Induced Acceleration of Phosphine Exchange in Metal Carbonyls by Pendant Groups of Coordinated Polyphosphines. Two Dangling Phosphine Arms Are Much Better Than One[1]

Richard L. Keiter,* John William Benson, Ellen A. Keiter,* Weiying Lin, Zhongjiang Jia, Donna M. Olson, Douglas E. Brandt, and Jeremy L. Wheeler

Department of Chemistry, Eastern Illinois University, Charleston, Illinois 61920

Received April 15, 1998

The kinetics and thermodynamics of isomerization of the linkage isomers $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH(PPh_2)_2]$ (**1**) and $(OC)_5W[\eta^1\text{-}PPh_2CH(PPh_2)CH_2PPh_2]$ (**2**) in chloroform have been studied by $^{31}P\{^1H\}$ NMR over the temperature range of 10−55 °C. Conversion of **1** to **2** is exothermic ($\Delta H = -12.25 \pm 0.1$ kJ mol^{-1}) and is accompanied by a large decrease in entropy ($\Delta S = -28.2 \pm 0.3$ J mol^{-1} K^{-1}). The reaction proceeds much faster than expected [$k = (1.18 \pm 0.01) \times 10^{-5}$ s^{-1}] at 25 °C, and its small activation enthalpy ($\Delta H^{\ddagger} = 92.6 \pm 1.9$ kJ mol^{-1}) and large negative activation entropy ($\Delta S^{\ddagger} = -28.2 \pm 6.2$ J mol^{-1} K^{-1}) suggest an associative mechanism. The reaction is 4 orders of magnitude faster than the isomerization of $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tol})_2]$ (**3**) to $(OC)_5W[\eta^1\text{-}P(p\text{-tol})_2CH_2CH_2PPh_2]$ (**4**). Exchange of coordinated and dangling phosphines is faster than chelation for each of the four complexes, but chelation of **1** or **2** is much faster than chelation of **3** or **4**. It appears that the second dangling phosphine arm present in **1** and **2** accelerates the exchange of all metal-attached ligands. Also observed is long-range phosphorus−carbon coupling, possibly enhanced by a "through-space" interaction, between the short-armed dangling phosphine and the equatorial carbonyl groups ($^4J_{PC} = 3.89$ Hz).

Introduction

Transition metal complexes in which polydentate phosphorus ligands are incompletely coordinated, sometimes known as "dangling" ligand complexes, have become important precursors for the synthesis of heterobimetallic compounds.[2] They were first observed spectroscopically[3] soon after the first chelated complexes of these ligands were isolated,[4] and within a few years random examples were obtained in pure form.[5] Not surprisingly, synthetic success was possible only when chelation was slow compared to the time required for isolation. Subsequently, selective syntheses based on controlling the number of metal sites available to the polydentate phosphine were developed for a number of these complexes.[6]

Robust complexes such as $(OC)_5M(\eta^1\text{-dppm})$ and $(OC)_5M(\eta^1\text{-dppe})$ (M = Cr, W; dppm = $Ph_2PCH_2PPh_2$; dppe = $Ph_2PCH_2CH_2PPh_2$) undergo chelation extremely slowly at room temperature with half-lives of many months.[6b,7] Early $^{31}P\{^1H\}$ NMR studies further confirmed their inert nature by showing that phosphorus exchange of coordinated and dangling phosphines was slow relative to the NMR time scale.[6b] Thus, all evidence indicated that the uncoordinated phosphine of these dangling ligand complexes is inactive until subjected to thermal or photolytic stimulation that leads to CO loss followed by chelation.

Recent qualitative results from our laboratory, however, demonstrated that for at least one mononuclear monoligated complex, $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH(PPh_2)_2]$, exchange between coordinated and uncoordinated phosphine occurs much more rapidly than chelation and is fast enough to measure conveniently even below room temperature.[8]

(1) Presented in part in the Symposium on Reactivity at Transition Metal-Nitrogen, Sulfur, and Phosphorus Bonds at the 211th ACS National Meeting, New Orleans, 1996.

(2) (a) Orth, S. D.; Terry, M. R.; Abboud, K. A.; Dodson, B.; McElwee-White. *Inorg. Chem.* **1996**, *35*, 916−922. (b) Carr, S. W.; Fontaine, X. L. R.; Shaw, B. L. J. *Chem. Soc., Dalton Trans.* **1991**, 1025−1027. (c) Carr, S. W.; Fowles, E. H.; Fontaine, X. L. R.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1990**, 573−579. (d) Fontaine, X. L. R.; Jacobsen, G. B.; Shaw, B. L.; Thronton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 741−750. (e) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191−243.

(3) Mawby, R. J.; Morris. D.; Thorsteinson, E. M.; Basolo, F. *Inorg. Chem.* **1966**, *5*, 27−33.

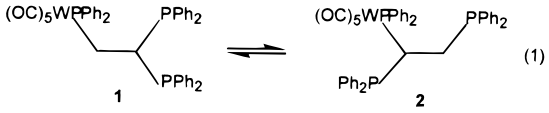
(4) Chatt, J.; Hart, F. A. *J. Chem. Soc.* **1960**, 1378.

(5) (a) King, R. B.; Efraty, A. *Inorg. Chem.* **1969**, *8*, 2374−2379. (b) Rigo, P. Longato, B.; Favero, G. *Inorg. Chem.* **1972**, *11*, 300−303. (c) Brown, M. L.; Cramer, J. L.; Ferguson, J. A.; Meyer, T. J.; Winterton, N. *J. Am. Chem. Soc.* **1972**, *94*, 8707−8710.

(6) (a) Keiter, R. L.; Shah, D. P. *Inorg. Chem.* **1972**, *11*, 191−193. (b) Connor, J. A.; Day, J. P.; Jones, E. M.; McEwen, G. K. *J. Chem. Soc., Dalton Trans.* **1973**, 347−354. (c) Grim, S. O.; Del Gaudio, J.; Molenda, R. P.; Tolman, C. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 3416−3422. (d) Keiter, R. L.; Sun, Y. Y.; Brodack, J. W.; Cary, L. W. *J. Am. Chem. Soc.* **1979**, *101*, 2638−2641. (e) Keiter, R. L.; Brodack, J. W.; Borger, R. D, Cary, L. W. *Inorg. Chem.* **1982**, *21*, 1256−1258. (f) Keiter, R. L.; Rheingold, A. L.; Hammerski, J. J.; Castle, C. K. *Organometallic* **1983**, *2*, 1635−1639. (g) Gan, K.-S.; Lee, H. K.; Hor, T. S. A. *J.* Organomet. *Chem.* **1993**, *460*, 197−201.

