Reaction of $W(CPh)X(CO)_2(PMe_3)_2$ (X = Cl, Br) with PMe_3 To Give $W(CPh)X(CO)(PMe_3)_3$: Characterization of a Ketenyltungsten Intermediate

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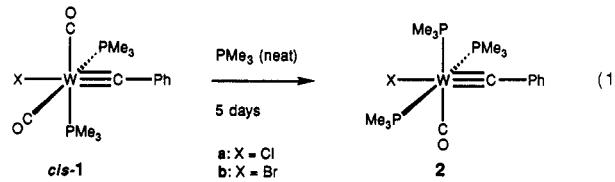
Summary: Treatment of $W(CPh)X(CO)_2(PMe_3)_2$, 1 (a, X = Cl; b, X = Br) with neat PMe_3 for several days gives $W(CPh)X(CO)(PMe_3)_3$, 2a and 2b. The ketenyltungsten complexes $W(OCCPh)X(CO)(PMe_3)_3$ are intermediates in this reaction. The complex $W(OCCPh)Cl(CO)(PMe_3)_3$ was isolated and characterized spectroscopically. Treatment of complex 2a with neat pyridine at 75 °C for several hours yields $W(CPh)Cl(CO)(py)(PMe_3)_2$.

Introduction

Substitution of one or two carbonyl ligands in alkylidyne(halo)tetracarbonylmetal complexes, $M(CR)X(CO)_4$ (M = Cr, W), by donor ligands is known to be facile.[4] Substitution of more than two carbonyl ligands is successful when the substituting ligands have π acceptor properties.[5,6] While these systems have not been studied in detail, the available experimental evidence suggests that these substitution reactions are dissociative in nature. This work describes the overall substitution of carbon monoxide in the complexes $W(CPh)X(CO)_2(PMe_3)_2$ (X = Cl, Br) by PMe_3, a strong donor ligand, which proceeds via ketenyltungsten complexes as intermediates.

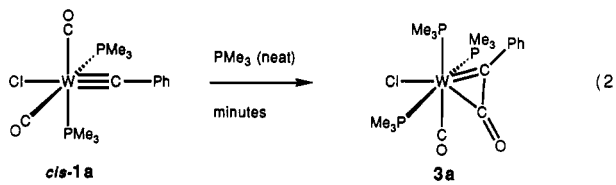
Results and Discussion

When *cis*-$W(CPh)Cl(CO)_2(PMe_3)_2$,[7] *cis*-**1a**, is dissolved in neat PMe_3, the yellow color of the solution of *cis*-**1a** turns purple-pink, and in most runs of the experiment a crystalline precipitate of a purple-pink intermediate, **3a**, forms within a few minutes. This precipitate redissolves in the course of several days to give an orange solution. Removal of the excess PMe_3 under vacuum leaves essentially pure $W(CPh)Cl(CO)(PMe_3)_3$, **2a** (eq 1).[8] Recrystallization from ether gives yellow-orange crystals. The bromo complex $W(CPh)Br(CO)(PMe_3)_3$,[9] **2b**, may be obtained in an analogous fashion starting from *cis*-$W(CPh)Br(CO)_2(PMe_3)_2$, *cis*-**1b**. Complexes **2a,b** have a strong IR absorption in the metal carbonyl region at 1895–



1900 cm^{-1}. The ^1H NMR spectra of complexes **2** exhibit a virtual triplet and a doublet for three trimethylphosphine ligands in a meridional arrangement. The ^{13}C NMR signal of the alkylidyne carbon appears as a quartet due to approximately equal coupling to the three phosphorus atoms. The signal of the carbonyl carbon atom is a doublet of triplets. Consequently, the alkylidyne ligand occupies a coordination site perpendicular to the plane containing the three phosphine ligands and the carbonyl ligand is located in the plane of the three phosphine ligands. The ^{31}P NMR features two signals, a triplet and a doublet, in a 1:2 relative ratio. These data are in agreement with the formulation of complexes **2a,b** as shown in eq 1. The synthesis of complexes **2a,b** according to eq 1 is a useful method. Since no solvent is used in addition to PMe_3, all unused PMe_3 is easily recovered.

