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Isomerization and Chelation Studies of $(OC)_5M[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$ and $(OC)_5M[\eta^1\text{-}P(p\text{-tolyl})_2CH_2CH_2PPh_2]$ (M = Cr, Mo, W)

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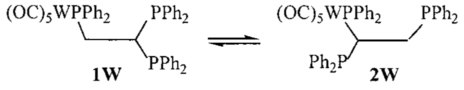
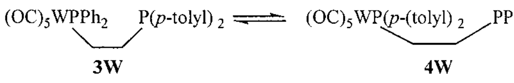
Six dangling phosphine complexes have been synthesized to provide three pairs of linkage isomers, $(OC)_5M[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$ (**3Cr**, **3Mo**, **3W**) and $(OC)_5M[\eta^1\text{-}P(p\text{-tolyl})_2CH_2CH_2PPh_2]$ **(4Cr**, **4Mo**, **4W).** Rate constants for isomerization in toluene of **3Cr**, **3Mo**, **3W**, **4Cr**, **4Mo**, and **4W** at 55 °C are 1.23×10^{-8}, 7.76×10^{-6}, 2.3×10^{-8}, 6.52×10^{-9}, 4.24×10^{-6}, and 9.7×10^{-9} s^{-1}, respectively. Rate constants for chelation of **3Cr**, **3Mo**, **4Cr**, and **4Mo** are 1.15×10^{-8}, 3.9×10^{-7}, 1.23×10^{-8}, and 3.9×10^{-7} s^{-1}, respectively. Chelation rates for **3W** and **4W** were too slow to conveniently measure. The position of equilibrium favors ditolylphosphino coordination with equilibrium constants of 1.88, 1.83, and 2.4 for the Cr, Mo, and W isomer pairs, respectively. Isomerization of **3Mo** and **4Mo** was studied at 25, 40, and 55 °C to give activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, of 102.4 and 103.6 kJ/mol and −32 and −33 J/(K mol), respectively. $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for chelation of **3Mo** and **4Mo** were determined to be 113.5 and 115.5 kJ/mol and −22 and −16 J/(K mol), respectively. These results suggest that the transition states for both isomerization and chelation are significantly associative and become more so in descending order through group 6.

Introduction

It has been a long-held assumption that exchange of coordinated and uncoordinated phosphines in dangling ligand complexes, $M(CO)_5(\eta^1\text{-L-L})$ (M = Cr, Mo, W; L-L = polydentate phosphine), is so slow as to be insignificant at modest temperatures. It was reasoned that stability with respect to chelation implied stability with respect to phosphine exchange as well. In 1994, however, we reported evidence that the rate of phosphorus exchange in $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH(PPh_2)_2]$ **1W** in chloroform is much faster than expected and significantly faster than chelation.[1] In fact, exchange could be monitored conveniently even below room temperature (reaction 1). Subsequently, quantitative kinetic and thermodynamic results were reported, from which it was concluded that the reaction proceeds essentially by an associative mechanism involving a quasi-seven-coordinate activated complex, perhaps stabilized by an interaction between the short phosphine arm and the equatorial carbonyl groups on tungsten.[2] The isomerization of $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$ (reaction 2) was also shown to be faster than chelation, but both processes proceed very slowly in comparison to reaction 1.



(1)



(2)

These results are intriguing because the phosphorus ligands of reactions 1 and 2 are electronically and sterically similar, and the exchanging phosphorus groups in both reactions are separated by two-carbon units. It is apparent, therefore, that the factors that influence the rate of phosphine exchange are rather subtle. To further understand the nature of phosphorus exchange in carbonyl complexes, we have now prepared the six $(OC)_5M[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$ and $(OC)_5M[\eta^1\text{-}P(p\text{-tolyl})_2CH_2CH_2PPh_2]$ (M = Cr, Mo, W) complexes in pure form and studied their rates of isomerization and chelation in toluene.

