2\text{-COMe})^{2+}$ (*cis*-**5**)	5.69 (d)	3.00 (d)	2.41 (s, 3H), 2.70 (d, 3H)		22.3 (s)
trans-$CpW(NCMe)_2)(PPh_3)(\eta^2\text{-COMe})^{2+}$ (*trans*-**5**)	5.79 (s)	3.52 (s)	2.48 (d, 6H)		14.9 (s)
$CpW(NCMe)(\eta^2\text{-dppe})(\eta^2\text{-COMe})^{2+}$ (**6a**)	5.58 (d)	2.51 (d)	1.86 (d)	274.2	30.6 (d), 35.7 (d)
$CpW(NCEt)(\eta^2\text{-dppe})(\eta^2\text{-COMe})^{2+}$ (**6b**)	5.58 (d)	2.55 (d)			31.5 (d), 36.0 (d)
$CpW(NCMe)(\eta^2\text{-dppp})(\eta^2\text{-COMe})^{2+}$ (**7a**)	5.53 (d)	2.79 (d)	1.80 (d)	266.2 (dd)	−5.7 (d), 4.1 (d)
$CpW(NCEt)(\eta^2\text{-dppp})(\eta^2\text{-COMe})^{2+}$ (**7b**)	5.52 (d)	2.79 (d)			−4.9 (d), 3.8 (d)
$CpW(NCMe)_2(\eta^3\text{-}Ph_2PCH_2PPh_2COMe)^{2+}$ (**8a**)	5.10 (d)	2.12 (d)	2.58 (s, 3H)[f]	66.5 (d)	17.2 (d), 47.9 (d)
$CpW(NCEt)_2(\eta^3\text{-}Ph_2PCH_2PPh_2COMe)^{2+}$ (**8b**)	5.10 (d)	2.12 (d)			
$CpW(NCCD_3)_2(PMePh_2)(\eta^2\text{-COMe(PMePh}_2))^{2+}$ (**9**)	5.39 (d)	2.22 (d)[g]			−15.2 (d), 30.0 (d)
$CpW(NCCD_3)_2(\eta^3\text{-}Ph_2PCH_2CH_2PPh_2COMe)^{2+}$ (**10**)	4.89 (d)	2.07 (d)			4.8 (d), 34.1 (d)

[a] In acetonitrile-d_3. [b] δ (ppm) relative to TMS. [c] δ (ppm) relative to 85% H_3PO_4. [d] Reference 7a. [e] Not detected; see text. [f] One acetonitrile ligand presumed to undergo rapid exchange; see text. [g] Assignment ambiguous; see text.

occurred via a preceding slow intramolecular exchange of cis and trans acetonitriles. Curiously, it was observed that substoichiometric quantities of PPh_3 efficiently *catalyzed* the exchange of the cis acetonitrile ligands but left the rate of exchange of the trans acetonitrile virtually unchanged. The rate of the catalyzed reaction showed a first-order dependence on the PPh_3 concentration. While the role of the PPh_3 was not understood at the time, it was speculated that the catalytic effect might arise from attack by PPh_3 at the metal, at the Cp, or at the carbonyl. A reversible nucleophilic displacement at the methyl group, with $CpW(CO)(NCMe)_3^+$ acting as the leaving group, was discounted.[7a]

The ligand substitution reactions of $CpW(NCMe)_3(\eta^2\text{-COMe})^{2+}$ and related η^2-acetyl complexes have now been investigated more closely. The PPh_3 catalysis has been efficiently exploited in the synthesis of more soluble propionitrile and phenylacetonitrile analogues. PPh_3, $PMePh_2$, dppm, dppe, and dppp[8b] derivatives of $CpW(NCMe)_3(\eta^2\text{-COMe})^{2+}$ have been prepared and characterized. Phosphine attack at the η^2-acetyl functionality generates η^2-acetylphosphonium ligands, side-on bonded through the carbonyl group. It will be shown that a cis-labilizing effect of the acetylphosphonium ligand formed in this reaction provides the key to the mechanisms of the phosphine-catalyzed ligand substitution reactions. Closely related nucleophilic catalysis of ligand substitution and CO insertion reactions at metal carbonyls,[4d,9] in particular by tertiary phosphine oxides, is well documented. These reactions have been suspected to take place via attack at a carbonyl ligand with concomitant labilization of another ligand, although the intermediates have not been observed. We report in this paper the first examples of such catalysis at η^2-acyl ligands, the first evidence that tertiary phosphines may act as the active nucleophile catalyst, and the first direct observation of intermediates in these reactions.

Results

I. Synthesis of New Compounds from $CpW(NCMe)_3(\eta^2\text{-COMe})^{2+}$ by Substitution. The poor solubility of BF_4^- or PF_6^- salts of $CpW(CO)_2(NCMe)_2Me^{2+}$ and $CpW(NCMe)_3(\eta^2\text{-COMe})^{2+}$ in solvents less polar than acetonitrile imposed undesired constraints on the exploration of their reactivities. Improved solubility in less polar solvents should result from the introduction of propionitrile, phenylacetonitrile, or tertiary phosphine ligands instead of acetonitrile. Different approaches that have been employed to synthesize such derivativs will be discussed in the following.

Oxidation of $CpW(CO)_3Me$ in Propionitrile and Phenylacetonitrile. The oxidation of $CpW(CO)_3Me$ with 2 equiv of $(\eta^5\text{-}C_5H_4COMe)(\eta^5\text{-}C_5H_5)Fe^+BF_4^-$ (**1**) in propionitrile and phenylacetonitrile proceeded smoothly to give good yields of $CpW(CO)_2(NCR)_2Me^{2+}$ (**2b**, R = Et; **2c**, R = CH_2Ph) as bis(tetrafluoroborate) salts. Key NMR spectroscopic data for new compounds as well as **2a** and **3a** are listed in Table 1. Complete IR and NMR spectroscopic data are given in the Experimental Section. Key spectroscopic data for **2a**–**c** are similar to those reported[7b] for $CpW(CO)_2(NCMe)_2Me^{2+}$ (**2a**). In agreement with the data, a cis,cis distorted-octahedral coordination sphere is assumed (Scheme 1). An unpublished X-ray structure determination of $\mathbf{2a}(PF_6^-)_2$ has verified the positioning of the ligands in the metal coordination sphere.[10] Similar coordination geometries

(8) (a) In order to avoid repeated lengthy and detailed descriptions of the relative orientations of the acetonitrile ligands throughout this paper, the term "cis nitrile" will refer to the nitrile ligand(s) which is (are) located in the cis position *relative to the η^2-acetyl ligand*. The converse applies to the "trans nitrile". (b) Abbreviations: dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane.

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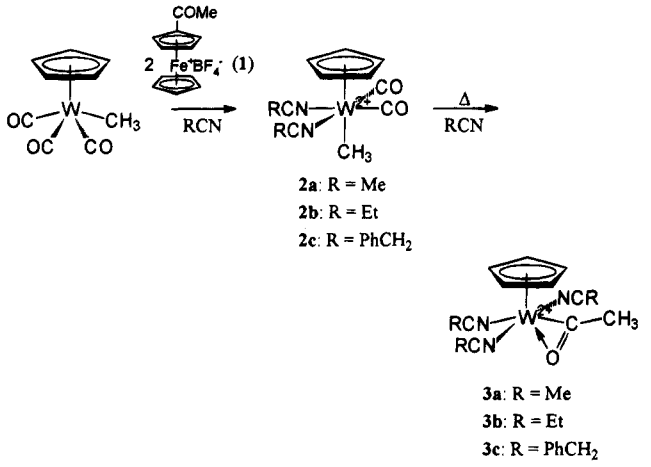
(10) The structure determination of $\mathbf{2a}(PF_6^-)_2$ appeared as a note added in proof in ref 7a. The refined structure verified the assumed coordination geometry and disposition of the ligands but was of insufficient quality for a detailed structural analysis. We have repeatedly experienced that, for this and related dicationic complexes that we have encountered, it has been notoriously difficult to obtain X-ray-quality crystals.

Scheme 1



are adopted by the Mo(IV) complexes *mer,trans*-CpMoCl$_3$(PMe$_2$Ph)$_2$,[11a] *mer,cis*-CpMoCl$_3$(η^2-dmpe),[11b] and *mer,cis*-CpMoCl$_3$(η^2-dppe).[11c]

When the reaction mixtures were heated at reflux before workup, the CO insertion and substitution products CpW(NCR)$_3$(η^2-COMe)$^{2+}$ **3b,c** resulted, although only **3b** was cleanly generated by this procedure (*vide infra*). The spectroscopic data resemble those of CpW(NCMe)$_3$(η^2-COMe)$^{2+}$ (**3a**).[7a] The coordination geometry of **3a** was assumed to be similar to the four-legged piano-stool structure of *cis*-CpW(CO)Cl$_2$(η^2-COMe),[12] characterized by X-ray crystallography. A recent structure determination of *trans*-CpW(NCMe)$_2$(Br)(η^2-COMe)$^+$ [13] in our laboratories lends further support to this assumption. In both structurally characterized complexes, the η^2-acetyl group is perpendicular to the basal plane of the piano stool. The ^{13}C NMR signals of the η^2-acetyl carbonyls appear at δ 278 and 269, respectively, for the two structurally characterized complexes, and leave little doubt that the dicationic species are in fact η^2-acetyl species. The methylene protons in each coordinated nitrile ligand in **2b,c** and in the cis nitriles[8a] in **3b,c** are diastereotopic but give rise to simple quartets in the ^{1}H NMR spectra. This must be due to very small chemical shift differences for the diastereotopic protons, since all evidence suggests that these compounds are rigid on the NMR time scale. In contrast, the isoelectronic four-legged piano-stool complex Cp*Mo(NO)(NCMe)$_3^{2+}$ (Cp* = η^5-C$_5$Me$_5$) was concluded to be stereochemically nonrigid in solution.[14] The infrared ν_{CO} bands for the η^2-acetyl groups have not been observed, but the ^{13}C{^{1}H} NMR spectra show resonances due to the η^2-acetyl carbonyls at δ 265–270.

When the reaction mixture containing **2c** had been heated at 130 °C for 4 h, the acetyl complex **3c** was obtained along with an unidentified product in a (1:1)–(2:1) ratio that did not change by prolonged heating.

Uncatalyzed Nitrile Exchange Reactions of 3a. When a propionitrile solution of **3a**(BF$_4^-$)$_2$ was heated at reflux for at least 3 h, complete exchange of all acetonitrile ligands occurred, and the conversion of **3a** to **3b** was achieved with good yields.

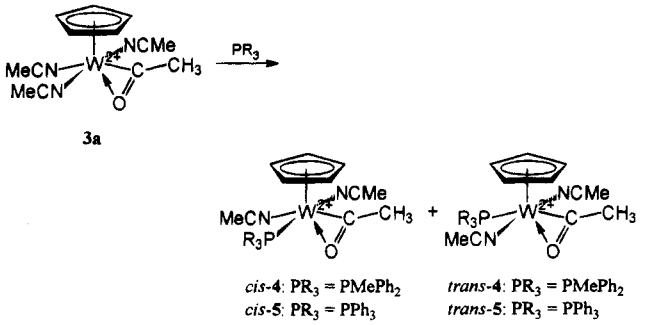
When a phenylacetonitrile solution of **3a**(BF$_4^-$)$_2$ was heated at 130 °C, a (2:1)–(4:1) mixture of **3c** and an unidentified complex was obtained. Other minor products were also seen by ^{1}H spectroscopy. The relative amounts of the two major products did not change when heating was continued.