(7) Benson, J. W.; Keiter, E. A.; Keiter, R. L. *J. Organomet. Chem.* **1995**, *495*, 77−81.

S0276-7333(98)00289-1 CCC: $15.00
Publication on Web 08/21/1998



We now report the quantitative kinetic and thermodynamic details of this reaction as determined by $^{31}P\{^1H\}$ NMR spectroscopy.

For purposes of comparison we have also synthesized both $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tol})_2]$ (**3**) and $(OC)_5W[\eta^1\text{-}P(p\text{-tol})_2CH_2CH_2PPh_2]$ (**4**) in pure form and monitored their rates of isomerization.

$$(OC)_5W[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tol})_2] \rightleftarrows \underset{\mathbf{3}}{} \quad (OC)_5W[\eta^1\text{-}P(p\text{-tol})_2CH_2CH_2PPh_2] \quad (2)$$
$$\mathbf{4}$$

Remarkably, reaction 1 is 4 orders of magnitude faster than reaction 2. In this paper we propose mechanistic models to account for the very different exchange rates and present evidence suggesting that reaction 1 proceeds primarily by an associative mechanism in which the transition state requires active participation of all three phosphino groups, one dangling phosphine arm interacting with the cis carbonyl groups and a second dangling phosphine arm displacing the coordinated phosphine. Reaction 2, on the other hand, lacking an accelerating short phosphine arm, proceeds at a normal rate, consistent with a mechanism in which ligand dissociation is of primary importance.

If interaction of an R group (in this case a dangling phosphine) of coordinated PR_3 with the equatorial carbonyl ligands of a complex such as $(OC)_5WPR_3$ leads to accelerated phosphine exchange, it would be expected that the same interaction would lead to accelerated carbonyl replacement. Thus, if the rate of isomerization in reaction 1 is accelerated by a phosphine−carbonyl interaction, the same interaction should lead to an accelerated rate of chelation. We have evaluated this hypothesis by measuring rates of chelation for both reaction 1 and 2 and comparing them to rates of isomerization.

These studies are of fundamental interest because they suggest that complex reactivity may be profoundly influenced by the nature of pendant groups attached to a coordinated ligand. Although it is widely recognized that steric repulsion between pendant groups and other ligands of a complex may significantly influence reaction rates, the importance of attractive interactions between these groups and coordinated ligands has received much less attention.[9] It would appear that for organometallic reactions in general it may be possible to influence substitution rates by employing ligands with pendant groups which have an affinity for other coordinated ligands of the complex.

Experimental Section

General Considerations. All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The compounds, $(Ph_2P)_2C{=}CH_2$,[10] $(OC)_5WPPh_2H$,[6d] $Cl_2Pt(PPh_2)_2C{=}CH_2$,[11] $P(p\text{-tol})_2H$,[12] $(Ph_2P)_2CHCH_2PPh_2$,[13] $(OC)_5WNH_2Ph$,[6a] and $(OC)_5WPPh_2CH{=}CH_2$[6d] were prepared according to published procedures. Phosphorus-31 NMR spectra (referenced to 85% phosphoric acid), carbon-13 spectra, and infrared spectra were recorded with GE QE-300 NMR and Nicolet 20 DXB FT-IR spectrometers, respectively. Elemental analyses were performed at the University of Illinois Microanalytical Laboratory, Urbana, Illinois.

Synthesis of $Cl_2Pt(PPh_2)_2CHCH_2PPh_2W(CO)_5$. A THF solution (25 mL) containing $Cl_2Pt(PPh_2)_2C{=}CH_2$ (0.700 g, 1.06 mmol), $(OC)_5WPPh_2H$ (0.539 g, 1.06 mmol), and $KOBu^t$ (0.0590 g, 0.528 mmol) was refluxed for 2 h. The residue remaining after the solvent was removed by vacuum was recrystallized from a 1:1 solution of CH_2Cl_2/CH_3OH to give 0.964 g (77.8%) of white needlelike crystals (dec 205−210 °C). IR ($CHCl_3$): E + A_1^1, 1940(s) cm^{-1}; A_1^2, 2073(m) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 17.7 ppm (t, $^1J_{WP} = 246$ Hz, $^3J_{PP} = 5.01$ Hz), δ −37.4 ppm (d, $^1J_{PtP} = 3077$ Hz, $^3J_{PP} = 5.01$ Hz[14]). Anal. Calcd for $C_{43}H_{33}Cl_2O_5P_3PtW$: C, 44.05; H, 2.84; P, 7.92. Found: C, 44.14; H, 2.88; P, 7.77.