Results and Discussion

Syntheses. Two general approaches can be imagined for the preparation of a linkage isomer of a unidentate phosphine complex such as $(OC)_5M[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2)]$. One could begin with the free ligand, $Ph_2PCH_2CH_2P(p\text{-tolyl})_2$, and use it to displace a neutral or anionic leaving group from $(OC)_5ML$ (e.g., L = amine, THF, Me_3NO, halide, MeCN).[3] This method has the disadvantage of producing a mixture of both linkage

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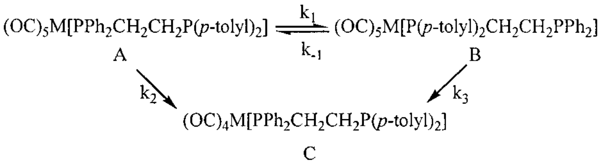
Scheme 1



isomers and requiring a difficult separation. The second, and preferred, approach allows one to selectively prepare the linkage isomer of choice. Rather than starting with the intact phosphine ligand, one builds the ligand of interest from coordinated phosphine fragments with vinyl addition reactions.

Symmetrical polyphosphines such as $Ph_2PCH_2CH_2PPh_2$ were first used in the early 1960s,[4] but within a few years unsymmetrical ligands (e.g., $Ph_2PCH_2CH_2PR_2$) were sought. Success was realized with the discovery that PR_2H could be added to $Ph_2PCH{=}CH_2$.[3d,5] However, it was not until the late 1970s that it became apparent that synthetic selectivity of dangling phosphine complexes could be achieved by coordinating vinyl or secondary phosphines *prior to addition*.[6] This was the approach used to prepare complexes **3** and **4** (M = Cr, Mo, W).

$$(CO)_5M[PPh_2CH{=}CH_2] + P(p\text{-tolyl})_2H \rightarrow (CO)_5M[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2] \quad (3)$$

3Cr,**3Mo**,**3W**

$$(OC)_5M[P(p\text{-tolyl})_2H] + PPh_2CH{=}CH_2 \rightarrow (OC)_5M[\eta^1\text{-}P(p\text{-tolyl})_2CH_2CH_2PPh_2] \quad (4)$$

4Cr,**4Mo**,**4W**

The reactions were free radical initiated (AIBN) and carried out in the absence of a solvent.[6a,7] The chromium and tungsten complexes **3Cr**, **4Cr**, **3W**, and **4W** isomerize and undergo chelation very slowly and can be subjected to temperatures of 80 °C for 24 h with little decomposition. Consistent with other reported work,[8] however, the molybdenum complexes, **3Mo** and **4Mo**, are much more reactive than those of chromium or tungsten, and as a result much milder conditions and shorter reaction times are needed to avoid chelation.

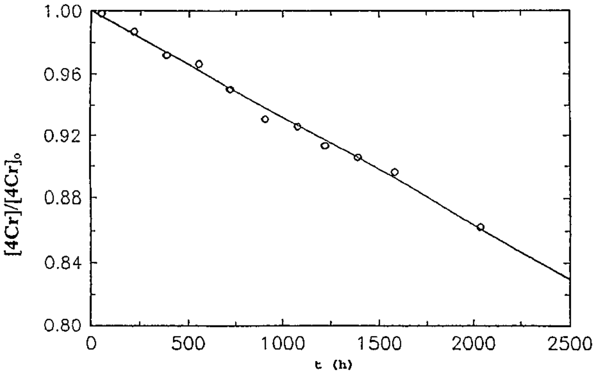


Figure 1. Plot of [**4Cr**]/[**4Cr**]$_0$ versus time at 55 °C in $C_6D_5CD_3$.