PPh$_3$-Catalyzed Nitrile Exchange Reactions of 3a. The earlier observation that substoichiometric quantities of PPh$_3$ catalyzed the exchange of the two cis acetonitriles in **3a** enabled the successful syntheses of **3b** and **3c** from **3a**.

With **3a**(BF$_4^-$)$_2$ as starting material, 10 min of reflux in propionitrile led to complete conversion to **3b** when 0.2 equiv of PPh$_3$ was present. The rate of this reaction was in sharp contrast to the 3 h needed for the reaction to proceed in the absence of PPh$_3$. In the same fashion, when **3a**(BF$_4^-$)$_2$ was heated in phenylacetonitrile at 130 °C for 10 min in the presence of 0.2 equiv of PPh$_3$, **3c** was cleanly formed. This constitutes a significant improvement of the uncatalyzed reaction, which produced **3c** contaminated with other, unidentified products.

We were somewhat concerned that adventitious traces of phosphine oxide, rather than the phosphine itself, could be involved in the catalyzed ligand exchange. However, this possibility was effectively eliminated, because the addition of Ph$_3$PO instead of PPh$_3$ to the reaction mixture had no observable catalytic effect on the exchange of acetonitrile-d_3 for acetonitrile in **3a**.

Reaction between 3a and PMePh$_2$ or PPh$_3$. Treatment of **3a**(BF$_4^-$)$_2$ with 2–3 equiv of PMePh$_2$ in acetonitrile at ambient temperature led to the isolation of a 4:1 mixture of the bis(tetrafluoroborate) salts of *cis*-CpW(NCMe)$_2$(PMePh$_2$)(η^2-COMe)$^{2+}$ (*cis*-**4**: ^{1}H NMR δ 2.05 (d, 3 H), 2.38 (s, 3 H), 2.71 (d, 3 H), 3.12 (d, 3 H), 5.69 (d, 5 H); ^{31}P{^{1}H} NMR δ 9.5 (s)) and *trans*-CpW(NCMe)$_2$(PMePh$_2$)(η^2-COMe)$^{2+}$ (*trans*-**4**: ^{1}H NMR δ 2.42 (d, 3 H), 2.58 (d, 6 H), 3.53 (s, 3 H), 5.69 (s, 5 H); ^{31}P{^{1}H} NMR δ −1.0 (s)). Distinct ^{183}W (14% natural abundance) satellites in the ^{31}P spectra showed that PMePh$_2$ was bonded directly to the metal in both isomers. The stereochemical designation indicates the relative positioning of the two acetonitrile ligands, assuming a four-legged piano-stool coordination geometry. The stereochemical assignments are based on the observation of two different coordinated acetonitrile signals of equal intensities in the ^{1}H NMR spectrum for the cis isomer and a single acetonitrile signal for the trans isomer. When a mixture of *cis*-**4**(BF$_4^-$)$_2$ and *trans*-**4**(BF$_4^-$)$_2$ was heated at reflux for 3 h in acetonitrile,



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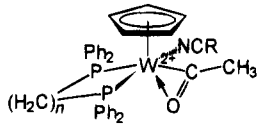
partial back-reaction to produce **3a** occurred. When the reaction between **3a**$(BF_4^-)_2$ and $PMePh_2$ was performed in acetonitrile-d_3, complete incorporation of acetonitrile-d_3 was found in the products.

For these and related phosphine-containing η^2-acetyl complexes that will be described in the following, resolvable couplings between a phosphine ligand and the Cp and acetyl ^1H NMR signals were seen only when the phosphine ligand was located cis to the acetyl group. This observation makes it possible to assign product stereochemistry even if one or more coordinated nitriles undergo exchange with the solvent during the ^1H NMR spectroscopic analysis. Furthermore, phosphorus coupling to a coordinated acetonitrile was observed when at least one nitrile in the complex was located cis to the phosphine. These spectroscopic differences agree with general features of ^1H NMR spectra of other phosphine-substituted four-legged piano-stool complexes. For example, $^3J_{PH}$ couplings in hydrides $CpM(CO)_2(PR_3)H$ (M = Mo, W) and related systems are much greater for the cis (ca. 60−75 Hz) than for the trans (ca. 20−30 Hz) isomers.[15] Couplings between phosphine and coordinated acetonitrile in $CpM(CO)_2(PR_3)(NCMe)^+$ species (M = Mo, W) are observed for the cis, but not for the trans, complexes.[16]

When **3a**$(BF_4^-)_2$ and 2 equiv of PPh_3 were left to react at ambient temperature in acetonitrile-d_3 for extended time periods, it was noted that PPh_3 does in fact catalyze the exchange not only of the cis, but also of the trans, acetonitrile of **3a**. The rate enhancement of the trans exchange was rather modest (ca. 5-fold rate increase at 112 mM PPh_3 for the trans exchange, to be compared with a 220-fold rate increase[7a] at 8 mM PPh_3 for the cis exchange) and this is the reason that the effect was not noticed in our previous work. At the high PPh_3 concentration, a slow substitution reaction also took place. After 16 h, NMR spectra indicated a mixture of $CpW(NCCD_3)_3(\eta^2\text{-}COMe)^{2+}$ (**3a**-d_9; 43%) and two products that are assumed to be *cis*-$CpW(NCCD_3)_2(PPh_3)(\eta^2\text{-}COMe)^{2+}$ (*cis*-**5**-d_6: 41%; ^1H NMR δ 3.00 (d, 3 H), 5.70 (d, 5 H); $^{31}P\{^1H\}$ NMR δ 22.3 (s)) and *trans*-$CpW(NCCD_3)_2(PPh_3)(\eta^2\text{-}COMe)^{2+}$ (*trans*-**5**-d_6: 15%; ^1H NMR δ 3.52 (s, 3 H), 5.79 (s, 5 H); $^{31}P\{^1H\}$ NMR δ 14.9 (s)). The cis isomer was produced faster than the trans isomer. After 12 days at ambient temperature, the same compounds were present but in a 21:43:36 ratio which underwent no change during a 1-month period. The same cis:trans ratio was reproduced in reactions with different PPh_3 concentrations, and this must reflect that equilibrium had been reached between the two isomers. Obviously, there is no strong thermodynamic preference for one isomer over the other. When an isolated mixture of **3a**$(BF_4^-)_2$, *cis*-**5**$(BF_4^-)_2$, and *trans*-**5**$(BF_4^-)_2$ was dissolved in acetonitrile-d_3, partial reversion of *cis*-**5** and *trans*-**5** to the precursor **3a** was observed. The initial rate of this reaction was seen to be about twice as great in the presence of ca. 0.05 equiv of added PPh_3 for both isomers.

Synthesis of dppe- and dppp-Substituted η^2-Acetyl Complexes. A clean reaction between **3a**$(BF_4^-)_2$ and dppe in acetonitrile yielded $CpW(NCMe)(\eta^2\text{-dppe})(\eta^2\text{-}COMe)^{2+}(BF_4^-)_2$ (**6a**$(BF_4^-)_2$). The ^1H NMR spectrum



6a: R = Me, n = 2 **7a**: R = Me, n = 3
6b: R = Et, n = 2 **7b**: R = Et, n = 3

displayed a doublet for the Cp at δ 5.58 and a doublet for the acetyl methyl at δ 2.51. The presence of an η^2-acetyl group was indicated by a resonance at δ 274.2 in the $^{13}C\{^1H\}$ NMR spectrum. In the ^{31}P NMR spectrum, two mutually coupled doublets ($^2J_{PP}$ = 2.4 Hz), both with ^{183}W satellites, were located at δ 30.6 and 35.7. Complete spectroscopic data are given in the Experimental Section. The ^1H and ^{31}P NMR spectra establish a cis-η^2-coordination of the chelating dppe ligand. The analogous compound $CpW(NCEt)(\eta^2\text{-dppe})(\eta^2\text{-}COMe)^{2+}$ (**6b**) was obtained from **3b** when the reaction was performed in propionitrile. The reactions between **3a,b** and dppp similarly yielded $CpW(NCMe)(\eta^2\text{-dppp})(\eta^2\text{-}COMe)^{2+}$ (**7a**) and $CpW(NCEt)(\eta^2\text{-dppp})(\eta^2\text{-}COMe)^{2+}$ (**7b**).

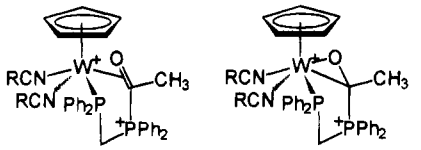
Reaction between 3a,b and dppm: Phosphine Attack at the η^2-Acetyl Ligand. The reactions between **3a**$(BF_4^-)_2$ and **3b**$(BF_4^-)_2$ and dppm in acetonitrile yielded the new products **8a**$(BF_4^-)_2$ and **8b**$(BF_4^-)_2$ which were quite different from the products of the reactions with dppe or dppp, as judged by their NMR spectroscopic data. For **8a**, the ^1H NMR spectrum displayed signals at δ 5.10 (Cp) and 2.12 (COMe). The Cp resonance appears at considerably higher field than the Cp signals of other dicationic W(IV) cyclopentadienyl complexes that have been investigated by us thus far, and this suggests that the metal carries only a single formal charge. The methyl resonance was coupled to only one P atom, and the coupling constant of 14.6 Hz was much greater than the 1.2−1.4-Hz couplings that were observed for the η^2-acetyl methyl groups in **4**−**7**. Only one coordinated acetonitrile ligand was detected by ^1H NMR spectroscopy at δ 2.58 (s, 3 H). A singlet (3 H) was superimposed on the residual solvent peak and signaled the presence of free acetonitrile, probably arising from exchange of a coordinated nitrile with the solvent. In dichloromethane-d_2, one well-defined acetonitrile signal was seen at δ 2.58 (s, 3 H). A broad signal centered at δ 2.1 (3 H) was superimposed on the resonance due to a methylene proton of the dppm ligand and a broadened doublet from the acetyl methyl. We assume that the signal is due to a labile acetonitrile ligand, broadened perhaps due to a rapid dissociation/association process. The $^{13}C\{^1H\}$ NMR spectrum of **8a** (acetonitrile-d_3) failed to show a signal due to an η^2-acetyl ligand but instead displayed a doublet (J = 55 Hz) at δ 66.5. The ^{31}P NMR spectrum showed two mutually coupled signals at δ 17.2 and 47.9. Only the former had the ^{183}W satellites that result from direct bonding to the metal. When **8a** was treated with dppe, **6a** was cleanly produced. This essentially proves that the constituents of the η^2-acetyl ligand are still present in **8a**.

We suggest that **8a** is described as $CpW(NCMe)_2(\eta^3\text{-}Ph_2PCH_2PPh_2COMe)^{2+}$, with a single formal charge

(15) (a) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852. (b) Kalck, P.; Pince, R.; Poilblanc, R. *J. Organomet. Chem.* **1970**, *24*, 445. (c) Flood, T. C.; Rosenberg, E.; Sarhangi, A. *J. Am. Chem. Soc.* **1977**, *99*, 4334.