Synthesis of $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH(PPh_2)_2]$, 1, and $(OC)_5W[\eta^1\text{-}PPh_2CH(PPh_2)CH_2PPh_2]$, 2. Method A. A mixture of $Cl_2Pt(PPh_2)_2CHCH_2PPh_2W(CO)_5$ (0.457 g, 0.390 mmol) and KCN (0.102 g, 1.56 mmol) in ethanol (25 mL) was stirred for 72 h at room temperature. During this time the color of the suspension changed from colorless to yellow. The insoluble material was collected by filtration and extracted with CH_2Cl_2 (10 mL). The solvent was removed, and the residue was shown to consist of a 1:5 mixture of isomers **1** and **2**.[13a] $^{31}P\{^1H\}$ NMR ($CDCl_3$) for **1**: δ 13.1 ppm (t, $^1J_{WP} = 242$ Hz, $^3J_{PP} = 7.5$ Hz), δ −3.1 ppm (d, $^3J_{PP} = 7.5$ Hz). $^{13}C\{^1H\}$ NMR: $\delta(CO)_{ax} = 199.8$ ppm (d, $^2J_{PC} = 23.1$ Hz); $\delta(CO)_{eq}$ 197.2 ppm (d, $^2J_{PC} = 7.27$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$) for **2**: δ 34.1 ppm (dd, $^1J_{WP} = 252$ Hz, $^2J_{PP} = 207$ Hz, $^3J_{PP} = 22.2$ Hz), δ −8.3 ppm (d, $^2J_{PP} = 207$ Hz), δ −16.6 ppm (d, $^3J_{PP} = 22.2$ Hz). $^{13}C\{^1H\}$ NMR for **2:** $\delta(CO)_{ax}$ 199.6 ppm (d, $^2J_{PC} = 23.7$ Hz, $^1J_{WC} = 142.1$ Hz), $\delta(CO)_{eq}$ 197.1 ppm (dd, $^2J_{PC} = 6.52$ Hz, $^4J_{PC} = 3.89$ Hz, $^1J_{WC} = 126.5$ Hz). The solvent was removed, and the residue was recrystallized from a mixture of 10 mL of CH_2Cl_2 and 15 mL of CH_3OH to give white crystals of the less soluble **2** (0.196 g, 55.4%, mp = 164.0−164.5 °C). IR ($CHCl_3$): A_1^1 + E = 1937(s) cm^{-1}, A_1^2 = 2070(m) cm^{-1}. It was not possible to obtain the more soluble **1** in pure form by either recrystallization or column chromatography; however, when the cyanide reaction was run for 4 h under the above conditions, the ratio of **1** to **2** was 3.6:1 as shown by $^{31}P\{^1H\}$ NMR, indicating that **1** formed initially and then partially isomerized to **2**. IR ($CHCl_3$): A_1^1 + E = 1936(s) cm^{-1}, A_1^2 = 2071 cm^{-1}. When pure **2** was placed in $CHCl_3$, isomerization took place to give a mixture of **1** and **2**.

Method B. To $(OC)_5WNH_2Ph$ (1.00 g, 2.33 mmol) and $(Ph_2P)_2CHCH_2PPh_2$ (1.36 g, 2.33 mmol) was added 20 mL of toluene. The solution was stirred for 12 h at room temperature, toluene was removed, and the residue was chromatographed on Al_2O_3 with CH_2Cl_2/hexane (1:2). The first fraction contained isomers **1** and **2** to give a combined yield of 1.1 g (52%).

Formation of $(OC)_4W[\eta^2\text{-}PPh_2CH(PPh_2)CH_2PPh_2]$, 5, and $(OC)_4W[\eta^2\text{-}PPh_2CH_2CH(PPh_2)_2]$, 6. These complexes slowly formed at 55 °C from mixtures of **1** and **2** in $CDCl_3$

(8) (a) Keiter, R. L.; Keiter, E. A.; Olson, D. M.; Bush, J. R.; Lin, W.; Benson, J. W. *Organometallics* **1994**, *13*, 3752−3754. (b) Evidence for phosphine exchange in $(OC)_5MoPPh_2CH{=}C(Me)PPh_2$ has been described recently. Maitra, K.; Catalano, V. J.; Nelson, J. H. *J. Organomet. Chem.* **1997**, 529, 409.

(9) (a) Brown, T. L. *Inorg. Chem.* **1992**, *31*, 1286−1294. (b) Woo, T. K.; Ziegler, T. *Inorg. Chem.* **1994**, *33*, 1857−1863.

(10) Colquhoun, I. J.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1982**, 1915−1921.

(11) Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1989**, 1527−1530.

(12) (a) Grim, S. O.; Yankowsky, A. W. *J. Org. Chem.* **1977**, *42*, 1236−1239. (b) Cotton, F. A.; Kitagawa, S. *Inorg.* Chem. **1987**, *26*, 3463−3468.

(13) (a) Bookham, J. L.; McFarlane, W., Colquhoun, I. J. *J. Chem. Soc., Dalton Trans.* **1988**, 503−507. (b) Schmidbaur, H.; Paschalidis, C.; Reber, G.; Muller, G. *Chem. Ber.* **1988**, *121*, 1241−1245.

(14) $^3J_{PP}$ was reported incorrectly in ref 8a.

solution in sealed NMR tubes (see kinetics results). $^{31}P\{^1H\}$ NMR ($CDCl_3$) for **5**:[13a] δ 3.9 ppm (t, $^1J_{WP} = 206$ Hz, $^3J_{PP} = 8.5$ Hz), δ −18.1 ppm (d, $^3J_{PP} = 8.5$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$) for **6**:[13a] δ 50.6 ppm (dd, $^1J_{WP} = 230.0$ Hz, $^3J_{PP} = 1.0$ Hz, $^2J_{PP} = 27.1$ Hz), δ 33.2 ppm (dd, $^1J_{WP} = 235$ Hz, $^3J_{PP} = 1.0$ Hz, $^3J_{PP} = 2.0$ Hz), δ −14.4 ppm (dd, $^3J_{PP} = 2.0$ Hz, $^2J_{PP} = 27.1$ Hz).

Synthesis of $(OC)_5W[P(p\text{-tol})_2H]$ and *cis*-$W(CO)_4[P(p\text{-tol})_2H]_2$. A solution containing $W(CO)_6$ (1.84 g, 5.23 mmol), $Me_3NO{\cdot}2H_2O$ (0.581 g, 5.23 mmol), $P(p\text{-tol})_2H$ (1.12 g, 5.23 mmol), and CH_2Cl_2 (50 mL) was stirred at room temperature for 72 h. The solvent was removed, and 80 mL of CH_2Cl_2/CH_3OH (1:3) was added to the residue followed by filtration to remove unreacted $W(CO)_6$. The filtrate was cooled to −5 °C, which gave a precipitate of 1.21 g of gray solid. Separation of products was achieved by eluting the sample on an alumina column (Brockman I deactivated with 5% water) with CH_2Cl_2/hexane (1:5). The first band was collected to yield 0.367 g (13.0%) of $(OC)_5WPPh_2(p\text{-tol})_2H$ (mp = 89−90 °C). IR (CH_2Cl_2), $A_1^1 + E = 1940$(s) cm^{-1}, $A_1^2 = 2074$(m) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ −15.5 ppm ($^1J_{WP} = 228$ Hz, $^1J_{PH} = 332$ Hz). Anal. Calcd for $C_{19}H_{15}O_5PW$: C, 42.41; H, 2.81. Found: C, 42.57; H, 2.88. From the second fraction *cis*-$W(CO)_4[P(p\text{-tol})_2H]_2$ was obtained (0.048 g, 2.5%; mp = 138−139 °C). IR (CH_2Cl_2): $A_1 = 2021$(m) cm^{-1}, $A_1 = 1916$(sh) cm^{-1}, $B_1 = 1903$(s) cm^{-1}, $B_2 = 1886$(sh) cm^{-1}. ^{31}P NMR ($CDCl_3$): δ −4.4 ppm ($^1J_{WP} = 224$ Hz, $^1J_{PH} = 337$ Hz). Anal. Calcd for $C_{32}H_{30}O_4P_2W$: C, 53.06; H, 4.17. Found: C, 52.90; H, 4.17. A trace of a third fraction, presumably *fac*-$W(CO)_3[P(p\text{-tol})_2H]_3$, was detected. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 4.6 ppm ($^1J_{WP} = 216$ Hz).