Kinetics and Thermodynamics. For each linkage isomer, isomerization and chelation are in competition (Scheme 1). The reactions for the chromium and tungsten complexes were exceedingly slow, and determination of their rate constants was not straightforward. Equilibrium was approached from both directions at 55 °C in $CD_3C_6D_5$ (and previously in $CDCl_3$ for **3W** and **4W**[2]), but even after months equilibrium had not been established. The rate equations, which can be solved by literature methods,[9] may be expressed as

$$d[A]/dt = -(k_1 + k_2)[A] + k_{-1}[B] \quad (5)$$

$$d[B]/dt = k_1[A] - (k_{-1} + k_3)[B] \quad (6)$$

$$d[C]/dt = k_2[A] + k_3[B] \quad (7)$$

The exact solutions to these equations are quite complex, but simplification is possible if $t \ll 1/(k_1 + k_2)$. Under these conditions, if one starts with pure A, the relationships between concentration and time can be approximated as

$$[A]/[A]_0 = 1 - (k_1 + k_2)t \quad (8)$$

$$[B]/[A]_0 = k_1 t \quad (9)$$

$$[C]/[A]_0 = k_2 t \quad (10)$$

It is possible, therefore, to obtain k_1 and k_2 from slopes that result by plotting concentration ratios versus time.

If one starts with pure B, an analogous set of equations results, from which one can extract k_{-1} and k_3:

$$[B]/[B]_0 = 1 - (k_{-1} + k_3)t \quad (11)$$

$$[A]/[B]_0 = k_{-1} t \quad (12)$$

$$[C]/[B]_0 = k_3 t \quad (13)$$

Thus, it becomes possible to obtain all four rate constants if both pure A and pure B are available, allowing the equilibrium to be approached from both directions. Plots for **4Cr** are shown in Figures 1 and 2. Isomerizations of the molybdenum complexes were much faster

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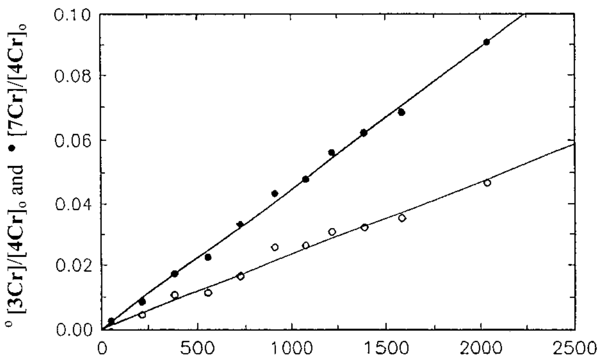

Figure 2. Plots of [**3Cr**]/[**4Cr**]$_0$ (○) and [**7Cr**]/[**4Cr**]$_0$ (●) versus time.

Table 1. Kinetic and Equilibrium Data for Isomerization and Chelation of (OC)$_5$M[η^1-PPh$_2$CH$_2$CH$_2$P(p-tolyl)$_2$] in CD$_3$C$_6$D$_5$

complex	T, K	10^8k_1 (s^{-1})	10^8k_{-1} (s^{-1})	10^8k_2 (s^{-1})	10^8k_3 (s^{-1})	K_{eq}
3Cr ⇄ **4Cr**	328	1.23(4)	0.652(3)	1.15(3)	1.23(2)	1.88(5)[a]
3W ⇄ **4W**	328	2.3(1)	0.97(5)	*b*	*b*	2.4(2)[a]
3Mo ⇄ **4Mo**	328	776(4)	424(4)	39(6)	39(6)	1.83(4)[c]
3Mo ⇄ **4Mo**	313	120(3)	64.8(3)	5.89(8)	5.53(8)	1.86(3)[c]
3Mo ⇄ **4Mo**	298	16.1(3)	8.4(3)	0.54(3)	0.50(3)	1.91(4)[c]

[a] K determined from ratio of rate constants, k_1/k_{-1}. [b] Only a trace of chelated product was present after 100 days. [c] Equilbrium constants are average results from approaching the equilibrium from both directions and were determined directly by monitoring the product/reactant ratio until there was no further change.

than those of chromium and tungsten, and as equilibrium concentrations could be measured directly, there was no need to employ the $t \ll 1/(k_1 + k_2)$ approximation. Results are presented in Table 1.