(16) (a) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618. (b) Smith, K.-T.; Tilset, M. *J. Organomet. Chem.* **1992**, *431*, 55.

each on W and one P atom. Two limiting formulations of this structure are shown:



8a: R = Me
8b: R = Et

The compound on the left may be viewed as a W(II) complex with a π-bonded acetylphosphonium ligand, whereas that on the right is a W(IV) metallaoxirane. The product arises from nucleophilic attack by the phosphine at the η^2-acetyl carbonyl carbon. Precedence exists for this type of reactivity at η^2-acyl groups.[17] For example, Cp*$TaCl_3(\eta^2$-$COSiMe_3$) undergoes reversible addition of PMe_3 to yield Cp*$TaCl_3(\eta^2$-$CO(SiMe_3)$-(PMe_3)).[17e] The carbonylation of $(\eta^5$-$C_5H_4PPh_2)_2ZrMeCl$ leads to a product in which the PPh_2 substituent at one of the Cp rings has intramolecularly added to an η^2-acetyl ligand.[17h] Variable-temperature NMR studies established that the latter addition was reversible and rapid on the NMR time scale. The ^{13}C NMR spectra of the acylphosphonium adducts[17a-d,f-i] display resonances at δ 52.0–83.0 for the carbonyl carbon atoms. The δ 66.5 value observed for **8a** clearly is in good agreement with these data and rules out an η^1-coordination of the carbonyl group through the oxygen atom (recently reported η^1-coordinated aldehyde complexes show ^{13}C NMR resonances at δ 160–220[18]). Attempts at obtaining X-ray-quality crystals of **8a,b** have not been successful; therefore, the orientation of the carbonyl group is not presently known.

II. NMR Spectroscopic Investigation of the Substitution Reactions. The structural diversity that was found among the products formed in the reactions between **3a** and different phosphines prompted us to monitor the progress of the reactions by NMR spectroscopy. It was hoped that the observation of intermediates could provide clues to a hopefully unifying reaction mechanism for all processes.

Monitoring of the Reaction between 3a and PPh_3. The early stages of the reaction between **3a** and PPh_3 were monitored by ^1H and ^{31}P NMR spectroscopy. In the ^1H NMR spectra, no intermediates or unusual features were seen in the reaction leading to *cis*-**5** and *trans*-**5**. However, an interesting observation was made in the ^{31}P NMR spectrum even immediately after mixing of the reactants. The normally sharp, well-defined resonance at δ −4.7 for free PPh_3 was unusually broad, with a half-height peak width of ca. 140 Hz. The signal broadening is likely due to a rapid and reversible attachment of the PPh_3 ligand at **3a**. Low equilibrium concentrations of the adduct, whatever its structure, combined with relatively small chemical shift differences (in Hz) for the Cp and acetyl signals in substrate and adduct, explain why at the same time the ^1H NMR spectrum of **3a** appeared to be unaffected by PPh_3. The greater chemical shift differences that are encountered in ^{31}P NMR spectra make this method more sensitive for detection of rapid equilibria of this type. The solution was cooled to −40 °C in an attempt to retard the exchange process. At this temperature, the broad signal attributed to free PPh_3 was still present. An additional faint, broadened resonance (ca. 5–10% of the intensity of the major signal) was seen at δ 2.5. This signal disappeared when ambient temperature was again attained. For two reasons, it is clear that the signal broadening and exchange process does not involve *cis*-**5** and *trans*-**5**. First, the broadening was observed at a time when no *cis*-**5** or *trans*-**5** could be detected; second, when observable quantities of **3a**, *cis*-**5**, and *trans*-**5** were present, both products displayed sharp ^{31}P resonances while the signal due to free PPh_3 was still broadened.

The progress of the reaction between **3a**$(BF_4^-)_2$ (0.068 M) and PPh_3 (0.136 M) in acetonitrile-d_3 at 30 °C was followed by ^1H NMR spectroscopy. Figure 1 shows the concentrations of **3a**, *cis*-**5a**, and *trans*-**5a**, relative to the initial concentration of **3a**, as a function of time. The solid lines show a simulated (by numerical integration) concentration vs time profile for a reaction taking place according to Scheme 2. Details about the simulation procedure are given in the Experimental Section. Figure 1 shows that the cis:trans ratio is much higher than

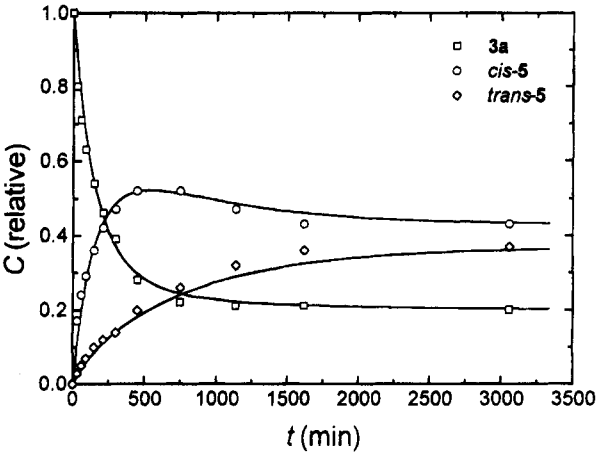
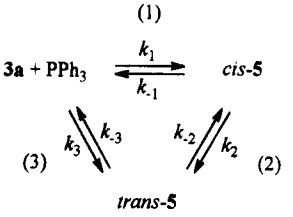


Figure 1. Relative concentrations of **3a**, *cis*-**5**, and *trans*-**5** as a function of time in the reaction between **3a**$(BF_4^-)_2$ (60 mM) and PPh_3 (127 mM) in acetonitrile-d_3 at 30 °C, as monitored by ^1H NMR spectroscopy.

Scheme 2



(17) (a) Labinger, J. A.; Miller, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 6856. (b) Labinger, J. A.; Bonfiglio, J. N.; Grimmett, D. L.; Masuo, S. T.; Shearin, E.; Miller, J. S. *Organometallics* **1983**, *2*, 733. (c) Grimmett, D. L.; Labinger, J. A.; Bonfiglio, J. N.; Masuo, S. T.; Shearin, E.; Miller, J. S. *Organometallics* **1983**, *2*, 1325. (d) Karsch, H. H.; Müller, G.; Krüger, C. *J. Organomet. Chem.* **1984**, *273*, 195. (e) Arnold, J.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5355. (f) Bonnesen, P. V.; Yau, P. K. L.; Hersh, W. H. *Organometallics* **1987**, *6*, 1587. (g) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 149. (h) Tikkanen, W.; Ziller, J. W. *Organometallics* **1991**, *10*, 2266. (i) Martin, A.; Mena, M.; Pellinghelli, M. A.; Rayo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1993**, 2117.

(18) (a) Méndez, N. Q.; Seyler, J. W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 2323 and references cited therein. (b) Klein, D. P.; Méndez, N. Q.; Seyler, J. W.; Arif, A. M.; Gladysz, J. A. *J. Organomet. Chem.* **1993**, *450*, 157. (c) Bianchini, C.; Linn, K.; Masi, D.; Peruzzini, M.; Polo, A.; Vacca, A.; Zanobini, F. *Inorg. Chem.* **1993**, *32*, 2366.

the equilibrium value at the early stages of the reaction. The concentration of *cis*-**5** even decreases after an initial buildup. These observations show that *cis*-**5** is the kinetically favored product of the reaction of **3a**. The direct interconversion (reaction 2) of *cis*-**5** and *trans*-**5** had to be incorporated for a reasonable fit to be achieved. A fit that excluded the direct formation of *trans*-**5** from **3a** (reaction 3) failed to reproduce the early stages of the experimental data. The deviation was particularly noticeable for *trans*-**5**, because an induction period should be observed for the buildup of *trans*-**5** in this case. The mere lack of an observable induction period suggests that *trans*-**5** cannot be generated from *cis*-**5** exclusively and that reaction 3 has to be incoporated.

Reaction between 4 and $PMePh_2$. The ^1H and $^{31}P\{^1H\}$ NMR spectra (acetonitrile-d_3) of a mixture of **4**$(BF_4^-)_2$ (4:1 cis/trans) and 2 equiv of $PMePh_2$ showed the presence of *cis*-**4**-d_6 and the new species **9** in a 1:4 ratio at −40 °C. No *trans*-**4**-d_6 could be detected. The new compound **9** is assigned the structure $CpW(NCCD_3)_2(PMePh_2)(\eta^2\text{-}COMe(PMePh_2))^{2+}$. One $PMePh_2$ moiety in **9** is attached to the metal and one to the acetyl group. In the ^1H NMR spectrum of **9**, the Cp signal appeared at δ 5.39, whereas the $WPMePh_2$, $COMePMePh_2$, and $COMePMePh_2$ methyl groups appeared as doublets at δ 1.75 (d, J = 15.5 Hz), 2.22 (d, J = 9.2 Hz), and 2.48 (d, J = 13.2 Hz), respectively. An unambiguous assignment of these signals cannot be made. The ^{31}P NMR spectrum of **9** displayed two mutually coupled (J_{PP} = 7 Hz) resonances at δ 30.0 and −15.2, the first of which had no ^{183}W satellites. Full NMR spectroscopic data are given in the Experimental Section. At 20 °C, the ^1H NMR spectrum showed the presence of *cis*-**4**-d_6 (ca. 50%) and indications of rapidly equilibrating *trans*-**4**-d_6 and **9** as humps barely discernible above the base line at δ ca. 5.7 and 5.4.

The interaction between **4**$(BF_4^-)_2$ (4:1 cis:trans) and ca. 0.5 equiv of $PMePh_2$ was monitored by ^1H NMR spectroscopy. At 20 °C, the ^1H NMR spectrum showed *cis*-**4**-d_6 and *trans*-**4**-d_6 in a 4:1 ratio. However, whereas the Cp and acetyl signals of *cis*-**4**-d_6 were sharp, the signals of *trans*-**4**-d_6 were significantly broadened and moved slightly upfield. The $PMePh_2$ doublet of *cis*-**4**-d_6 appeared normal, while the signals of *trans*-**4**-d_6 and free $PMePh_2$ had coalesced to one broad signal at δ 1.75. When the sample was cooled, the signals due to *cis*-**4**-d_6 gradually lost intensity but remained well defined. At −20 °C, a ca. 3:2 mixture of *cis*-**4**-d_6 and **9** was seen. Signals due to *trans*-**4**-d_6 were not observable at this temperature. At −40 °C, the *cis*-**4**-d_6:**9** ratio was ca. 2:3. Small quantities of *trans*-**4**-d_6 could now be observed. The *cis*-**4**:*trans*-**4** ratio was essentially unchanged from that at 20 °C, indicating that the cis/trans equilibrium is not strongly temperature dependent. The observed dynamic processes were reversible; when the temperature was returned to ambient, the original spectrum was restored.

NMR spectra with the same general features were obtained when **3a**$(BF_4^-)_2$ was treated with $PMePh_2$ at −40 °C. The substitution of acetonitrile by $PMePh_2$ therefore is a very fast reaction, in contrast to the behavior of PPh_3.

These observations establish the occurrence of temperature-dependent equilibria between *cis*-**4**, *trans*-**4**, and **9**. The *cis*-**4**:*trans*-**4** ratio was independent of the temperature, and therefore, the effect must reflect temperature-dependent concentrations of **9**. The exchange line broadening shows that a rapid equilibrium exists between *trans*-**4** and **9**. The adduct **9** is entropically disfavored relative to *trans*-**4** at high temperatures, whereas at low temperatures, **9** is preferred. The equilibrium involving *cis*-**4** is established more slowly, judged from the presence of well-defined NMR resonances at low and high temperatures, but at least is established on the time scale of a few minutes.