The purple-pink intermediate **3a** of the reaction of **1a** with PMe_3 can be obtained in the form of beautiful purple-pink platelets, if the reaction solution is gently swirled (eq 2). The platelets were found to be too thin for an X-ray



crystallographic study, but the available spectroscopic information is sufficient to characterize compound **3a** as a ketenyl tungsten complex.[10] The IR spectrum of **3a** in CH_2Cl_2 exhibits a strong signal at 1917 cm^{-1} with a shoulder at 1947 cm^{-1} for a carbonyl ligand and a weak absorption at 1667 cm^{-1} for a ketenyl ligand. The ^1H NMR spectrum shows the presence of three trimethylphosphine ligands in a meridional arrangement. The two mutually trans PMe_3 ligands give rise to a virtual triplet at δ 1.41, and the signal of the central PMe_3 ligand is a doublet at δ 1.59. The ^{13}C NMR spectrum shows no signal in the region characteristic of alkylidyne ligands. Three signals are found between δ 220 and 200. Only two of these signals exhibit observable coupling to the phosphorus atoms. A

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(9) **2a** and **2b** may also be obtained by irradiation of $[W(CPh)X(CO)_2(TMEDA)]$ (X = Cl, Br; TMEDA = tetramethylethylenediamine) in the presence of PMe_3. Steil, P.; Mayr, A. *Z. Naturforsch. B* **1991**, *47*, 656.

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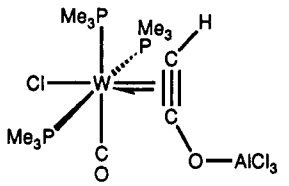
resonance at δ 216.8 appears as a doublet of triplets and consequently belongs to a ligand located in the plane of the three trimethylphosphine ligands. It is assigned to the carbonyl ligand. A second resonance at δ 215.2 appears as a quartet due to approximately equal coupling to three phosphorus atoms and consequently belongs to a ligand coordinated perpendicular to the plane of the three phosphine ligands. This signal is assigned to the phenyl-substituted carbon atom of the ketenyl ligand. A third resonance at δ 207.9 exhibits no observable coupling to the phosphorus atoms. This signal is assigned to the carbonyl group of the ketenyl ligand.[10] The respective assignment of the signals at δ 216.8 and 215.2 to the carbonyl ligand and to the phenyl-substituted ketenyl carbon is not unambiguous. It is, however, consistent with the structure of the closely related and crystallographically characterized complex **4**.[11] For electronic reasons, the



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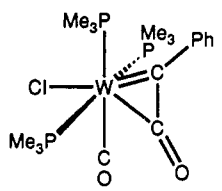
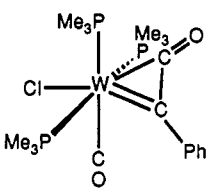
ketenyl ligand in **3a** is expected to be most stable in the orientation parallel to the axis of the metal–carbonyl bond whereby the ketenyl carbonyl group is oriented toward the carbonyl ligand and the phenyl group toward the central trimethylphosphine ligand (rotamer **A**).[12] This



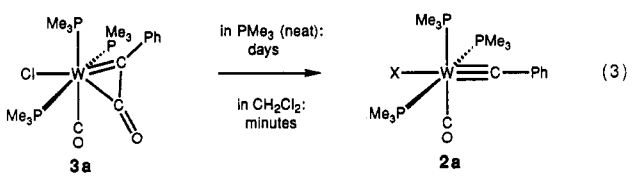
3a, A



3b, B

orientation, however, is probably destabilized due to steric interactions between the phenyl group and the central trimethylphosphine ligand. Thus rotamer **B** may be similar in energy to rotamer **A**. The appearance of a shoulder in the IR absorption of the carbonyl ligand could be due to the presence of two rapidly interconverting species (only a single species is observed by NMR). We propose that these are the rotamers **A** and **B**.