Few studies have been carried out in which the rate of substitution of the phosphine ligand in (OC)$_5$M(PR$_3$) has been measured. Substitution of PPh$_3$ by CO in (OC)$_5$Cr(PPh$_3$) has been reported and shown to proceed very slowly, as expected for a d^6 low-spin complex.[10] The first-order rate constant for dissociation of PPh$_3$ at 55 °C (obtained by extrapolation) is 3×10^{-9} s^{-1}, about an order of magnitude slower than the isomerization of **3Cr** and about half as fast as the isomerization of **4Cr.** The faster rates of substitution for isomerization of **3Cr** and **4Cr** suggest that these reactions may be more associative than displacement of PPh$_3$ by CO. It is also noted that isomerization **3W** ⇄ **4W** is somewhat faster than **3Cr** ⇄ **4Cr.** If the isomerization processes were strictly dissociative, it might be expected that the smaller Cr atom in **3Cr** and **4Cr** and the expected greater M−P bond energy for **3W** and **4W** would lead to the opposite result. It would appear that the associative contribution to the mechanism of exchange plays a significant role and becomes more important in descending order within group 6. The much faster rates of isomerization of **1W** and **2W**, however, in comparison to those of **3Cr**, **4Cr**, **3W**, and **4W** lead us to continue to believe that the second phosphine arm present in the former complexes plays a role in their transition states.

Many studies have confirmed that second-row metal carbonyls are much more reactive than those of the first or third row. For example, k_{obs} values for the reactions of Mo(CO)$_6$, Cr(CO)$_6$, and W(CO)$_6$ with P(OEt)$_3$ at 130 °C are 2.0×10^{-3}, 1.4×10^{-4}, and 4.0×10^{-6} s^{-1}, respectively.[8] Thus, it is expected that **3Mo** and **4Mo** will undergo isomerization and chelation much faster than their chromium and tungsten analogues. As can be seen from the data, the half-lives to equilibrium ($0.693/(k_1 + k_{-1})$) for isomerization of the chromium, molybdenum, and tungsten complexes at 55 °C are 3.7×10^7 s (428 days), 5.8×10^4 s (0.67 days), and 2.1×10^7 s (243 days), respectively.

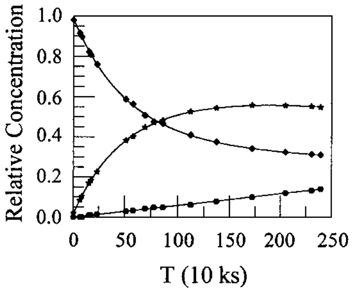

Figure 3. Plots of concentration versus time: (◆) disappearance of (OC)$_5$Mo[η^1-PPh$_2$CH$_2$CH$_2$P(p-tolyl)$_2$] (**3Mo**); (★) appearance of (OC)$_5$Mo[η^1-P(p-tolyl)$_2$CH$_2$CH$_2$PPh$_2$] (**4Mo**); (●) appearance of (OC)$_4$Mo[η^2-PPh$_2$CH$_2$CH$_2$P(p-tolyl)$_2$] (**7Mo**).

Early chelation studies of (OC)$_5$Cr[η^1-PPh$_2$CH$_2$CH$_2$PPh$_2$] and (OC)$_5$W[η^1-PPh$_2$CH$_2$CH$_2$PPh$_2$] were interpreted in terms of a concerted mechanism: i.e., one in which stretching of the M−CO bond is accompanied by metal−phosphorus bond formation.[3b] The rate constants (extrapolated) from these studies for the formation of (OC)$_4$Cr[η^2-PPh$_2$CH$_2$CH$_2$PPh$_2$] and (OC)$_4$W[η^2-PPh$_2$CH$_2$CH$_2$PPh$_2$] at 55 °C in octane are 5×10^{-8} and 5×10^{-9} s^{-1}, respectively, remarkably close to the k values found for the chelation of the chromium complexes **3Cr** ($k_2 = 1.15 \times 10^{-8}$ s^{-1}) and **4Cr** ($k_3 = 1.23 \times 10^{-8}$ s^{-1}) and consistent with our inability to measure the rate of chelation of the tungsten complexes **3W** and **4W** over the time period of investigation. Both of the isomerizations **3Mo** ⇄ **4Mo** and **3W** ⇄ **4W** are significantly faster than chelation. However, the rate of chelation of the chromium complexes, **3Cr** and **4Cr**, is competitive with the rate of isomerization.