Synthesis of $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tol})_2]$, 3. A mixture of $(OC)_5WPPh_2CH{=}CH_2$ (3.0 g, 5.6 mmol), $P(p\text{-tol})_2H$ (1.1 g, 5.1 mmol), and 2,2′-azobisisobutyronitrile (AIBN) (0.13 g) was heated without solvent at 60° C for 24 h. Recrystallization of the crude product gave **3** (1.71 g, 44%) (mp = 112−115 °C). IR (CH_2Cl_2): $A_1^1 + E = 1937$(s) cm^{-1}, $A_1^2 = 2071$(m) cm^{-1}, $B_2 = 1981$(w) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.6 ppm (d, $^1J_{WP} = 239.3$ Hz, $^3J_{PP} = 37.6$ Hz), δ −13.7 ppm (d, $^3J_{PP} = 37.6$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta(CO)_{ax}$ 199.3 ppm (d, $^2J_{PC} = 21.4$ Hz, $^1J_{WC} = 143.7$ Hz), $\delta(CO)_{eq}$ 196.9 ppm (d, $^2J_{PC} = 6.46$ Hz, $^1J_{WC} = 125.6$ Hz). Anal. Calcd for $C_{33}H_{28}O_5P_2W$: C, 52.82; H, 3.76. Found: C, 52.64; H, 3.75.

Synthesis of $(OC)_5W[\eta^1\text{-}P(p\text{-tol})_2CH_2CH_2PPh_2]$, 4. A mixture of $(OC)_5W[P(p\text{-tol})_2H]$ (0.31 g, 0.57 mmol), $PPh_2CH{=}CH_2$ (0.15 mL, 0.66 mmol), and AIBN (0.12 g) without solvent was heated to 80 °C for 24 h. The crude reaction mixture was recrystallized from CH_2Cl_2/CH_3OH (3:1) to give 0.33 g of **6**, which was further purified chromatographically (Brockman I deactivated with 5% water) by eluting with a hexane/CH_2Cl_2 solution (1:3) (0.19 g, 44%). IR (CH_2Cl_2): $A_1^1 + E = 1936$(s) cm^{-1}, $A_1^2 = 2071$(m) cm^{-1}, $B_2 = 1981$(w) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.5 ppm (d, $^3J_{PP} = 38.0$ Hz, $^1J_{WP} = 238.4$ Hz), δ −12.0 ppm (d, $^3J_{PP} = 38.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta(CO)_{ax}$ 199.5 ppm (d, $^2J_{PC} = 20.9$ Hz, $^1J_{WC} = 143.7$ Hz); $\delta(CO)_{eq}$ 197.2 (d, $^2J_{PC} = 7.01$ Hz, $^1J_{WC} = 125.2$ Hz). Anal. Calcd for $C_{33}H_{28}O_5P_2W$: C, 52.82; H, 3.76. Found: C, 52.65; H, 3.64.

Equilibrium and Kinetics Measurements. A mixture of **1** and **2** (65.0 mg, 0.0717 mmol) and $CDCl_3$ (0.50 mL) was flame sealed under vacuum at liquid nitrogen temperature in an NMR tube, thawed, and thermostated in a constant-temperature bath at the appropriate temperature. The NMR probe was brought to the same temperature, and the $^{31}P\{^1H\}$ NMR spectrum was recorded. Meaningful spectral integrations were obtained by using a delay time of 15 s and a pulse sequence that gave ^1H decoupling but eliminated NOE effects on ^{31}P signal intensities. Integrations were carried out following standard procedures[15] in which the width at half-height was obtained for each signal and multiplied by ±31.8 to give an integral that included 99% of the intensity. Each spectrum was integrated four times, and the average value was used in subsequent calculations. Equilibrium was assumed to have been reached when the integral ratio of isomers remained unchanged after three consecutive runs spaced by several days. Equilibrium and kinetics experiments with **3** and **4** were carried out as described for **1** and **2**, except that pure **3** (20.0 mg, 0.0263 mmol) and pure **4** (20.0 mg, 0.0263 mmol) were placed in separate NMR tubes; thus, the equilibrium between **3** and **4** was approached from both directions starting with pure reactants.

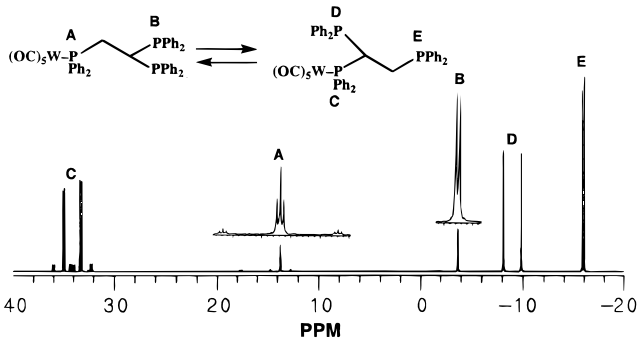


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of a $CDCl_3$ solution of **1** and **2** at 10 °C. Signals A and B belong to isomer **1**, while signals D, C, and E belong to **2**.