When complex **3a** is dissolved in methylene chloride, it decomposes within a few minutes to give **2a** as the major product (eq 3). Depending on the reaction conditions, but not reproducibly in our hands, several byproducts are



3a **2a** (3)

formed as well. Complex *cis*-**1a** and W{C(PMe$_3$)Ph}Cl(CO)$_2$(PMe$_3$)$_2$[13] have been characterized as byproducts in several runs. The observation that **3a** decomposes faster in the absence of a high concentration of PMe$_3$ suggests that dissociation of PMe$_3$ initiates the transformation of **3a** to **2a**. The phosphine ligand in the central position of the meridional arrangement is sterically encumbered due to the presence of two trimethylphosphine ligands and the ketenyl ligand in cis coordination sites. It is therefore most likely to be this phosphine ligand which dissociates from the metal center. This assumption is supported by the small size of the ^{183}W–^{31}P coupling constant of 122 Hz for this ligand. In comparison, the ^{183}W–^{31}P coupling constant for the two mutually trans phosphine ligands is 268 Hz, a value typical for PMe$_3$ coordinated to tungsten.[14] Pyrolysis of solid **3a** at 98 °C under vacuum for several hours also gives **2a** among other unidentified products.

If dissociation of PMe$_3$ is the first step in the decomposition of **3a** in CH_2Cl_2, then a possible pathway for the formation of **2a** could consist of cleavage of the ketenyl ligand to give the dicarbonyl complex W(CPh)Cl(CO)$_2$(PMe$_3$)$_2$, **1**, in either its cis or trans form. Intuitively, we would expect formation of *trans*-**1a**. Subsequent substitution of carbon monoxide by PMe$_3$ could then lead to **2a**. Facile substitution of a carbonyl ligand in *trans*-**1a** had previously been documented.[8] To probe the possible intermediacy of *cis*- or *trans*-**1a**, several test reactions were performed. The reaction of a sample of *cis*-**1a** with 1 equiv of PMe$_3$ in CH_2Cl_2 does afford **2a**, but only very slowly, requiring about 9 days to go to completion.[15] *cis*-**1** can therefore be excluded as an intermediate in the decomposition of **3a** to **2a**. The reaction of a sample of *trans*-**1a** with 1 equiv of PMe$_3$ in CH_2Cl_2 also affords **2a** quantitatively (IR), taking about 11 h to go to completion. The reaction of *trans*-**1a** with neat PMe$_3$, leading to the quantitative formation of **2a**, takes about 7 h to go to completion. In this latter reaction, **3a** is not observed as an intermediate. Obviously, the formation of **2a** from *trans*-**1** and PMe$_3$ in CH_2Cl_2 is much slower than the decomposition of **3a** in CH_2Cl_2 to form **2a** as the major product. Consequently, *trans*-**1a** is also not an intermediate in the main pathway of the decomposition of **3a** to **2a**.

A proposed mechanism for the loss of carbon monoxide, which is compatible with the experimental observations, is shown in Scheme 1. It involves dissociation of PMe$_3$ from **3a** and cleavage of the ketenyl ligand into alkylidyne and carbonyl ligands, but in a way not to afford *cis*- or *trans*-**1a**. Since the rotamer **A** of **3a** is electronically more favorable than rotamer **B**, dissociation of PMe$_3$ from **3a** to give the unsaturated intermediate **C**, in which the carbonyl group of the ketenyl ligand is proximal to the carbonyl ligand, would appear to be a likely event. Cleavage of the ketenyl ligand in **C** would then result in the formation of **D**, in which the alkylidyne ligand occupies the coordination site trans to the previously present carbonyl ligand. That carbonyl ligand would be strongly labilized and consequently dissociate to give **E**. Trapping of **E** by PMe$_3$ would then afford **2a**.