The faster rates of isomerization and chelation of the molybdenum complexes allowed their kinetic parameters to be measured at room temperature, which made it possible to conduct variable-temperature studies within a temperature range that minimized hazards associated with following a gas-evolving process in a sealed NMR tube. In addition, the faster reaction allowed the equilibrium concentrations of the two isomers, **3Mo** and **4Mo**, to be determined directly, something that was not possible for the chromium or tungsten isomers. Figures 3 and 4 show concentration versus time plots of isomerization and chelation at 40 °C for **3Mo** and **4Mo**, respectively. Rate constants and the measured equilibrium constants are reported in Table 1.

The equilibrium constants show that linkage isomers with coordinated ditolylphosphino groups are more stable than those with coordinated diphenylphosphino groups (Table 1). A plot of ln K versus $1/T$ provides values for ΔH and ΔS. The reaction, **3Mo** ⇄ **4Mo**, is slightly exothermic ($\Delta H = -1.2(1)$ kJ/mol). Thermody-

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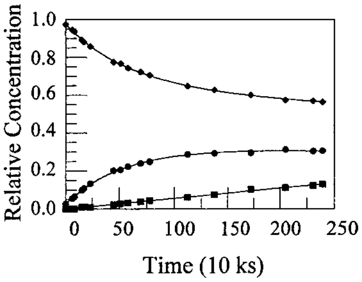

Figure 4. Plots of concentration versus time: (◆) disappearance of $(OC)_5Mo[\eta^1\text{-}P(p\text{-tolyl})_2CH_2CH_2PPh_2]$ (**4Mo**); (●) appearance of $(OC)_5Mo[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$ (**3Mo**); (■) appearance of $(OC)_4Mo[\eta^2\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$ (**7Mo**).

namic comparisons of M−PPh$_3$ with M−P(*p*-tolyl)$_3$ show that formation of complexes of PPh$_3$ is less exothermic than formation of complexes of P(*p*-tolyl)$_3$. For example, replacing PPh$_3$ with P(*p*-tolyl)$_3$ in $Fe(CO)_3(PR_3)_2$ leads to a release of 5.4 kJ/mol of energy, or an average of 2.7 kJ/mol per ligand,[11] and protonation of P(*p*-tolyl)$_3$ is more exothermic than protonation of PPh$_3$ by 8.4 kJ/mol.[12] Our isomerization reaction is accompanied by only a very small increase in entropy ($\Delta S = 1.5(4)$ J/K mol), showing that the difference in disorder for the two isomers in solution is very small. As shown in Table 1, the equilibrium constant for isomerization of the molybdenum complexes is not very temperature-dependent, as expected for a reaction for which ΔH and ΔS are small.

The activation enthalpies, $\Delta H^{\ddagger}$, for the isomerization **3Mo** ⇄ **4Mo** were found to be 102.4(6) kJ/mol for the forward reaction and 103.6(3) kJ/mol for the reverse. The difference between the two numbers (−1.3 kJ/mol) is in good agreement with ΔH for the reaction (−1.2 kJ/mol). Likewise, the values of $\Delta S^{\ddagger}$, −32(2) J/(K mol) for the forward reaction and −33(1) J/(K mol) for the reverse reaction, are in agreement with ΔS for the reaction (1.5 J/(K mol)).