Table 1. Equilibrium Constants (*K*) for Isomerization of Linkage Isomers 1 ⇆ 2 and 3 ⇆ 4 in $CDCl_3$

temp (K)	*K*
1 ⇆ 2	
283	6.14 ± 0.04
298	4.74 ± 0.01
313	3.76 ± 0.05
328	3.01 ± 0.02
3 ⇆ 4	
328	1.62 ± 0.08

Results and Discussion

Thermodynamics. Equilibrium constants for reaction 1 were obtained from $^{31}P\{^1H\}$ NMR spectra of $CDCl_3$ solutions at 10, 25, 40, and 55 °C (Table 1). Phosphorus signals of the first-order spectra of **1** and **2** are well-separated, as shown in Figure 1, allowing straightforward integration. From a van't Hoff plot ($R^2 = 0.999\,86$), calculations of ΔH, ΔS, and ΔG (298 K) for the isomerization gave values of -12.25 ± 0.1 kJ mol^{-1}, -28.2 ± 0.3 J mol^{-1} K^{-1}, and -3.86 ± 0.14 kJ mol^{-1}, respectively.

Electronic considerations would lead us to believe that the basicities of the nonequivalent phosphorus groups of $(PPh_2)_2CHCH_2PPh_2$ are quite similar, as each phosphorus atom has two phenyl substituents and is separated from other phosphorus atoms by either one or two methylene groups. For example, the pK_a values of $Ph_2PCH_2CH_2PPh_2$ and $Ph_2CH_2PPh_2$ are 3.86 and 3.81,[16] respectively, and photoelectron spectroscopy studies show that $Me_2PCH_2CH_2PMe_2$ and $Me_2PCH_2PMe_2$ are electronically nearly identical in $LMo(CO)_5$ complexes.[17]

Interestingly, the more sterically congested end of the phosphine ligand is coordinated in the more stable

(15) Rabenstein, D. L.; Keire, D. A. In *Modern NMR Techniques and Their Application in Chemistry*; Popov, A. I., Hellenga, K., Eds.; Marcel Dekker: New York, 1991.

(16) Sowa, J. R., Jr.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 3534−3537.

(17) Lichtenberger, D. L.; Jatcko, M. E. *Inorg. Chem.* **1992**, *31*, 451−455.

complex, **2**. Furthermore, the decrease in entropy is far greater than can be rationalized on the basis of simple conformational changes. These intriguing thermodynamic results can be accounted for if one assumes that the short dangling phosphine which is separated from the coordinated phosphine by one carbon atom experiences some attractive interaction for the four equatorial carbonyl groups. Thus **2** may be stabilized by a van der Waals interaction between the short phosphine arm and the carbonyl groups. The latter interaction, which diminishes the mobility of the dangling arm, would also explain the large entropy decrease for the reaction (eq 1). As the temperature of the reaction is increased, isomer **1** gains in stability relative to isomer **2** (the equilibrium constant decreases), consistent with the breakdown of the weak phosphine−carbonyl interaction present in isomer **2** (but not in **1**) and with the favorable entropy increase for the reverse reaction. The origin of the weak interaction that exists between the dangling phosphine and the carbonyl groups is uncertain; it may be a forced consequence of the steric demands of a pentacarbonyltungsten and four phenyl groups in close proximity.

Although a single crystal of **2** has not been obtained, the molecular structure[18] of $(OC)_5W[\eta^1\text{-}PPh_2CH_2PPh_2]$, a complex similar to **2,** shows that the unshared pair of electrons of the dangling phosphine is tilted toward two of the equatorial carbonyl groups, bisecting the C−W−C angle and giving a phosphorus−carbon separation (3.55 Å) equal to the approximate sum of the van der Waals radii for C and P (3.50−3.55 Å).[19] Long-range phosphorus−carbon coupling is also observed for this molecule ($^4J_{PC}$ = 3.0 Hz, $CDCl_3$) and for **2**, suggesting that they have similar structures in solution. The $^{13}C\{^1H\}$ NMR spectrum of the equatorial carbonyl region of each consists of a doublet of doublets ($^4J_{PC}$ = 3.89 Hz for **2**), a pattern without precedent in $(OC)_5W$(phosphine) complexes.[20] The possibility of endo and exo isomers was considered but ruled out because neither the remainder of the $^{13}C\{^1H\}$ NMR or the $^{31}P\{^1H\}$ NMR spectra provided evidence for their existence. The possibility of two sets of nonequivalent CO groups resulting from restricted rotation about the W−P bond was also considered as an explanation for the four-line equatorial carbonyl C-13 patterns (two doublets rather than a doublet of doublets) but dismissed because $^{13}C\{^{31}P\}$ established the presence of long-range phosphorus−carbon coupling.[21] The close approach of the phosphine to the equatorial carbonyl groups, as shown by the structure of $(OC)_5W[\eta^1\text{-}PPh_2CH_2PPh_2]$, would not allow space for an intervening solvent molecule. Five-bond phosphorus−carbon coupling involving the longer phosphine arm present in **1** or **2** is not observed. Similarly no long-range phosphorus−carbon coupling is observed in complexes **3** and **4,** neither of which contains a short phosphine arm.

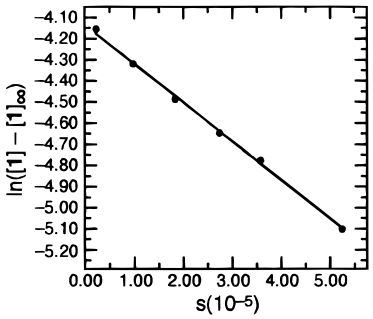


Figure 2. Plot of ln([**1**] − [$\mathbf{1}_\infty$]) vs time for the reaction, **1** ⇄ **2**, at 10 °C in $CDCl_3$.

The possibility of "through-space" coupling between the short dangling phosphine arm in **2** was considered because it seemed unlikely that coupling would be observed through four bonds, a 90° angle, and a transition metal atom.[22] Also, long-range phosphorus coupling to the axial carbonyl ligand was not observed even though it would be expected to be larger than coupling to equatorial carbonyl groups. The infrared spectrum of **2** in the carbonyl region, however, is consistent with C_{4v} symmetry, implying that any interaction that exists between the dangling phosphine of **2** and its equatorial carbonyl groups is not localized. Furthermore, the carbonyl spectra of **1** and **2** are identical within experimental error, suggesting that any interaction that exists in **2** must be rather weak. It has been noted, however, that vibrational spectroscopy is not very sensitive to small electronic differences in $LW(CO)_5$ (L = $PMe_n\text{-}Ph_{3-n}$).[20b] The observed long-range coupling may arise from a particularly favorable conformational arrangement of the dppm ligand or from a through-space interaction or a combination of both.