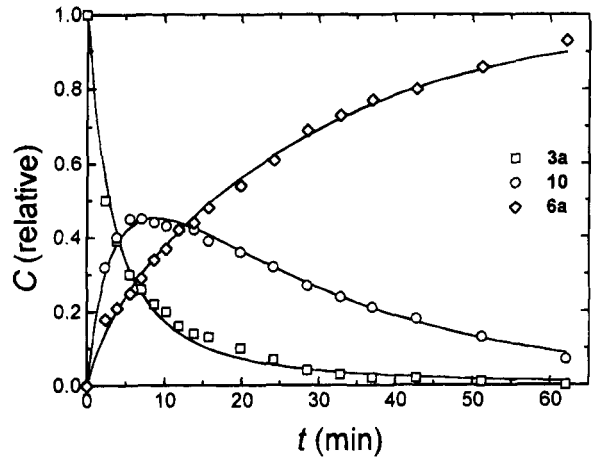
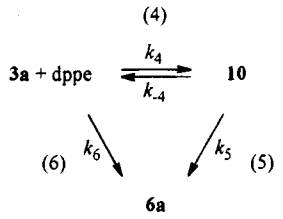


Figure 2. Relative concentrations of **3a**, **6a**, and **10** as a function of time in the reaction between **3a**$(BF_4^-)_2$ (26 mM) and dppe (37 mM) in acetonitrile-d_3 at 21 °C, as monitored by ^1H NMR spectroscopy.

Monitoring of the Reaction between 3a and dppe. When a ^1H NMR spectrum was recorded 5 min after the mixing of **3a** and dppe in acetonitrile-d_3 at ambient temperature, the spectrum revealed the presence of **3a** (80%), **6a**-d_3 (5%), and the new species **10** (15%). The dppe-catalyzed exchange of the two cis acetonitriles in **3a** was complete within 5 min after sample preparation. Dppe catalyzed the exchange of the trans acetonitrile also, but ca. 30 min was required for complete exchange in this position. The new complex **10** was present as long as unreacted **3a** still was available, but eventually **3a** and **10** were quantitatively transformed to **6a**. The ^1H NMR spectrum of **10** displayed a Cp doublet at δ 4.89 and a methyl doublet (J = 13.3 Hz) at δ 2.07. In the ^{31}P NMR spectrum, two mutually coupled doublets (J = 11.5 Hz) were seen at δ 4.8 and 34.1. Only the former had ^{183}W satellites. It is assumed that **10** has a structure similar to that proposed for the dppm analogue **8a**. While the signals due to **10** and **6a** were sharp and well-defined, the signal due to free dppe was broadened.

The progress of the reaction between **3a** (0.026 M) and dppe (0.037 M) in acetonitrile-d_3 at 21 °C was monitored by ^1H NMR spectroscopy. Figure 2 shows the concentrations of **3a**, **6a**, and **10** relative to the initial concentration of **3a** as a function of time. Good correspondence between observed and simulated data was again observed when a three-step reaction mechanism (Scheme 3) was modeled (see Experimental Section for details). In this scheme, **10** is an intermediate for the formation of **6a** (reaction 5). An additional pathway (reaction 6) that leads to **6a** without this intermediate has been included. It was not possible to obtain acceptable fits for alternative mechanisms where **6a** is exclusively

Scheme 3



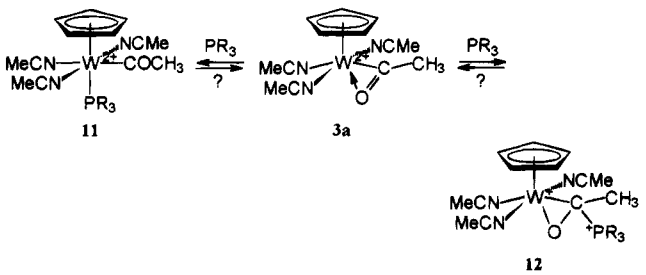
generated from **10** (i.e., reaction 6 is ignored) or where **6a** is directly generated from **3a** while **10** is produced from **3a** and dppe in a nonproductive side equilibrium (i.e., reaction 5 is ignored). As was the case for the reaction between **3a** and PPh_3, the lack of an observable induction period for the buildup of the thermodynamically favored product is strong evidence for the operation of two parallel reaction pathways.

Monitoring of the Reactions between 3a and dppm and dppp. No intermediates were detected during the reaction between **3a** and dppm by ^1H and ^{31}P spectroscopy. The only unusual feature again was the broadened ^{31}P signal due to free phosphine. During the reaction between **3a** and dppp, the ^{31}P resonance due to free dppp was also broadened. As the reaction proceeded, no evidence for species analogous to **8a** or **10** was seen. However, in this reaction a compound that appeared to be structurally related to the final product **7a**, perhaps by way of some type of geometrical isomerism, was observed. Eventually, this compound was converted to **7a** without the intervention of detectable intermediates.

Discussion

In this section, we will attempt to provide a unifying mechanism for the reactions that were described in the Results. Certain general observations pertained to all reactions between **3a**$(BF_4^-)_2$ and tertiary phosphines included in this study. First, *all* free phosphines exhibited broadened resonances in the ^{31}P NMR spectra in the presence of **3a**. Second, *all* phosphines efficiently catalyzed the exchange of solvent acetonitrile-d_3 for the two cis acetonitrile ligands in unconsumed starting material **3a**. Third, less efficient catalysis of the exchange of the trans acetonitrile in unconsumed starting material **3a** occurred.

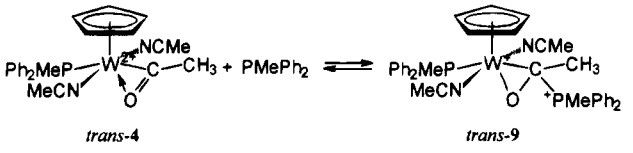
We initially considered that the generation of an open coordination site by a reversible interconversion of η^2 and η^1 acetyl bonding modes,[6] followed by reversible PR_3 coordination to yield the pseudooctahedral intermediate **11**, might be the key to some of the observations. This



process could cause the broadening of the ^{31}P NMR signals of free phosphines in the presence of **3a**. The preferred labilization of the cis acetonitrile ligands should then be rationalized by a cis-labilizing effect of the η^1-acetyl group. The η^1-acetyl group has been previously shown to exert a strong cis labilizing effect on CO dissociation and substitution reactions in *octahedral* group 6 and 7 metal carbonyl complexes.[2d,19]

However, the observed phosphine attachment at the acetyl group in several products or intermediates led us to consider that all the reactions could occur with acetylphosphonium compounds **12** as key intermediates. We concur that observations made for phosphine substitution reactions may not necessarily be relevant for the mechanism of catalyzed nitrile exchange or that the observation of transient species during the phosphine substitution reactions does not prove that these species are on the product-forming reaction pathway. However, having expressed these reservations, we will show in the following discussion that by considering the involvement of species like **12**, and assuming that the acetylphosphonium group exerts a cis-labilizing effect, the experimental observations may be rationalized with a simple mechanistic model.

Evidence for Reversible Attack by PR_3 at the η^2-Acetyl Group. Reversible phosphine addition to η^2-acyl ligands has been previously documented.[17g,h] In the reactions of **3a** with phosphines, the expected adducts $CpW(NCMe)_3(\eta^2\text{-}COMe(PR_3))^{2+}$ were never directly observed, since substitution of coordinated acetonitrile had always occurred in the first detectable products. Evidence for a rapid and reversible phosphine addition at **3a** was indicated by the broadened ^{31}P NMR resonances of the free phosphine in the presence of **3a**. Definitive support that this attack does in fact take place at the acetyl group was provided by the observed equilibrium between *trans*-**4** and $PMePh_2$ to yield **9**. Presumably, steric effects contribute to make attack at *trans*-**4** more favorable than at *cis*-**4**; we assume that complex **9** is also a trans isomer:



It is likely that *all* the line-broadening effects observed for free phosphines in the presence of **3a** have a similar origin, i.e. a reversible attack at the η^2-acetyl group of **3a** to yield η^2-acetylphosphonium complexes.

Evidence for Cis-Labilizing Effect of the η^2-Acetylphosphonium Ligand. The cis-labilizing effect of the acetylphosphonium ligand was at first manifested by the PPh_3-catalyzed exchange of acetonitrile-d_3 for acetonitrile in **3a** selectively in the positions cis to the acetyl. In fact, the catalytic effect and the cis selectivity pertained to all phosphines in this study. The effect was exploited in the synthesis of the propionitrile and phenylacetonitrile analogues of **3a** using PPh_3 catalysis. In these particular reactions, the low concentrations of PPh_3 made the formation of the phosphine substitution products *cis*-**5** and *trans*-**5** highly unfavorable.

The cis-labilizing effect of the acetylphosphonium ligand is further implied by the observation that one

(19) Theoretical studies of the cis-labilizing effects of ligands in octahedral complexes have appeared: (a) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366. (b) Davy, R. D.; Hall, M. B. *Inorg. Chem.* **1989**, *28*, 3524.

acetonitrile ligand in the dppm product **8a** underwent complete exchange with acetonitrile-d_3 before ^{1}H NMR spectra could be recorded and by the fact that in dichloromethane-d_2 one acetonitrile ligand appeared as a broad ^{1}H NMR signal, presumably due to broadening resulting from a rapid coordination/decoordination equilibrium.

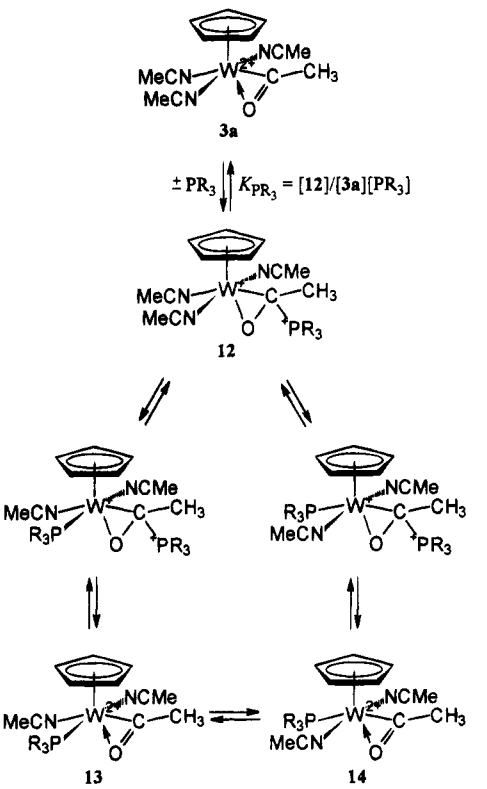
Relative to the η^2-acetyl ligand in **3a**, the acetylphosphonium ligand also exerts a labilizing effect on the trans acetonitrile, as evidenced by the increased rate of acetonitrile-d_3 exchange into this position in the presence of phosphines. The effect was clearly less pronounced than the cis effect. Qualitatively, it may not be too surprising that the attack by phosphine at the η^2-acetyl group labilizes the acetonitrile ligands. The phosphine addition reduces the formal charge at the metal from +2 to +1, and this in turn favors the dissociation of a good donor ligand such as acetonitrile. The high selectivity for cis labilization in the complexes studied here remains to be explained.[19]

The phenomenon is reminiscent of the well-known nucleophile- or base-catalyzed substitution reactions of metal carbonyls.[4d,9] Nucleophilic attack at CO and ligand substitution are closely related in many reactions.[20] The catalytic effect of phosphine oxides in such reactions is suspected to be due to nucleophilic attack at coordinated CO.[2a] Substitution of pyridine for acetonitrile in $Mn(CO)_5(NCMe)^+$ is believed to occur via rapid, reversible attack of pyridine at a cis carbonyl,[9g] yielding a cis-labilizing adduct ligand which initiates rate-limiting acetonitrile dissociation. The purported intermediate adducts in these reactions have not been observed. We are not aware of any previous reports that tertiary phosphines are capable of catalyzing similar reactions.