The enthalpies of activation are considerably less than the average M−P bond dissociation energies reported for $Mo(CO)_3(PPh_2Me)_3$ (147 kJ/mol) and $Mo(CO)_4(PPh_2Me)_2$ (158 kJ/mol), supporting a mechanism with a significant associative contribution.[13] The entropies of activation for both the forward and reverse isomerization reactions are significantly negative and also strongly suggest a mechanism in which there is significant association in the transition state. Thus, it appears that both reactions 1 and 2 proceed by interchange mechanisms but, as postulated earlier, the former reaction is accelerated by the presence of a labilizing short phosphine arm.[2]

The rates of chelation of **3Mo** and **4Mo** (Table 1) were nearly identical for each of the three temperatures reported. Activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, for chelation of **3Mo** were 113.5(5) kJ/mol and −22(15) J/(K mol), respectively, while for **4Mo** they were 115.5(4) kJ/mol and −16(12) J/(K mol), suggesting a transition state in which bond making is important. The M−CO dissociation energy of $Mo(CO)_6$ is 167 kJ/mol, considerably larger than $\Delta H^{\ddagger}$ for our system, also suggesting that bond making is important.[14] The activation parameters may be compared to those obtained previously from infrared studies for the chelation of $(OC)_5Mo[\eta^1\text{-}PPh_2CH_2CH_2PPh_2]$ and $(OC)_5Mo[\eta^1\text{-}PMe_2PCH_2CH_2PMe_2]$.[15] Values of 120 kJ/mol and 14 J/(K mol), respectively, were reported for the former and 118 kJ/mol and −7.0 J/(K mol) for the latter. In those studies it was concluded that a concerted mechanism of chelation best explains the results, consistent with our conclusions.

Conclusions. Isomerization of $(OC)_5M[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$ and of $(OC)_5M[\eta^1\text{-}P(p\text{-tolyl})_2CH_2CH_2PPh_2]$ is faster than chelation for molybdenum and tungsten complexes but comparable to chelation for chromium complexes. In all cases bond making in the transition state appears to be important, but especially so for the molybdenum and tungsten complexes. Although exchange of coordinated and dangling phosphines in pentacarbonyl complexes of group 6 metals has received little previous attention, it appears to be a common phenomenon.

Experimental Section

General Considerations. Reactions and manipulations of air-sensitive materials were carried out under a dry nitrogen atmosphere with standard Schlenk techniques. Preparations of P(*p*-tolyl)$_2$H,[16] $(OC)_5Cr[PPh_2CH{=}CH_2]$,[17] $(OC)_5Mo[PPh_2CH{=}CH_2]$,[17] $(OC)_5W[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$,[2] and $(OC)_5W[\eta^1\text{-}P(p\text{-tolyl})_2CH_2CH_2PPh_2]$[2] were as described previously. NMR and IR spectra were recorded with GE QE-300 and Nicolet 20 DXB FT-IR spectrometers, respectively. Phosphorus-31 NMR spectra are referenced to 85% phosphoric acid. Elemental analyses were performed at the University of Illinois Microanalytical Laboratory, Urbana, IL.

$(OC)_5Cr[P(p\text{-tolyl})_2H]$ (5). A solution consisting of $Cr(CO)_6$ (4.02 g, 18.3 mmol) and THF (250 mL) was irradiated in a quartz vessel with a 400 W UV lamp for 6 h, after which was added P(*p*-tolyl)$_2$H (4.0 mL, 18.6 mmol). The solution was stirred for 1.5 h, the solvent was removed, and the product was dissolved in a 1:1 v/v ratio of CH_2Cl_2/CH_3OH. Unreacted $Cr(CO)_6$ was removed by filtration and, after refrigeration at −5 °C for 48 h, $(OC)_5Cr[P(p\text{-tolyl})_2H]$ (1.2 g; 32%) crystallized (mp 91−92 °C). IR (CH_2Cl_2): $A_1^1 + E$, 1943 cm^{-1}; A_1^2, 2066 cm^{-1}; B_2, 1984 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 30.9 ppm ($^1J_{PH}$ = 338 Hz). Anal. Calcd for $C_{19}H_{15}O_5PCr$: C, 56.17; H, 3.72. Found: C, 56.54; H, 3.60.