Linkage isomers **3** and **4** are easily distinguished from one another with phosphorus-31 NMR spectroscopy, the former having a coordinated phosphine chemical shift lying over 2 ppm downfield and a dangling phosphine chemical shift lying nearly 2 ppm upfield from the corresponding signals in the latter. Because isomers **3** and **4** move to equilibrium extremely slowly, even at 55 °C, time requirements made it impractical to obtain *K* at lower temperatures. Isomer **4** is thermodynamically more stable than **3**, in agreement with our expectation that coordination of the more basic ditolylphosphino end of $Ph_2PCH_2CH_2P(p\text{-tol})_2$ will lead to a more stable complex in solution than coordination of the isosteric diphenylphosphino group.[23]

Kinetics. Rate constants and half-lives to equilibrium for reactions 1 (10, 25, and 40 °C) and 2 (55 °C) are shown in Table 2. A plot of ln{[**1**] − [$\mathbf{1}_8$]} vs *t* at 10

(18) Benson, J. W.; Keiter, R. L.; Keiter, E. A.; Rheingold, A. L.; Yap, G. P. A.; Mainz, V. V. *Organometallics*, in press.

(19) Huheey, J. E.; Keiter, R. L.; Keiter, E. A. *Inorganic Chemistry*, 4th ed.; HarperCollins: New York, 1993.

(20) (a) Nelson, J. H. *Coord. Chem. Rev.* **1995**, *139*, 245−280. (b) Bancroft, G. M.; Dignard-Bailey, L.; Puddephatt, R. J. *Inorg. Chem.* **1986**, 25, 3675−3680. (c) Buchner, W.; Schenk, W. A. *Inorg.* Chem. **1984**, *23*, 132−137. (d) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951−1958. (e) Inubushi, Y.; Huy, N. H. T.; Mathey, F. *Chem. Commun.* **1996**, 1903−1904. (f) Streubel, R.; Kusenberg, A.; Jeske, J.; Jones, P. G. *Angew. Chem.* **1994**, *33*, 2427−2428. (g) Huang, J.-T.; Chand, P.; Fronczek, F. R.; Watkins, S.F.; Lammertsma, K. *Organometallics* **1993**, *12*, 1401−1405.

(21) The $^{13}C\{^{31}P\}$ NMR spectrum was provided by Vera Mainz of the Varian Oxford Instrument Center for Excellence in NMR Laboratory at the University of Illinois at Urbana.

(22) (a) Holmes, R. R.; Prakasha, T. K.; Pastor, S. D. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkade, J. G., Eds.; VCH: New York, 1994. (b) Mathey, F.; Mercier, F.; Nief, F.; Fischer, J.; Mitschler, A. *J. Am. Chem.* Soc. **1982**, *104*, 2077. (c) Pastor, S. D.; Shum, S. P.; DeBellis, A. D.; Burke, L. P.; Rodebaugh, R. K.; Clarke, F. H.; Rihs, G. *Inorg. Chem.* **1996**, *35*, 949. (d) Szalontai, G.; Bakos, J.; Toth, I.; Heil, B. *Magn. Reson. Chem.* **1987**, *25*, 761. Günther, H. *NMR Spectroscopy*, 2nd ed.; John Wiley: New York, 1995; p 129.

(23) Li, C.; Nolan, S. P. *Organometallics* **1995**, *14*, 1327−1332.

Table 2. Rate Constants for Isomerization of Linkage Isomers, 1, 2, 3, and 4 and for the Chelation of 1 and 2 in ($CDCl_3$)

temp (K)	k_1 (s^{-1})	k_{-1} (s^{-1})	ln 2/($k_1 + k_{-1}$)
	1 ⇆ 2		
283	$(1.60 \pm 0.04) \times 10^{-6}$	$(2.61 \pm 0.06) \times 10^{-7}$	4.31 days
298	$(1.18 \pm 0.01) \times 10^{-5}$	$(2.50 \pm 0.01) \times 10^{-6}$	13.5 h
313	$(7.95 \pm 0.3) \times 10^{-5}$	$(2.11 \pm 0.1) \times 10^{-5}$	2.4 h
	3 ⇆ 4		
328	$(2.03 \pm 0.06) \times 10^{-8}$	$(1.25 \pm 0.06) \times 10^{-8}$	245 days
	1 → 5 + CO		
328	$(1.29 \pm 0.03) \times 10^{-6}$		
	1 + 2 → 6 + CO		
328	$(1.35 \pm 0.1) \times 10^{-6}$		

Table 3. Activation Parameters for Isomerization of Linkage Isomers 1 ⇆ 2

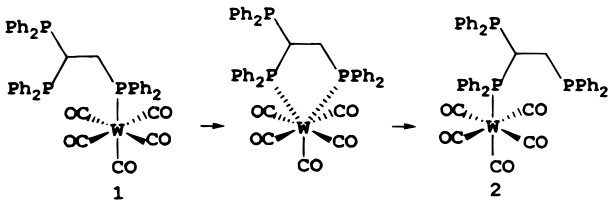
$\Delta H^{\ddagger}$(forward) = 92.6 ± 1.9 kJ mol^{-1}
$\Delta S^{\ddagger}$(forward) = −28.2 ± 6.2 J mol^{-1} K^{-1}
$\Delta G^{\ddagger}_{298}$(forward) = 101.0 ± 2.6 kJ mol^{-1}
E_a(forward) = 95.3 ± 1.8 kJ mol^{-1}
$\Delta H^{\ddagger}$(reverse) = 104.5 ± 1.8 kJ mol^{-1}
$\Delta S^{\ddagger}$(reverse) = −1.0 ± 6 J mol^{-1} K^{-1}
$\Delta G^{\ddagger}_{298}$(reverse) = 104.8 ± 2.5 kJ mol^{-1}
E_a(reverse) = 107.0 ± 1.6 kJ mol^{-1}

°C is shown in Figure 2. Activation parameters, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}_{298}$, for both forward and reverse directions of eq 1 as obtained from Eyring plots, are given in Table 3. It was not possible to determine k for reaction 1 at 55 °C with phosphorus-31 NMR because the reaction proceeds too quickly, relative to the time required for signal accumulation, to allow direct determination, but not fast enough to be determined by ^{31}P 2D-EXSY experiments.[24] However, the calculated k_{for} (3.7×10^{-4} s^{-1}) at that temperature is 4 orders of magnitude faster than k_{for} (3.3×10^{-8} s^{-1}) for reaction 2.