Mechanisms for Reactions with Monodentate Phosphines. The cis-labilizing effect leads to facile generation of a cis vacant coordination site, and this should kinetically favor the formation of cis, rather than trans, substitution products. In fact, this is exactly what has been observed. For the reaction between **3a** and PPh_3, it was *cis*-**5** that was the first observable product. The trans isomer was generated more slowly, in part by isomerization of *cis*-**5**.

The kinetics for the PPh_3 substitution reactions was presented in the Results. The mechanism in Scheme 2 may now be described in some more detail. In Scheme 4, a preequilibrium involving the acetylphosphonium intermediate **12** is assumed to be involved. In this scheme, PPh_3 is seen to catalyze its own substitution reactions. Kinetically, Scheme 4 is indistinguishable from Scheme 2, provided that PR_3 addition to **3a** is a rapidly established preequilibrium with a small value for the equilibrium constant K_{PR_3}, and therefore the kinetic data cannot be used to definitely distinguish between catalyzed and uncatalyzed substitution pathways. The kinetic treatment of Scheme 4 (and 2) takes into account that [PPh_3], and therefore [**12**], decreases as the reaction proceeds. Two separate reaction channels leading to the cis (**13**) and trans (**14**) substitution products are available. The cis product is formed from the intermediate adduct **12** following the dissociation of a cis acetonitrile ligand, phosphine coordination, and liberation of the acetyl-bound phosphine unit. The trans

Scheme 4



product is similarly produced from **12** via dissociation of the trans acetonitrile ligand.

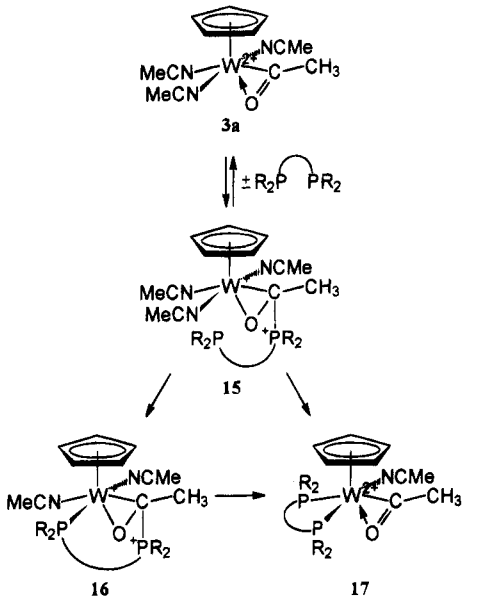
It is an important consequence of the catalytic phosphine effect that the reverse reactions (i.e., generation of **3a** from the substitution products **13** and **14**) must also be catalyzed by phosphines. In fact, this is exactly what was qualitatively observed: the back-reactions of *cis*-**5a** and *trans*-**5a** initially proceeded more rapidly in the presence of PPh_3 than in its absence. The notion that a catalyzed, rather than uncatalyzed, phosphine substitution pathway is operative is therefore supported by this finding.

The rate of product formation in the reaction between **3a** and PPh_3 is slower than the uncatalyzed acetonitrile exchange into the trans position of **3a**. Therefore, for this reaction, kinetics do not dictate that the trans product must be formed via **12**. A simple dissociation of a trans acetonitrile from **3a** is in principle possible. However, for the reaction of **3a** with $PMePh_2$, which also led to substitution of the trans acetonitrile, the rates of formation *trans*-**4** and *cis*-**4** were significantly greater than the rate for uncatalyzed trans acetonitrile exchange. We hold it likely that all substitution reactions, including the one with PPh_3, occur via the general intermediate **12**.

Mechanisms for Reactions with Bidentate Phosphines. The reactions between **3a** and dppm, dppe, and dppp are readily understood in terms of the reactions in Scheme 5, which is obviously closely related to Scheme 4. The dppm product **8** results from intramolecular ring closure from the dangling end of dppm in the intermediate **15** to a vacant cis coordination site which was generated as a result of the cis-labilizing effect of the acetylphosphonium ligand. In the reaction with dppe, the kinetically favored but thermodynamically disfavored acetylphosphonium product **16** is produced by the same route. The direct formation of the

(20) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160.

Scheme 5



chelate product **17** from **15** may take place via opening of a trans coordination site in **15**. Rate-limiting acetonitrile dissociation from **15** followed by rapid coordination of free dppe is consistent with the kinetics and may constitute key steps of this reaction. An alternative mechanism involving initial capture of the open trans coordination site by an intramolecular ring closure is unlikely (but not impossible) for ring-strain reasons.

Combined steric and ring-strain effects presumably determine whether the reactions between **3a** and diphosphines lead to acetylphosphonium complex **16** or the disubstituted chelate **17** as the favored product. Steric effects are not readily assessed without molecular models based on X-ray structures of the complexes. The absence of chelate products for the reaction with dppm probably reflects that the four-membered ring in the resulting product **17** will be relatively strained in comparison with the five-membered ring in the preferred product **16**. Recent calorimetry measurements have indicated that the four-membered chelate $Fe(CO)_3$(dppm) contains ca. 12 kcal/mol more ring strain than does the five-membered $Fe(CO)_3$(dppe) and the six-membered $Fe(CO)_3$(dppp) analogues.[21a] Similar trends pertain to the $Mo(CO)_4L_2$ series (L_2 = dppm, dppe, dppp).[21b]

Concluding Remarks. The reversible attack by tertiary phosphines at the η^2-acetyl carbonyl group of **3a** catalyzes the ligand-substitution reactions of **3a** via the selective, but not exclusive, labilization of acetonitrile ligands located cis to the acetyl group. This appears to be the first observation of nucleophilic catalysis of ligand substitution reactions in η^2-acetyl complexes and the first report that phosphines participate in such catalysis. *The phosphines effectively catalyze their own substitution reactions.* Work in progress is aimed at exploring the new complexes described in this paper and at utilizing the catalytic effect in the synthesis of new relatively high oxidation state tungsten organometallics.

(21) (a) Luo, L.; Nolan, S. P. *Inorg. Chem.* **1993**, *32*, 2410. (b) Mukerjee, S. L.; Nolan, S. P.; Hoff, C. D.; de la Vega, R. *Inorg. Chem.* **1988**, *27*, 81.

Experimental Section

General Procedures. Organometallic complexes were handled under an inert atmosphere by use of standard vacuum line, Schlenk, syringe, and drybox techniques. Acetonitrile, propionitrile, and phenylacetonitrile were distilled from P_2O_5, and acetonitrile-d_3 and dichloromethane-d_2 were distilled from CaH_2. ^1H NMR spectra were recorded on Varian Gemini-200 or Varian XL-300 instruments. $^{13}C\{^1H\}$ NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-300 instrument operating at 50 and 120 MHz, respectively. ^1H and ^{13}C NMR chemical shifts are reported downfield from tetramethylsilane using the solvent resonances as internal standards (for acetonitrile-d_3 ^1H NMR δ 1.93, $^{13}C\{^1H\}$ NMR δ 1.3; for dichloromethane ^1H NMR δ 5.32). $^{31}P\{^1H\}$ 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 (δ −4.7 vs H_3PO_4). IR spectra were obtained on a Perkin-Elmer 1310 infrared spectrophotometer. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany.

The compounds $Cp(\eta^5\text{-}C_5H_4COMe)Fe^+BF_4^-$ (**1**),[22a] $CpW(CO)_3Me$,[22b] $CpW(CO)_2(NCMe)_2Me^{2+}(BF_4^-)_2$ (**2a**$(BF_4^-)_2$),[7b] and $CpW(NCMe)_3(\eta^2\text{-}COMe)^{2+}(BF_4^-)_2$ (**3a**$(BF_4^-)_2$)[7a] were prepared according to published procedures. Tertiary phosphines were purchased from commercial suppliers. PPh_3, bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), and 1,3-bis(diphenylphosphino)propane (dppp) were recrystallized from ethanol. $PMePh_2$ was used as received.

$CpW(CO)_2(NCEt)_2Me^{2+}(BF_4^-)_2$(2b$(BF_4^-)_2$). This complex was prepared by following the procedure described for **2a**$(BF_4^-)_2$.[7b] A solution of **1** (182 mg, 0.58 mmol) in propionitrile (10 mL) was added dropwise to a vigorously stirred solution of $CpW(CO)_3Me$ (100 mg, 0.29 mmol) in propionitrile (40 mL) at 0 °C. The solution was concentrated by vacuum transfer. Slow addition of ether at −20 °C gave an oily product which eventually crystallized over a period of 2−3 days at room temperature. The crystals were washed with ether (3 × 10 mL) and dried in vacuo. The product was obtained as an orange powder (142 mg, 82%): ^1H NMR (acetonitrile-d_3) δ 1.34 (t, J = 7.4 Hz, 6 H, $NCCH_2CH_3$), 1.49 (s, 3 H, WCH_3), 2.94 (q, J = 7.6 Hz, 4 H, $NCCH_2CH_3$), 6.39 (s, 5 H, Cp); IR (acetonitrile) ν_{CO} 2110, 2070 cm^{-1}.

$CpW(CO)_2(NCCH_2Ph)_2Me^{2+}(BF_4^-)_2$ (2c$(BF_4^-)_2$). This compound was prepared by following the same procedure described for **2b**$(BF_4^-)_2$ above, except that phenylacetonitrile was used as the solvent for the oxidation. Even with repetitive recrystallizations and ether washings, well-defined crystals could not be obtained, and the ^1H NMR spectra of the red oil always showed the presence of some free phenylacetonitrile: ^1H NMR (acetonitrile-d_3) δ 1.43 (s, 3 H, WCH_3), 4.39 (s, 4 H, $PhCH_2CN$), 6.43 (s, 5 H, Cp), 7.4 (m, 10 H, Ph); IR (acetonitrile) ν_{CO} 2114, 2075 cm^{-1}.

$CpW(NCEt)_3(\eta^2\text{-}COMe)^{2+}(BF_4^-)_2$(3b$(BF_4^-)_2$). This complex was prepared by three different methods.