$(OC)_5Mo[P(p\text{-tolyl})_2H]$ (6). A solution of $Mo(CO)_6$ (3.56 g, 36.0 mmol) and dimethoxyethane (60 mL) was heated to reflux for 1 h. To this solution was added P(*p*-tolyl)$_2$H (2.9 mL, 36 mmol), and the resulting solution was heated under reflux for an additional 2.5 h. Recrystallization from a 1:1 v/v ratio of CH_2Cl_2 and CH_3OH after solvent removal gave $(OC)_5Mo[P(p\text{-tolyl})_2H]$ (3.60 g, 58.3%; mp 81−82 °C). IR (CH_2Cl_2): $A_1^1 + E$, 1948 cm^{-1}; A_1^2, 2075 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ 4.5 ppm ($^1J_{PH}$ = 332 Hz). Anal. Calcd for $C_{19}H_{15}O_5PMo$: C, 50.69; H, 3.36. Found: C, 50.59; H, 3.25.

$(OC)_5Cr[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$ (3Cr). A mixture of $(OC)_5Cr[PPh_2CH{=}CH_2]$ (1.10 g, 2.72 mmol), P(*p*-tolyl)$_2$H (0.55 mL, 2.57 mmol), and 2,2′-azobis(isobutyronitrile) (AIBN; 0.15 g) was heated without solvent at 80 °C for 24 h. Recrystalli-

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zation from dichloromethane/methanol gave **7** (0.41 g; 25.9%) as white crystals (mp 133−144 °C). IR (CH_2Cl_2): $A_1{}^1 + E$, 1939 cm^{-1};$A_1{}^2$, 2063 cm^{-1}; B_2, 1983 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_{CrP} 50.5 (d, $^3J_{PP}$ = 35.1 Hz), −13.6 ppm (d, $^3J_{PP}$ = 35.1 Hz). Anal. Calcd for $C_{33}H_{28}O_5P_2Cr$: C, 64.08; H, 4.56. Found: C, 63.82; H, 4.22.

$(OC)_5Mo[\eta^1\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$ (3Mo). A mixture of $(OC)_5Mo[PPh_2CH{=}CH_2]$ (1.52 g, 3.38 mmol), $P(p\text{-tolyl})_2H$ (0.80 mL, 3.7 mmol), and 2,2′-azobis(isobutyronitrile) (AIBN; 0.21 g) was heated without solvent at 43 °C for 1.5 h. Recrystallization from dichloromethane/methanol gave **3Mo** (0.82 g, 36.6%) as white crystals (mp 130 °C). IR (CH_2Cl_2): $A_1{}^1 + E$, 1945 cm^{-1}; $A_1{}^2$, 2073 cm^{-1}; B_2, 1989 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_{MoP} 31.7 (d, $^3J_{PP}$ = 37.0 Hz), −13.6 ppm (d, $^3J_{PP}$ = 37.0 Hz). Anal. Calcd for $C_{33}H_{28}O_5P_2Cr$: C, 59.83; H, 4.26. Found: C, 59.84; H, 4.18.

$(OC)_5Cr[\eta^1\text{-}P(p\text{-tolyl})_2CH_2CH_2PPh_2]$ (4Cr). A mixture of $(OC)_5Cr[P(p\text{-tolyl})_2H]$ (1.09 g, 2.68 mmol), $PPh_2CH{=}CH_2$ (0.55 mL, 2.57 mmol), and 2,2′-azobis(isobutyronitrile) (AIBN; 0.15 g) was heated without solvent at 80 °C for 24 h. Recrystallization from dichloromethane/methanol gave **9** (0.98 g, 58.9%) as light yellow crystals (mp 103−104 °C). IR (CH_2Cl_2): $A_1{}^1 + E$, 1937 cm^{-1}; $A_1{}^2$, 2062 cm^{-1}; B_2, 1982 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_{CrP} 48.4 (d, $^3J_{PP}$ = 35.0 Hz), δ −11.8 ppm (d, $^3J_{PP}$ = 35.0 Hz). Anal. Calcd for $C_{33}H_{28}O_5P_2Cr$: C, 64.08; H, 4.56. Found: C, 63.71; H, 4.58.