The loss of carbon monoxide from ketenyl complexes of the type M(η^5-C$_5$H$_5$)(η^2-RCCO)(CO)(PR′$_3$) (M = Mo,

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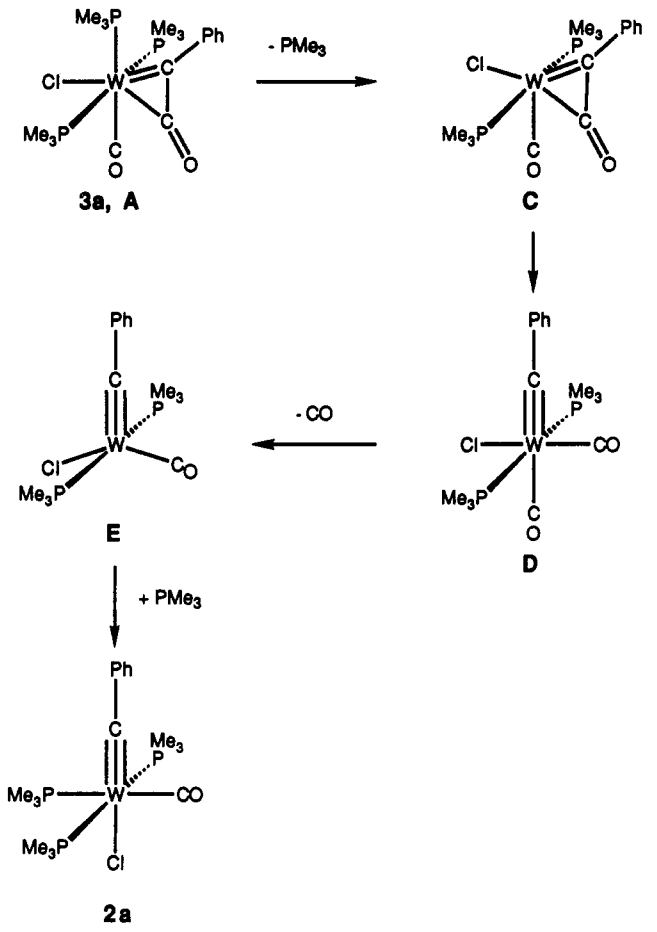
(13) The bromo analogue has previously been described (ref 4). IR, ν(CO): 1927 and 1827 cm^{-1}.

(14) Pregosin, P. S. in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: New York, 1987; p 465.

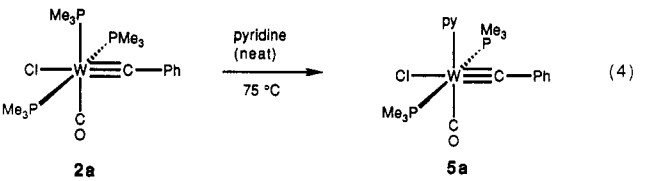
(15) *cis*-**1a** very slowly transforms thermally into *trans*-**1a** (unpublished results). It was not established whether cis–trans isomerization is significant under the conditions of this experiment.

Scheme 1



W) has been observed in mass spectroscopic studies and upon attempted sublimation.[10b] The ketenyl complex [W{C(PMePh$_2$)CO}(Cl)$_2$(CO)(PMePh$_2$)$_2$] loses carbon monoxide upon gentle heating.[16a] Several examples of unusually facile substitution of carbon monoxide in alkylidyne-metal complexes have been reported in the literature.[17] For example, the cyclopentadienyl-substituted alkylidyne complexes M(CR)(η^5-C$_5$H$_5$)(CO)$_2$ (M = Mo, W) react at or below room temperature with strongly nucleophilic phosphines, such as PMe$_3$, to give the ketenyl complexes M(η^5-C$_5$H$_5$)(η^2-RCCO)(CO)(PR'$_3$). Depending on the conditions, these reactions may be accompanied by the formation of the carbonyl substitution products M(CR)-(η^5-C$_5$H$_5$)(CO)(PR'$_3$).[17] Since the reaction conditions are mild, it is unlikely that the substitution of carbon monoxide occurs via dissociation. In light of the present results and in view of the facile alkylidyne–carbonyl coupling in these systems, it appears possible that ketenylmetal species may be involved in the formation of the carbonyl substitution products.