I. Oxidation of $CpW(CO)_3Me$ in Propionitrile. A propionitrile solution of **2b**$(BF_4^-)_2$ was prepared from $CpW(CO)_3Me$ (100 mg, 0.29 mmol) as described above, whereupon the solution was heated at reflux for 3 h. The solution was concentrated by vacuum transfer. Addition of ether at −20 °C provided an oily product which formed orange microcrystals over 2−3 days (128 mg, 70%): ^1H NMR (acetonitrile-d_3) δ 1.20 (t, J = 7.4 Hz, 6 H, *cis*-$NCCH_2CH_3$[8a]), 1.42 (t, J = 7.4 Hz, 3 H, *trans*-$NCCH_2CH_3$), 2.77 (q, J = 7.4 Hz, 4 H, *cis*-$NCCH_2CH_3$), 3.04 (q, J = 7.4 Hz, 2 H, *trans*-$NCCH_2CH_3$), 3.41 (s, 3 H, $COMe$), 5.82 (s, 5 H, Cp); $^{13}C\{^1H\}$ NMR (acetonitrile-d_3) δ 9.4, 10.6, 11.2, 13.3, 28.8 ($COMe$), 95.8 (Cp), 130.2, 265.3 ($COMe$). Anal. Calcd for $C_{16}H_{23}B_2F_8N_3OW$: C, 30.46; H, 3.67. Found: C, 30.59; H, 3.45.

(22) (a) Carty, P.; Dove, M. F. A. *J. Organomet. Chem.* **1971**, *28*, 125. (b) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 304.

II. Uncatalyzed Ligand Substitution on CpW(NCMe)$_3$(η^2-COMe)$^{2+}$(BF_4^-)$_2$. **3a**(BF_4^-)$_2$ (50 mg, 0.085 mmol) was dissolved in propionitrile (20 mL), and the solution was heated at reflux for 3 h. The product (40 mg, 74%) was precipitated as a yellow powder by the addition of ether.

III. PPh_3-Catalyzed Ligand Substitution on CpW(NCMe)$_3$(η^2-COMe)$^{2+}$(BF_4^-)$_2$. **3a**(BF_4^-)$_2$ (50 mg, 0.085 mmol) and PPh_3 (4.4 mg, 0.017 mmol) were dissolved in propionitrile (20 mL) and heated at reflux for 5 min. Precipitation by the addition of ether provided the product as a yellow powder (45 mg, 84%).

PPh_3-Catalyzed Synthesis of CpW(NCCH$_2$Ph)$_3$(η^2-COMe)$^{2+}$(BF_4^-)$_2$ (3c(BF_4^-)$_2$). A solution of **3a**(BF_4^-)$_2$ (106 mg, 0.168 mmol) and PPh_3 (17 mg, 0.065 mmol) in phenylacetonitrile (5 mL) was heated at 130 °C for 5 min. The solution was cooled, layered with ether (30 mL), and stored at −20 °C for 20 h. During this period, an oily material formed. The oil was brought to crystallize by allowing the solution to stand for 7 days at room temperature. The solvent was decanted, and the product was washed with ether (3 × 10 mL) and dried under vacuum. The product was obtained as a red powder (109 mg, 79%): ^{1}H NMR (acetonitrile-d_3) δ 3.42 (s, 3 H, CO*Me*), 4.22 (s, 4 H, *cis*-PhC*H*$_2$CN[8a]), 4.50 (s, 2 H, *trans*-PhC*H*$_2$CN), 5.90 (s, 5 H, Cp), 7.4−7.6 (m, 15 H, Ph). The ^{1}H NMR spectrum showed noncoordinated phenylacetonitrile at δ 3.80. Repeated recrystallizations (dichloromethane/ether) or drying in vacuo for extended time periods failed to remove the free phenylacetonitrile.

Heating of a Solution of CpW(NCMe)$_3$(η^2-COMe)$^{2+}$(BF_4^-)$_2$ in Phenylacetonitrile. A solution of **3a**(BF_4^-)$_2$ (25 mg, 0.043 mmol) in phenylacetonitrile (5 mL) was heated at 130 °C for 4 h. The product mixture was obtained as a red oil by addition of ether (30 mL) at −20 °C. The ^{1}H NMR spectrum of the oil (acetonitrile-d_3) showed a mixture of CpW(NCCH$_2$Ph)$_3$(η^2-COMe)$^{2+}$ (**3c**) and a product of unknown structure in a (2:1)−(4:1) ratio. ^{1}H NMR for unknown (acetonitrile-d_3): δ 5.86 (s, 5 H), 7.4−7.6 (m).

Reaction of CpW(CO)$_2$(NCCH$_2$Ph)$_2$Me^{2+}(BF_4^-)$_2$ (3c(BF_4^-)$_2$) in Phenylacetonitrile. A solution of **3a**(BF_4^-)$_2$ (25 mg, 0.043 mmol) in phenylacetonitrile (5 mL) was heated at 130 °C for 4 h. The product was precipitated as an oil by addition of ether (30 mL) at −20 °C. The ^{1}H NMR spectrum of the oil showed a mixture of **3c** and an unknown species in a 1:1 ratio. ^{1}H NMR for unknown (acetonitrile-d_3): δ 3.39 (s, 3 H), 4.26 (s, 4 H), 4.50 (s, 2 H), 5.88 (s, 5 H), 7.4−7.6 (m).

CpW(NCMe)$_2$(PMePh$_2$)(η^2-COMe)$^{2+}$(BF_4^-)$_2$ (4(BF_4^-)$_2$). A solution of **3a**(BF_4^-)$_2$ (85 mg, 0.14 mmol) and $PMePh_2$ (45 mg, 0.23 mmol) in acetonitrile (3.0 mL) was stirred at room temperature for 5 min. Ether (20 mL) was added with stirring. A yellow crystalline precipitate formed over 5−6 h at −20 °C. The solvent was decanted, and the residue was washed with ether. Drying under vacuum yielded **4**(BF_4^-)$_2$ as a yellow powder (80 mg, 76%) as a 4:1 mixture of the cis and trans isomers. Spectroscopic data for *cis*-**4**: ^{1}H NMR (acetonitrile-d_3) δ 2.05 (d, J = 9.6 Hz, 3 H, P*Me*Ph$_2$), 2.38 (s, 3 H, *trans*-*Me*CN), 2.71 (d, J = 1.0 Hz, 3 H, *cis*-*Me*CN), 3.12 (d, J = 1.2 Hz, 3 H, CO*Me*), 5.69 (d, J = 2.8 Hz, 5 H, Cp), 7.5−7.9 (m, 10 H, Ph); ^{13}C{^{1}H} NMR δ 13.4 (d, J = 33 Hz, P*Me*Ph$_2$), 28.9 (CO*Me*), 93.9 (Cp), 125−128, 267.2 (d, J = 7.3 Hz, *C*OMe); ^{31}P{^{1}H} NMR (120 MHz, acetonitrile-d_3) δ 9.5 (s, $^1J_{PW}$ = 128 Hz). Spectroscopic data for *trans*-**4**: ^{1}H NMR (acetonitrile-d_3) δ 2.42 (d, J = 9.6 Hz, 3 H, P*Me*Ph$_2$), 2.58 (d, J = 1.0 Hz, 6 H, *Me*CN), 3.53 (s, 3 H, CO*Me*), 5.79 (s, 5 H, Cp), 7.5−7.9 (m, 10 H, Ph); ^{13}C{^{1}H} NMR (acetonitrile-d_3) δ 94.7 (Cp) (due to the low concentration of the trans isomer, only the Cp signal was observable); ^{31}P{^{1}H} NMR (120 MHz, acetonitrile-d_3) δ −1.0 (s, $^1J_{PW}$ = 134 Hz). Anal. Calcd for $C_{24}H_{27}B_2F_8N_2OW$: C, 38.54; H, 3.64. Found: C, 38.59; H, 3.75.

Heating of a Mixture of *cis*-4 and *trans*-4 in Acetonitrile. An NMR tube equipped with a ground-glass joint was loaded with a 4:1 mixture of *cis*-**4**(BF_4^-)$_2$ and *trans*-**4**(BF_4^-)$_2$ (20 mg, 0.023 mmol). Acetonitrile-d_3 (0.7 mL) was added by vacuum transfer, and the tube was sealed under vacuum. A ^{1}H NMR spectrum recorded after 3 h at reflux revealed the presence of <10% **3a** and a 4:1 mixture of *cis*-**4** and *trans*-**4**.

Reaction between 3a(BF_4^-)$_2$ and PPh_3. A solution of **3a**(BF_4^-)$_2$ (30 mg, 0.051 mmol) and PPh_3 (26.7 mg, 0.10 mmol) in acetonitrile (5 mL) was stirred for 3 days. The mixture of products was precipitated by the addition of ether (20 mL). The ^{1}H NMR spectrum indicated the formation of a mixture of **3a** (43%), *cis*-CpW(NCMe)$_2$(PPh_3)(η^2-COMe)$^{2+}$ (*cis*-**5**: 41%; ^{1}H NMR δ 2.41 (s, 3 H, *trans*-*Me*CN), 2.70 (3 H; J not resolved due to overlapping with a signal from **3a**, *cis*-*Me*CN), 3.00 (d, J = 1.0 Hz, 3 H, CO*Me*), 5.69 (d, J = 2.8 Hz, 5 H, Cp); ^{31}P{^{1}H} NMR δ 22.3 ($^1J_{WP}$ = 120 Hz)), and *trans*-**5** (15%; ^{1}H NMR δ 2.48 (d, J = 0.9 Hz, 6 H, *Me*CN), 3.52 (s, 3 H, CO*Me*), 5.79 (s, 5 H, Cp); ^{31}P{^{1}H} NMR δ 14.9 ($^1J_{WP}$ = 130 Hz)).

Heating of a Mixture of 3a, *cis*-5, and *trans*-5 in Acetonitrile. When a mixture of the BF_4^- salts of **3a**, *cis*-**5**, and *trans*-**5** was isolated by precipitation with ether and dissolved in acetonitrile-d_3, a slow but incomplete conversion of *cis*-**5** and *trans*-**5** to **3a**-d_9 was seen by ^{1}H NMR spectroscopy. This reaction was seen to initially occur twice as fast when 0.1 equiv of PPh_3 was added to the solution.

CpW(NCMe)(η^2-dppe)(η^2-COMe)$^{2+}$(BF_4^-)$_2$ (6a(BF_4^-)$_2$). An acetonitrile (40 mL) solution of **3a**(BF_4^-)$_2$ (100 mg, 0.17 mmol) and dppe (76 mg, 0.19 mmol) was heated at reflux for 10 min. The solution was layered with ether and kept at −20 °C for 12 h. During this period an oily precipitate formed. The solvent was decanted, and the residue was taken up in dichloromethane (5 mL). Ether was added while the flask was swirled to ensure quick mixing of the solvents. A yellow crystalline precipitate formed. The solvent was decanted, and the precipitate was washed with ether. Drying under vacuum yielded **6a**(BF_4^-)$_2$ (128 mg, 83%) as a yellow powder: ^{1}H NMR (acetonitrile-d_3) δ 1.86 (d, J = 1.8 Hz, 3 H, *Me*CN), 2.51 (d, J = 1.2 Hz, 3 H, CO*Me*), 2.60 (m, 2 H, dppe C*H*$_2$), 3.10 (m, 2 H, dppe C*H*$_2$), 5.58 (d, J = 2.4 Hz, 5 H, Cp), 7.00 (m, 2 H, Ph), 7.9−7.5 (m, 18 H, Ph); ^{13}C{^{1}H} NMR (50 MHz, acetonitrile-d_3) δ 4.3, 24.0 (dd, J = 7, 34 Hz, dppe *C*H$_2$), 28.8 (CO*Me*), 29.4 (dd, J = 6, 30 Hz, dppe *C*H$_2$), 96.4 (Cp), 127−133, 274.2 (*C*OMe); ^{31}P{^{1}H} NMR (120 MHz, acetonitrile-d_3) δ 35.7 (d, $^2J_{PP}$ = 2.4 Hz, 1 P, $^1J_{PW}$ = 115 Hz), 30.6 (d, $^2J_{PP}$ = 2.4 Hz, 1 P, $^1J_{PW}$ = 115 Hz). Anal. Calcd for $C_{35}H_{35}B_2F_8NOP_2W$: C, 46.45; H, 3.90. Found: C, 46.44; H, 4.05.