Many studies have confirmed the expectation that d^6 low-spin complexes will be substitutionally inert.[25] For example, the dissociative rate constant (k_1) for CO substitution by phosphines in $W(CO)_6$ at 30 °C is 1×10^{-14} s^{-1}.[26] The reverse reactions in which phosphines are replaced by CO have received much less attention.[27] The rate constant for PPh_3 dissociation from $(OC)_5CrPPh_3$ is 3×10^{-11} s^{-1} at 30 °C,[27a] about 6 orders of magnitude slower than the rate of isomerization in reaction 1. Phosphine dissociation for tungsten carbonyl complexes would be expected to be even slower than for chromium complexes if generally observed trends are followed.[28]

Reaction Mechanisms. Most transition metal carbonyl complexes undergo substitution by ligand dissociation.[29] Notable exceptions include associative mechanisms involving nitrosyl (linear to bent) or cyclopentadienyl (η^5 to η^3) complexes in which the ligands change hapticity during the course of the reaction. As in these cases, a dissociative (D) mechanism for reaction 1 may be ruled out for several reasons: (1) the rate of the reaction is much faster than the rate of phosphine exchange in similar $LM(CO)_5$ complexes, as indicated in the previous section,[27] and enthalpies of activation for both forward and reverse reactions are much smaller than expected for a D mechanism.[27a] Values for the forward and reverse reactions are 93 and 105 kJ mol^{-1}, respectively. Hoff and Nolan have shown that for a series of phosphines in $L_3M(CO)_3$ complexes the W−P bond energy is 1.48 times the Cr−P bond energy.[30] Assuming that a similar ratio exists in $LM(CO)_5$ complexes and using the Cr−P bond energy reported for $(OC)_5CrPPh_3$ (151 kJ mol^{-1}),[27a] a W−P bond energy of about 223 kJ mol^{-1} is predicted, much larger than our observed activation enthalpies. (2) When the reaction is carried out in the presence of a 5-fold excess of PPh_3, no $(OC)_5WPPh_3$ is formed, indicating that a vacant coordination site does not become available during phosphine exchange. (3) The isomerization takes place without the formation of phosphine-bridged complexes such as $(OC)_5W[\mu\text{-}PPh_2CH_2CH(PPh_2)PPh_2]W(CO)_5$, also arguing against the availability of a coordination site to an external ligand.

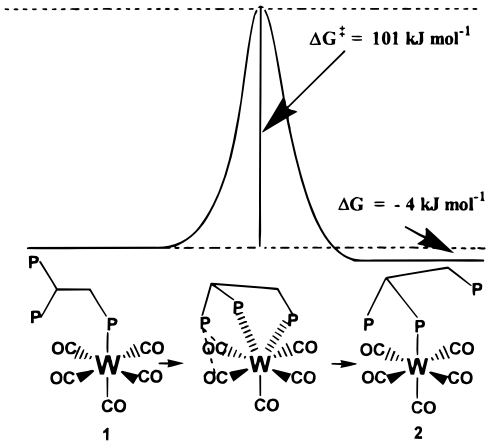
Scheme 1



Abel and co-workers have examined a number of fluxional dithioether complexes, $(OC)_5W(\eta^1\text{-}RSCH_2SR)$ (R = alkyl), with variable-temperature proton NMR spectroscopy and have proposed a pseudo-seven-coordinate transition state for the observed 1,3-metal sulfur shift.[31] It would appear that to a first approximation reaction 1 requires a similar transition state, one involving a 1,4-metal phosphorus shift (Scheme 1). In our view, however, a simple associative (A) mechanism does not satisfactorily explain why reaction 1 is 4 orders of magnitude faster than reaction 2. In both reactions the exchange that takes place involves diphenylphosphino groups separated by two carbon atoms and the exchanging phosphines would be expected to be electronically very similar. The large difference in rates of isomerization for reactions 1 and 2 must in some manner depend on the presence of the short CH_2PPh_2 arm in reaction 1. A modification of the transition state in Scheme 1, as shown in Scheme 2, nicely accounts for the observed results. The weakening of the existing W−P bond and the formation of the new W−P bond are accompanied by the onset of an interaction between the

(24) Orrell, K. G.; Sik, V.; Stephenson, D. *Prog. Nucl. Magn. Reson. Spectrosc.* **1990**, 22, 141.
(25) (a) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH: New York, 1991. (b) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, 1985. (c) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; John Wiley: New York, 1967.
(26) (a) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160−3166. (b) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366−373.
(27) Darensbourg, D. J. Graves, A. H. *Inorg. Chem*. **1979**, *18*, 1257−1261. Yang, G. K.; Peters, K. S.; Vaida, V. *Chem. Phys. Lett*. **1986**, *125*, 566.
(28) Kirtley, S. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982.
(29) (a) Basolo, F. *Polyhedron* **1990**, *13*, 1503−1535. (b) Darensbourg, D. J. *Adv. Organomet. Chem*. **1982**, *21*, 113−150.
(30) Mukerjee, S. L.; Lang, R. F.; Ju, T.; Kiss, G.; Hoff, C. D.; Nolan, S. P. *Inorg. Chem*. **1992**, *31*, 4885−4889.
(31) Abel, E. W.; Blackwall, E. S.; Orrell, K. G.; Sik, V. *J. Organomet. Chem*. **1994**, *464*, 163−170.