Complexes **2a,b** are useful starting materials in metal alkylidyne chemistry due to the coordinative lability of the central trimethylphosphine ligand.[18] A weaker coordination of this phosphine ligand, compared to the two mutually trans phospine ligands, is indicated by its smaller ^{184}W–^{31}P coupling constant (219.4 Hz versus 269.3 Hz). Selective substitution at the position of the central PMe$_3$ ligand is feasible. For example, heating of complex **2a** in neat pyridine to 75 °C for several hours affords the pyridine-substituted complex **5a** in essentially quantitative yield (eq 4).



(4)

Experimental Section

Standard inert-atmosphere techniques were used in the execution of the experiments. The solvents methylene chloride (CaH$_2$), tetrahydrofuran (Na/benzophenone), and hexane (CaH$_2$) were dried and distilled prior to use.

Materials. [W(CPh)(Cl)(CO)$_2$(PMe$_3$)$_2$], **1a**,[19] was prepared as previously described. PMe$_3$ was obtained from commercial sources or prepared by a modification[20] of a literature procedure.[21] The NMR spectra were measured at magnetic field strengths of 5.87 or 7.05 T (250 or 300 MHz for ^{1}H NMR) in CDCl$_3$ at room temperature unless otherwise noted; solvent peaks were used as the internal reference, the data are reported in δ relative to TMS. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

[W(CPh)(Br)(CO)$_2$(PMe$_3$)$_2$], 1b. [W(CPh)Br(CO)$_2$(pyridine)$_2$][4,19] (1.102 g, 1.94 mmol) is dissolved in 35 mL of THF and PMe$_3$ (0.04 mL, 294 mg, 3.86 mmol) is added. The solution is heated to 50 °C for 1.5 h. Completion of the reaction is monitored by IR. The solvent is removed under vacuum, and the residue is washed twice with hexane. The product is recrystallized from CH$_2$Cl$_2$/hexane (yellow crystals). Yield: 542 mg (49.7%). IR (CH$_2$Cl$_2$, cm^{-1}): 2003 (s, CO), 1930 (s, CO). ^{1}H NMR (CDCl$_3$, 298 K): δ 7.30–7.17 (m, 5 H, Ph), 1.75–1.63 (m, 18 H, P(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): δ 265.1 (CPh), 210.9 (dd, $^2J_{PCtrans}$ = 36 Hz, $^2J_{PCcis}$ = 18 Hz, CO), 149.5 (*i*-Ph), 129.0, 128.0, 127.4 (C$_6$H$_5$), 19.7 (d, J_{PC} = 15.0 Hz, P(CH$_3$)$_3$). ^{31}P NMR (CDCl$_3$, 298 K): δ −31.4 (d, J_{WP} = 238.13 Hz, PMe$_3$).