CpW(NCEt)(η^2-dppe)(η^2-COMe)$^{2+}$(BF_4^-)$_2$ (6b(BF_4^-)$_2$). This complex was prepared as described for **6a**(BF_4^-)$_2$, except that **3b**(BF_4^-)$_2$ was reacted with dppe in propionitrile. This provided **6b**(BF_4^-)$_2$ as a yellow powder in 88% yield. ^{1}H NMR (acetonitrile-d_3) δ 0.66 (t, J = 7.4 Hz, 3 H, C*H*$_3$CH$_2$CN), 2.30 (m, 2 H, dppp C*H*$_2$), 2.55 (d, J = 1.2 Hz, 3 H, CO*Me*), 2.8−3.1 (m, 4 H, dppp C*H*$_2$), 5.58 (d, J = 2.4 Hz, 5 H, Cp), 6.8−7.0 (m, 2 H, Ph), 7.3−7.9 (m, 18 H, Ph); ^{31}P{^{1}H} NMR (120 MHz, acetonitrile-d_3) δ 31.5 (d, $^2J_{PP}$ = 2.4 Hz, 1 P, $^1J_{PW}$ = 122 Hz), 36.0 (d, $^2J_{PP}$ = 2.4 Hz, 1 P, $^1J_{PW}$ = 122 Hz). Anal. Calcd for $C_{36}H_{37}B_2F_8NOP_2W$: C, 47.05; H, 4.06. Found: C, 47.61; H, 4.12.

CpW(NCMe)(η^2-dppp)(η^2-COMe)$^{2+}$(BF_4^-)$_2$ (7a(BF_4^-)$_2$). An acetonitrile (30 mL) solution of **3a**(BF_4^-)$_2$ (100 mg, 0.17 mmol) and dppp (77 mg, 0.19 mmol) was heated at reflux for 10 min, and the product was isolated as described for **6a**(BF_4^-)$_2$. This provided **7a**(BF_4^-)$_2$ as deep yellow microcrystals (138 mg, 88%): ^{1}H NMR (acetonitrile-d_3) δ 1.80 (d, J = 1.6 Hz, 3 H, *Me*CN), 2.35 (m, 2 H, dppp C*H*$_2$), 2.70 (m, 2 H, dppp C*H*$_2$), 2.79 (d, J = 1.4 Hz, 3 H, CO*Me*), 3.20 (m, 2 H, dppp C*H*$_2$), 5.53 (d, J = 2.4 Hz, 5 H, Cp), 6.8−6.9 (m, 2 H, Ph), 7.1−7.8 (m, 18 H, Ph); ^{13}C{^{1}H} NMR (50 MHz, acetonitrile-d_3) δ 4.8, 17.9 (dppp *C*H$_2$), 25.2 (d, J = 28 Hz, dppp *C*H$_2$), 26.2 (d, J = 28 Hz, dppp *C*H$_2$), 28.2 (CO*Me*), 94.4 (Cp), 128−135, 266.2 (dd, J = 7.5, 7.5 Hz, *C*OMe); ^{31}P{^{1}H} NMR (120 MHz, acetonitrile-d_3) δ −5.7 (d, $^2J_{PP}$ = 27 Hz, 1 P, $^1J_{PW}$ = 113 Hz), 4.1 (d, $^2J_{PP}$ = 27 Hz, 1 P, $^1J_{PW}$ = 113 Hz). Anal. Calcd for $C_{36}H_{37}B_2F_8NOP_2W$: C, 47.05; H, 4.06. Found: C, 46.68; H, 4.15.

CpW(NCEt)(η^2-dppp)(η^2-COMe)$^{2+}$(BF_4^-)$_2$ (7b(BF_4^-)$_2$). A solution of dppp and CpW(NCEt)$_3$(η^2-COMe)$^{2+}$(BF_4^-)$_2$ (**5**(BF_4^-)$_2$) was heated in propionitrile as described for the preparation of **3b**(BF_4^-)$_2$. The synthesis provided **7b**(BF_4^-)$_2$ as deep yellow microcrystals (80%): ^{1}H NMR (acetonitrile-d_3) δ 0.80 (t, J = 7.4 Hz, 3 H, CH_3CH$_2$CN), 2.35 (m, 2 H, dppp CH_2), 2.70 (m, 2 H, dppp CH_2), 2.79 (d, J = 1.4 Hz, 3 H, CO*Me*), 3.20 (m, 2 H, dppp CH_2), 5.52 (d, J = 2.4 Hz, 5 H, Cp), 6.8–6.9 (m, 2 H, Ph), 7.1–7.8 (m, 18 H, Ph); ^{31}P{^{1}H} NMR (120 MHz, acetonitrile-d_3) δ −4.9 (d, $^2J_{PP}$ = 29 Hz, 1 P, $^1J_{PW}$ = 112 Hz), 3.8 (d, $^2J_{PP}$ = 27 Hz, 1 P, $^1J_{PW}$ = 112 Hz).

CpW(NCMe)$_2$(η^3-Ph$_2$PCH$_2$PPh$_2$COMe)$^{2+}$(BF_4^-)$_2$ (8a(BF_4^-)$_2$). A solution of **3a**(BF_4^-)$_2$ (200 mg, 0.34 mmol) and dppm (142 mg, 0.37 mmol) in acetonitrile (30 mL) was heated at reflux for 10 min, and the product was isolated by following the procedure that was described for **6a**(BF_4^-)$_2$. This yielded **8a**(BF_4^-)$_2$ as pale yellow microcrystals (248 mg, 80%): ^{1}H NMR (acetonitrile-d_3) δ 2.12 (d, J = 14.6 Hz, 3 H, CO*Me*), 2.58 (s, 3 H, *Me*CN), 3.40 (m, 1 H, dppm CH_2), 4.05 (m, 1 H, dppm CH_2), 5.10 (d, J = 3.6 Hz, 5 H, Cp), 7.5–7.9 (m, 20 H, Ph) (the rate of exchange of one acetonitrile ligand with solvent was rather fast, and as a consequence, the chemical shift for this ligand could not be identified by ^{1}H NMR in acetonitrile-d_3 and only a broad signal was seen in dichloromethane-d_2 as explained in the Results); ^{13}C{^{1}H} NMR (50 MHz, acetonitrile-d_3) δ 4.8, 25.7 (d, J = 26 Hz, CO*Me*), 26.8 (dd, J = 14.2, 65 Hz, dppm *C*H$_2$), 66.5 (d, J = 55 Hz, *C*OMe), 93.2 (Cp), 128–135; ^{31}P{^{1}H} NMR (120 MHz, acetonitrile-d_3) δ 17.2 (d, J_{PP} = 11.5 Hz, 1 P, $^1J_{PW}$ = 149 Hz), 47.9 (d, $^2J_{PP}$ = 11.7 Hz, 1 P). The ^{1}H NMR spectrum indicated that the crystals contained 0.5 equiv of ether, which also was suggested by elemental analysis data for **7a**(BF_4^-)$_2$·0.5Et$_2$O: Anal. Calcd for $C_{38}H_{41}B_2F_8N_2O_{1.5}P_2W$: C, 47.08; H, 4.23. Found: C, 47.49; H, 4.14.

No intermediates were observed when this reaction was monitored by ^{1}H NMR spectroscopy.

CpW(NCEt)$_2$(η^3-Ph$_2$PCH$_2$Ph$_2$PCOMe)$^{2+}$(BF_4^-)$_2$ (8b(BF_4^-)$_2$). A solution of **3b**(BF_4^-)$_2$ (80 mg, 0.13 mmol) and dppm (54 mg, 0.14 mmol) in propionitrile (20 mL) was heated at reflux for 10 min, and the product was isolated by the same procedure as that described for **6b**(BF_4^-)$_2$. This yielded **8b**(BF_4^-)$_2$ as pale yellow microcrystals (90 mg, 78%): ^{1}H NMR (acetonitrile-d_3) δ 1.16 (t, J = 7.4 Hz, 3 H, CH_3CH$_2$CN), 2.12 (d, J = 14.6 Hz, 3 H, CO*Me*), 2.91 (dq, J = 2.8, 7.6 Hz, 1 H, CH$_3$CH_2CN), 2.96 (dq, J = 2.9, 7.5 Hz, 1 H, CH$_3$CH_2CN), 3.40 (m, 1 H, dppm CH_2), 4.05 (m, 1 H, dppm CH_2), 5.10 (d, J = 3.6 Hz, 5 H, Cp), 7.5–7.9 (m, 20 H, Ph). (The rate of exchange of one propionitrile ligand with solvent is rather fast. As a consequence, the chemical shifts for this ligand could not be determined by ^{1}H NMR spectroscopy in acetonitrile-d_3 and *the reported spectrum is in fact that due to the mixed nitrile complex* CpW(NCEt)(NCCD$_3$)(η^3-Ph$_2$PCH$_2$Ph$_2$PCOMe)$^{2+}$. The identification of two coordinated propionitriles is based on the integrated intensities of the signals due to one coordinated and one uncoordinated propionitrile in the acetonitrile-d_3 ^{1}H NMR spectrum of **8b**. Sample decomposition occurred in dichloromethane-d_2). ^{31}P{^{1}H} NMR (120 MHz, acetonitrile-d_3) δ 17.3 (d, $^2J_{PP}$ = 11.2 Hz, 1 P, $^1J_{PW}$ = 150 Hz), 47.8 (d, $^2J_{PP}$ = 11.2 Hz, 1 P).

NMR Monitoring of the Reaction between CpW(NCMe)$_3$(η^2-COMe)$^{2+}$(BF_4^-)$_2$ and PPh$_3$. An NMR tube equipped with a ground-glass joint was loaded with **3a**(BF_4^-)$_2$ (30 mg, 0.051 mmol) and PPh$_3$ (27 mg, 0.10 mmol). Acetonitrile-d_3 (0.7 mL) was added by vacuum transfer and the tube was sealed under vacuum. A ^{1}H NMR spectrum recorded after 16 h at ambient temperature revealed the presence of **3a**-d_6 (43%; complete exchange of the two as acetonitrile ligands had occurred), *cis*-**5**-d_6, and *trans*-**5**-d_6. The PPh$_3$ resonance appeared as a *broadened* signal at δ −3.50 in the ^{31}P{^{1}H} spectrum and did not give sharpened signals at temperatures down to −40 °C.

NMR Monitoring of the Exchange of Trans Acetonitrile in CpW(NCMe)$_3$(η^2-COMe)$^{2+}$(BF_4^-)$_2$ in the Presence of PPh$_3$. An NMR tube equipped with a ground-glass joint was loaded with **3a**(BF_4^-)$_2$ (20 mg, 0.024 mmol) and PPh$_3$ (18 mg, 0.069 mmol). Acetonitrile-d_3 (0.6 mL) was added by vacuum transfer, and the tube was sealed under vacuum. Under these conditions, the exchange of the trans acetonitrile ligand was seen to occur at a rate ca. 5–6 times greater than in the absence of PPh$_3$.