Scheme 2



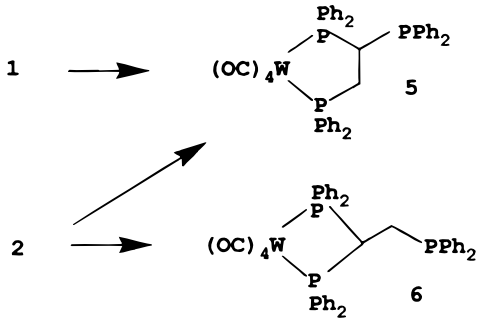
equatorial carbonyl groups and the dangling CH_2PPh_2. The large decrease in entropy for the forward activation step ($\Delta S^{\ddagger}_{for} = -28.2$ J mol^{-1} K^{-1}) is consistent with an interaction involving all three associated arms in the transition state. When the reverse reaction takes place, however, as the new W−P bond forms, the weak dangling phosphine−carbonyl interaction diminishes in strength, as does the existing W−P bond. The combination of two interactions decreasing while a third is increasing leads to opposing entropy changes which nearly nullify each other ($\Delta S^{\ddagger}_{rev} = -1.0$ J mol^{-1} K^{-1}).

There are a number of examples in the literature in which the interaction of an approaching nucleophile with coordinated CO accelerates the rate of ligand substitution. For example, Basolo has shown that CO substitution by $AsPh_3$ in $Fe(CO)_2(NO)_2$ is catalyzed by a variety of bases [R_4NX (X = Cl, Br, I, N_3), NaOMe, pyrrolidine].[29a] Similarly, Darensbourg's studies have shown that ligand substitution in $M(CO)_6$ (M = Cr, Mo, W) is catalyzed by OH^-.[29b] In each example acceleration is believed to occur because of a transient interaction between the base and coordinated CO, which in turn leads to labilization of carbonyl groups. Furthermore, it is well-known that substitution rates in metal carbonyls are greatly influenced by the nature of ligands cis to the ligand that is replaced.[26] The transition state in these substitution reactions is stabilized by the presence of cis ligands that are π donors.[32] We are suggesting a neighboring group cis labilization effect in which the transition state is stabilized by an interaction between the short dangling phosphine and the cis carbonyl groups.

Rate constants for reaction 2 at 55 °C in $CDCl_3$ are 2.03×10^{-8} and 1.25×10^{-8} s^{-1} for the forward and reverse reactions, respectively, about 4 orders of magnitude slower than for reaction 1. The mechanistic model presented in Scheme 2 requires the existence of an exchange-accelerating short phosphine arm not found in isomers **3** and **4**. Isomerization rates for reaction 2, although an order of magnitude faster than PPh_3 dissociation from $(OC)_5CrPPh_3$ ($k_{calc} = 2.9 \times 10^{-9}$ s^{-1}), do not clearly distinguish between an A, I_A, or I_D mechanism, although the slowness of the reaction suggests a significant dissociative component.

If phosphine exchange in **1** and **2** is accelerated by the presence of a dangling phosphine, it would be expected that rate acceleration would also be observed for CO substitution. Loss of CO by either isomer would result in the formation of a chelated complex. Only one product, **5,** is possible when isomer **1** undergoes chelation, but two products, **5** and **6**, result when **2** loses CO (Scheme 3). Within the temperature range used for the phosphine exchange experiments (10−40 °C), chelation was too slow to monitor in practical time periods. At 55 °C, however, it was possible to obtain k_{obs} for the irreversible formation of both **5** and **6** (Table 2). Comparison with chelation rates from previous studies substantiates that **1** and **2** undergo chelation much faster than expected. Kinetic studies of chelation of $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH_2PPh_2]$ at 123, 134, and 150 °C[6b,33] allow calculation of k at 55 °C to give a direct comparison with chelation rates for **1** and **2**. A value of 3×10^{-10} s^{-1} is obtained, which is about 6 orders of magnitude slower than chelation of **1** and **2**. Isomers **3** and **4** undergo chelation so slowly that chelated products were seen only in trace concentrations even after several hundred days. It was not possible to extract meaningful rate constants from these baseline concentrations. However, as we were able to measure phosphine exchange rates of **3** and **4** as described earlier, we can say with certainty that chelation is much slower than exchange and that k_{obs} for chelation of **3** and **4** is at least an order of magnitude smaller than 10^{-8} s^{-1}. Thus, chelation rates as well as phosphine exchange rates are much faster in **1** and **2** than in **3** and **4**, leading us to conclude that the presence of the short phosphine arm in reaction 1 accelerates both phosphine and carbonyl replacement.

Scheme 3



Conclusions

In this work we have found that the rate of exchange of coordinated and terminal phosphines in $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH(PPh_2)_2]$ is 4 orders of magnitude faster than the rate of exchange in $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tol})_2]$, a striking result when one considers the electronic similarities of the two phosphorus ligands. Chelation rates for the two complexes also differ by at least 4 orders of magnitude but are significantly slower in each than the rate of phosphine exchange. We believe that phosphine exchange in $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH(PPh_2)_2]$ proceeds primarily by an associative mechanism in which the transition state exhibits three phosphine interactions, one in which the reactant W−P bond is weakening, one in which the incoming dangling

(32) Darensbourg, D. J.; Joyce, J. A.; Bischoff, C. J.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 1137.

(33) Connor, J. A.; Riley, P. I. *J. Organomet. Chem.* **1975**, *94*, 55−60.

phosphine is interacting with tungsten to form a new bond, and one in which the short arm experiences an interaction with the equatorial carbonyl groups. The latter interaction may help to stabilize the product isomer, $(OC)_5W[\eta^1\text{-}PPh_2CH(PPh_2)PPh_2]$, and help account for the large decrease in entropy associated with the isomerization, as well as the long-range coupling between the short arm and the equatorial carbonyl groups. We believe that the acceleration of the reaction occurs because the interaction of the dangling phosphine arm with a carbonyl ligand in the transition state leads to a weakening (cis labilization) of the metal−phosphorus bond, allowing the other dangling phosphine arm to displace the coordinated phosphine. The isomerization of $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tol})_2]$, lacking an accelerating arm, proceeds at the expected slower pace. These results suggest that complex reactivity may be greatly influenced by the extent to which R groups of a bound ligand can interact with other ligands of the complex. The principles involved should be applicable to a wide range of organometallic reactions and have important catalytic implications.

Acknowledgment. We thank the Camille and Henry Dreyfus Foundation for a Scholar/Fellow grant, and the National Science Foundation (CHE-9708342 and CHE 8851619) for support of this work and for the purchase of a General Electric QE300 NMR spectrometer. D.M.O. is the recipient of a Council on Undergraduate Research AIURP Fellowship sponsored by Eli Lilly and Co.

OM980289H