[W(CPh)(Cl)(CO)(PMe$_3$)$_3$], 2a. A mixture of **1a** (6.75 g, 13 mmol) and 75 mL trimethylphosphine is stirred in a 300-mL flask, which is equipped with an oil bubbler. After a few minutes a purple-pink precipitate forms. Stirring is continued for 5 days. Then, the trimethylphosphine is removed under vacuum (recovered in a cold-trap) and the product is recrystallized from diethyl ether (orange crystals). Yield: 6.8 g (92%). Mp 106 °C dec. IR (CH$_2$Cl$_2$, cm^{-1}): 1896 (s, CO). ^{1}H NMR (CDCl$_3$, 298 K): δ 7.08 (m, 3 H, *o,p*-Ph), 7.01 (m, 2 H, *m*-Ph), 1.63 (virtual t, 18 H, 3.4 Hz, P(CH$_3$)$_3$), 1.59 (d, 9 H, $^2J_{PH}$ = 6.7 Hz, P(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K): δ 261.5 (q, J_{WC} = 201.1 Hz, $^2J_{PC}$ = 10.8 Hz, CPh), 227.5 (dt, J_{WC} = 154.4 Hz, $^2J_{PCtrans}$ = 43.5 Hz, $^2J_{PCcis}$ = 6.7 Hz, CO), 151.3 (*i*-Ph), 127.6 (*o,m*-Ph), 124.6 (*p*-Ph), 20.8 (m, P(CH$_3$)$_3$). ^{31}P NMR (CDCl$_3$, 298 K): δ −23.12 (d, J_{WP} = 269.3 Hz, $^2J_{PPcis}$ = 21.8 Hz, 2 PMe$_3$), −26.54 (t, J_{WP} = 219.4 Hz, $^2J_{PP}$ = 21.8 Hz, 1 PMe$_3$). Anal. Calcd for C$_{17}$H$_{32}$ClOP$_3$W (MW 564.66): C, 36.16; H, 5.71. Found: C, 36.31; H, 5.81.

[W(CPh)(Br)(CO)(PMe$_3$)$_3$], 2b. Complex **2b** is prepared in an analogous fashion from **1b** (98 mg, 0.18 mmol). The reaction is complete after 64 h (100% conversion based on IR). The product is recrystallized from hexane (orange crystals). Yield: 64 mg (60.2%). IR (CH$_2$Cl$_2$, cm^{-1}): 1900 (s, CO). ^{1}H NMR (CDCl$_3$, 298 K): δ 7.25–7.05 (m, 5 H, Ph), 1.66 (virtual t, 18 H, 3.33 Hz, P(CH$_3$)$_3$), 1.63 (d, 9 H, $^2J_{PH}$ = 6.9 Hz, P(CH$_3$)$_3$). ^{13}C{^{1}H}

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(21) Wolfsberger, W.; Schmidbaur, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149.

NMR ($CDCl_3$, 298 K): δ 260.6 (q, $^2J_{PC}$ = 11.8 Hz, CPh), 226.5 (dt, $^2J_{PCtrans}$ = 42.7 Hz, $^2J_{PCcis}$ = 6.1 Hz, CO), 150.7 (*i*-Ph), 127.6, 127.4, 124.7 (C_6H_5), 1.67 (m, $P(CH_3)_3$). ^{31}P NMR ($CDCl_3$, 298 K): δ −27.4 (d, J_{WP} = 268.5 Hz, $^2J_{PPcis}$ = 23.9 Hz, 2 PMe_3), −31.1 (t, J_{WP} = 219.6 Hz, $^2J_{PP}$ = 23.9 Hz, 1 PMe_3). Anal. Calcd for $C_{17}H_{32}BrOP_3W$ (M_r 609.11): C, 33.52; H, 5.30. Found: C, 33.41; H, 5.26.

Isolation of 3a. Complex **1a** (0.5 g, 0.97 mmol) is dissolved in 10 mL of trimethylphosphine in a 50-mL flask by swirling for approximately 15 min. Purple crystals start to form before or shortly after all of the starting material is dissolved. After the formation of the crystals, the trimethylphosphine solution is decanted. The crystals are washed several times with cold diethyl ether (0 °C) and then dried under vacuum. The solid slowly decomposes at room temperature. IR (CH_2Cl_2, cm^{-1}): 1947 (sh, CO), 1917 (s, CO) 1667 (w, CCO). ^1H NMR (CD_2Cl_2, 213 K): δ 7.14 (m, 5 H, Ph), 1.59 (d, 9 H, $^2J_{PH}$ = 7.7 Hz, 1 $P(CH_3)_3$), 1.41 (t, 18 H, $^2J_{PH}$ = 3.9 Hz, 2 $P(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 213 K): δ 216.8 (dt, $^2J_{PCtrans}$ = 32.6 Hz, $^2J_{PCcis}$ = 6.7 Hz, CO), 215.2 (q, $^2J_{PC}$ = 18.2 Hz, PhCCO), 207.9 (PhCCO), 147.2 (*i*-Ph), 127.8 (*o*-Ph), 124.8 (*p*-Ph), 122.4 (*m*-Ph), 17.6 (J_{PC} = 13.7 Hz, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 210 K): δ −21.4 (d, J_{WP} = 268.4 Hz, $^2J_{PP}$ = 19.3 Hz, 2 PMe_3), −33.4 (t, J_{WP} = 122.0 Hz, $^2J_{PP}$ = 19.3 Hz, 1 PMe_3). Anal. Calcd for $C_{18}H_{32}ClO_2P_3W$ (M_r 592.78): C, 36.48; H, 5.44; P, 15.68. Found: C, 36.64; H, 4.92; P, 14.77.