NMR Observation of the Reaction between CpW(NCMe)$_2$(PMePh$_2$)(η^2-COMe)$^{2+}$(BF_4^-)$_2$ and 2 Equiv of PMePh$_2$. A solution of the isolated 4:1 cis:trans mixture of **4**(BF_4^-)$_2$ (10 mg, 0.013 mmol) and PMePh$_2$ (5.6 mg, 0.028 mmol) in acetonitrile-d_3 (0.7 mL) was added to an NMR tube which was sealed under vacuum. The ^{1}H NMR spectrum revealed a 1:4 mixture of *cis*-**4**-d_6 (complete exchange of coordinated acetonitrile with acetonitrile-d_3 had occurred) and a new compound, assumed to be CpW(NCCD$_3$)$_2$(η^2-CO(PMePh$_2$)Me)$^{2+}$ (**9**). The new compound displayed ^{1}H NMR signals at δ 1.75 (d, J = 15.5 Hz, 3 H), 2.22 (d, J = 9.2 Hz, 3 H), 2.48 (d, J = 13.2 Hz, 3 H), and 5.39 (d, J = 1.2 Hz, 5 H, Cp). An assignment of the δ 1.75, 2.22, and 2.48 doublets to the WP*Me*Ph$_2$, CO*Me*PMePh$_2$, and COMeP*Me*Ph$_2$ groups cannot be unambiguously made. The *cis*-**4**-d_6:**9** ratio was ca. 1:4. The ^{31}P NMR spectrum showed the δ 10.0 singlet of *cis*-**4**-d_6, and two somewhat broadened but mutually coupled signals were seen at δ −15.2 (d, J_{PP} = 7 Hz, 1 P, 1J_{WP} = 144 Hz) and 30.0 (d, J_{PP} = 7.0 Hz, no observable J_{WP}). We attribute these signals to **9**. Free PMePh$_2$ appeared as a broadened peak centered at δ −27.0.

The ambient-temperature ^{1}H NMR spectrum revealed the presence of *cis*-**4**-d_6, the signals of which were normal and well-defined. Two broad humps barely discernible above the base line were located at δ 5.4 and 5.6. The methyl signal of free PMePh$_2$ appeared as a broad peak (half-height peak width ca. 40 Hz). The ambient-temperature ^{31}P NMR spectrum displayed a broad signal at δ 32, a reasonably sharp signal at δ 10.0 attributed to *cis*-**4**-d_6, and a major extremely broad signal centered at δ −25, attributed to rapidly exchanging bound and largely free PMePh$_2$. The changes in the NMR spectra caused by temperature differences were reversible.

NMR Observation of the Reaction between CpW(NCMe)$_2$(PMePh$_2$)(η^2-COMe)$^{2+}$(BF_4^-)$_2$ and 0.3–0.5 Equiv of PMePh$_2$. A solution of the isolated 4:1 cis:trans mixture of **4**(BF_4^-)$_2$ (20 mg, 0.027 mmol) in acetonitrile-d_3 (0.5 mL) was transferred to an NMR tube, PMePh$_2$ (ca. 2 μL, 0.01 mmol) was added, and the tube was sealed under vacuum. The Cp and acetyl part of the ^{1}H NMR spectrum showed the presence of *cis*-**4**-d_6 (well-defined signals) and *trans*-**4**-d_6 (broadened signals) in a 4:1 ratio. The PMePh$_2$ methyl signal of *cis*-**4**-d_6 was sharp; that of the trans isomer had coalesced with the signal due to free PMePh$_2$ and appeared as a broad peak at δ 1.75. When the temperature was lowered, the amount of *cis*-**4**-d_6 decreased but its signals retained their sharpness. The signals of *trans*-**4**-d_6 were replaced by signals due to CpW(NCCD$_3$)$_2$(PMePh$_2$)(η^2-CO(PMePh$_2$)Me)$^{2+}$ (**9**). The *cis*-**4**-d_6:**9** ratio was 3:2 at −20 °C. At −40 °C, *cis*-**4**-d_6, *trans*-**4**-d_6, and **9** were seen in a ca. 1:4:6 ratio. When the temperature was returned to ambient, the original spectrum was restored.

NMR Observation of the Reaction between CpW(NCMe)$_3$(η^2-COMe)$^{2+}$(BF_4^-)$_2$ and 3 Equiv of PMePh$_2$. An NMR tube equipped with a ground-glass joint was loaded with **3a**(BF_4^-)$_2$ (20 mg, 0.034 mmol) and PMePh$_2$ (20 mg, 0.10 mmol). Acetonitrile-d_3 (0.7 mL) was added by vacuum transfer, and the tube was sealed under vacuum. NMR spectra were recorded immediately at −40 °C. The ^{1}H and ^{31}P NMR spectra were nearly identical with those recorded for the reaction of **4**(BF_4^-)$_2$ and 2 equiv of PMePh$_2$.

NMR Monitoring of the Reaction between CpW(NCMe)$_3$(η^2-COMe)$^{2+}$(BF_4^-)$_2$ and dppe. A hot solution of dppe (7.6 mg, 0.019 mmol) in acetonitrile-d_3 (0.7 mL) was cooled to 20 °C, and **3a**(BF_4^-)$_2$ (10.0 mg, 0.017 mmol) was added. The NMR tube was immediately placed in the NMR probe at 20 °C, and ^{1}H NMR spectra were recorded. After 5

min, the spectrum showed the presence of **3a** (80%; significant phosphine-catalyzed exchange of the cis acetonitrile ligands had occurred), $CpW(NCCD_3)(\eta^2\text{-dppe})(\eta^2\text{-COMe})^{2+}$ (**6a**-d_3; 5%), and $CpW(NCCD_3)_2(\eta^3\text{-}Ph_2PCH_2CH_2PPh_2COMe)^{2+}$ (**10**; 15%), δ 2.07 (d, J = 13.3 Hz, 3 H, CO*Me*), 4.89 (d, J = 3.3 Hz, 5 H, Cp)). **10** was present throughout the reaction but was eventually transformed to **6a**-d_3 at the end. The reaction was also followed by ^{31}P NMR spectroscopy. After 5 min, the spectrum showed well-defined, sharp signals attributed to **10** (δ 4.8 (d, $^2J_{PP}$ = 11.5 Hz, 1 P, $^1J_{WP}$ = 115 Hz), 34.1 (d, J = 4.8 Hz, 1 P, no observable J_{WP})). In addition, a *broad* signal due to free dppe, in presumed rapid equilibrium with small amounts of coordinated dppe, was seen at δ −12.3.

NMR Monitoring of the Reaction between $CpW(NCMe)_3(\eta^2\text{-COMe})^{2+}(BF_4^-)_2$ and dppp. A hot solution of dppp (7.8 mg, 0.019 mmol) in acetonitrile-d_3 (0.7 mL) was cooled to 20 °C, and **3a**$(BF_4^-)_2$ (10.0 mg, 0.017 mmol) was added. The NMR tube was immediately placed in the NMR probe at 20 °C, and spectra were recorded. The reaction was fast, and after 5 min the spectrum showed **3a**-d_6 (15%; exchange of the cis acetonitrile ligands was complete), $CpW(NCCD_3)(\eta^2\text{-dppp})(\eta^2\text{-COMe})^{2+}$ (**8a**-d_3; 49%), and a complex (36%), presumably a geometrical isomer of **8a**, giving rise to signals at δ 2.92 (d, J = 1.3 Hz, 3 H) and 5.55 (d, J = 2.6 Hz, 5 H). This reaction was also followed by ^{31}P NMR (120 MHz, acetonitrile-d_3). After 5 min, the spectrum showed the signals due to **8a** and a *broad* signal attributed to free dppp in rapid equilibrium with minute amounts of coordinated dppp at δ −16.0.

Reaction of $CpW(NCMe)_2(\eta^3\text{-}Ph_2PCH_2PPh_2COMe)^{2+}(BF_4^-)_2$ (8a$(BF_4^-)_2$) with dppe in Acetonitrile. An NMR tube equipped with a ground-glass joint was loaded with **8a**$(BF_4^-)_2$ (10 mg, 0.01 mmol) and dppe (40 mg, 0.10 mmol). Acetonitrile-d_3 (0.7 mL) was added by vacuum transfer, and the tube was sealed under vacuum. The contents of the tube were heated at reflux for 12 h, and the ^1H NMR spectrum revealed the presence of **6a** (80%) and **8a** (20%). Prolonged heating did not change this ratio.

Simulation of the Kinetics of the Reactions between 3a and PPh_3 or dppe. The concentration vs time profiles for the observed species in these reactions were calculated by numerical integration of the simultaneous differential equations defined by the rate laws pertaining to the single steps in Schemes 2 and 3. In the computation of the $C-t$ profiles, each concentration derivative dC/dt was approximated as $\Delta C/\Delta t$, with the time increment Δt chosen sufficiently small so as to make errors arising from this approximation negligible.[23] In practice, the conversion of any species amounted to less than 5% per time step and no discernible difference was seen when the per-pass conversion was reduced to 2%. In addition, for much improved accuracy, the fourth-order Runge−Kutta integration method was employed. The use of this technique in kinetics simulations has been thoroughly explained by Wiberg.[23] The appropriate independent rate constants and the time-step size were used as adjustable input parameters. Best-fit conditions were determined by visual inspection of instantaneously produced graphs displaying simulated and experimental data. Unless noted otherwise, changes in values for a given rate constant by more than ±10−20% of the values reported below and optimization through variation of the other constants led to considerably poorer fits of simulated vs experimental data for a given run.

For the reaction between **3a** (0.060 M) and PPh_3 (0.127 M), the equilibrium constants K_1, K_2, and K_3 ($=K_1K_2$) were readily available because equilibrium between the reacting species was eventually achieved. The equilibrim constants link k_{-1} to k_1, k_{-2} to k_2, and k_{-3} to k_3; therefore, the only adjustable parameters needed for the simulation are k_1, k_2, and k_3. For the solid line in Figure 1, the following values were used: $k_1 = 6.0 \times 10^{-4}$ M^{-1} s^{-1}, $k_{-1} = 2.1 \times 10^{-5}$ s^{-1}, $k_2 = 7.0 \times 10^{-6}$ s^{-1}, $k_{-2} = 8.1 \times 10^{-6}$ s^{-1}, $k_3 = 1.3 \times 10^{-4}$ M^{-1} s^{-1}, and $k_{-3} = 8.1 \times 10^{-6}$ s^{-1}. A kinetic run at 238 mM PPh_3 resulted in a similar set (to within ±25%) of rate constants.

For the reaction between **3a** (0.026 M) and dppe (0.037 M), the solid lines in Figure 2 correspond to $k_4 = 1.1 \times 10^{-1}$ M^{-1} s^{-1}, $k_{-4} = 1.5 \times 10^{-4}$ s^{-1}, $k_5 = 6.0 \times 10^{-4}$ s^{-1}, and $k_6 = 4.0 \times 10^{-2}$ M^{-1} s^{-1}. The k_{-4} value is rather uncertain (±50%), as it is very sensitive to the selected values for k_4, k_5, and k_6.

Acknowledgment. This work was supported by Statoil under the VISTA program, administered by the Norwegian Academy of Science and Letters, and by the Norwegian Council for Science and the Humanities.

OM9400199

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