Decomposition of 3a. **3a** (15 mg, 0.026 mmol) is dissolved in 3 mL of CH_2Cl_2 at -78 °C. The reaction flask is put into a water bath (21.0 °C). Complex **3a** is completely decomposed after about 10–15 min. Complex **2a** is formed as the major product (30–70%, based on IR and ^1H NMR). Complex *cis*-**1a** could be identified as a significant byproduct (15–40%, IR and ^1H NMR) in most runs. In some runs, a third product with IR absorptions at 1924 and 1822 cm^{-1} was formed (0–40%). On the basis of the IR absorptions of the known complex $[W(C(PMe_3)Ph)Br(CO)_2(PMe_3)_2]$ at 1927 and 1827 cm^{-1}, this third product is assumed to be $[W\{C(PMe_3)Ph\}Cl(CO)_2(PMe_3)_2]$. Additional, minor byproducts were not identified.

Three 5-mg samples of **3a**, which are contained in NMR tubes, are placed into a Schlenk flask. A dynamic oil pump vacuum is applied, and the Schlenk flask is placed into an oil bath at 98 °C. The three samples are removed from the Schlenk flask after 5, 28, and 50 h. After addition of $CDCl_3$, the ^1H NMR spectra are recorded. The ^1H NMR spectra of the samples (orange solutions; some insoluble parts in the sample heated for 28 h; the sample heated for 50 h is almost completely insoluble) indicate the presence of several PMe_3-containing compounds of which only **2a** could be identified. The presence of neither *cis*- nor *trans*-**1a** could be detected.

$[W(CPh)(Cl)(CO)(py)(PMe_3)_2]$, 5a. Complex **2** (2.8 g, 5.0 mmol) is dissolved in 20 mL of pyridine in a 50-mL flask and heated to 75 °C in a hot water bath. Nitrogen is blown over the solution periodically (to remove liberated PMe_3) until IR indicated that the reaction is complete (about 3–4 h). The pyridine is evaporated under a stream of nitrogen. The solid is dried under vacuum and then washed with a small amount of pentane. Yield: 2.7 g (96%). Mp 94 °C dec. IR: (CH_2Cl_2, cm^{-1}) 1870 (s, CO), (KBr, cm^{-1}) 1859 (s, CO). ^1H NMR ($CDCl_3$, 298 K): δ 9.52 (d, 2 H, α-py), 7.77 (t, 1 H, γ-py), 7.30 (m, 2 H, β-py), 7.20 (m, 5 H, Ph), 1.40 (virtual t, 18 H, 13.1 Hz, $P(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 255.6 (t, J_{WC} = 201.1 Hz, $^2J_{PC}$ = 11.2 Hz, CPh), 238.8 (J_{WC} = 172.4 Hz, CO), 150.7 (α-py), 148.6 (*i*-Ph), 136.8–124.2 (py, Ph), 17.4 (virtual t, 13.1 Hz, $P(CH_3)_3$). Anal. Calcd for $C_{19}H_{28}ClNOP_2W$ (M_r 567.68): C, 40.20; H, 4.97; N, 2.47. Found: C, 39.98; H, 5.02; N, 2.37.

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