$(OC)_5Mo[\eta^1\text{-}P(p\text{-tolyl})_2CH_2CH_2PPh_2]$ (4Mo). A mixture of $(OC)_5Mo[P(p\text{-tolyl})_2H]$ (2.00 g, 4.42 mmol), $PPh_2CH{=}CH_2$ (0.94 mL, 4.42 mmol), and 2,2′-azobisisobutyronitrile, AIBN, (0.15 g) was heated without solvent at 40 °C for 1.5 h. Recrystallization from dichloromethane/methanol gave **4Mo** (2.18 g, 74.5%) as white crystals (mp 90−91 °C). IR (CH_2Cl_2): $A_1{}^1 + E$, 1943 cm^{-1}; $A_1{}^2$, 2072 cm^{-1}; B_2, 1989 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_{MoP} 29.7 (d, $^3J_{PP}$ = 35.9 Hz), −11.8 ppm (d, $^3J_{PP}$ = 35.9 Hz). Anal. Calcd for $C_{33}H_{28}O_5P_2Mo$: C, 59.83; H, 4.26. Found: C, 59.68; H, 4.16.

$(OC)_4Mo[\eta^2\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$ (7Mo).[18] A mixture of $(OC)_5Mo[PPh_2CH{=}CH_2]$ (2.50 g, 5.59 mmol), $P(p\text{-tolyl})_2H$ (1.2 mL, 5.6 mmol), and 2,2′-azobis(isobutyronitrile) (AIBN; 0.16 g) was heated without solvent at 80 °C for 24 h. Recrystallization from dichloromethane/methanol gave **7Mo** (1.50 g, 42.3%) as white crystals (mp 147−148 °C). IR (CH_2Cl_2): 2021 (m), 1909 (vs), 1882 cm^{-1} (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_{MoPPh} 55.5 ppm (d, $^3J_{PP}$ = 5.7 Hz); $\delta_{MoP(tolyl)}$ 53.6 ppm (d, $^3J_{PP}$ = 5.7 Hz). Anal. Calcd for $C_{32}H_{28}O_4P_2Mo$: C, 60.58; H, 4.45. Found: C, 60.74; H, 4.33.

$(OC)_4Cr[\eta^2\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$ (7Cr) and $(OC)_4W[\eta^2\text{-}PPh_2CH_2CH_2P(p\text{-tolyl})_2]$ (7W).[18] These complexes slowly formed in solution at 55 °C from complexes **3Cr** and **4Cr** and from **3W** and **4W,** respectively (see Kinetics and Thermodynamics), and were identified by comparison of their $^{31}P\{^1H\}$ NMR spectra to that of **7Mo**. $^{31}P\{^1H\}$ NMR ($CDCl_3$): **7Cr**, δ_{CrPPh} 80.8 ppm (d, $^3J_{PP}$ = 11.3 Hz), $\delta_{CrP(tolyl)}$ 78.6 ppm (d, $^3J_{PP}$ = 11.3 Hz); **7W**, δ_{WPPh} 41.1 ppm (d, $^3J_{PP}$ = 5.6 Hz), $\delta_{WP(tolyl)}$ 39.1 ppm (d, $^3J_{PP}$ = 5.6 Hz).

Equilibrium and Kinetics Measurements. Pure samples (30 mg) of **3Cr**, **3Mo, 3W**, **4Cr**, **4Mo**, and **4W** in $C_6D_5CD_3$ (0.40 mL) were flame-sealed under vacuum at liquid-nitrogen temperature and thermostated in a constant-temperature bath at the appropriate temperature. The NMR probe was brought to the same temperature, and $^{31}P\{^1H\}$ NMR spectra were recorded at selected time intervals. A delay time of 15 s and a pulse sequence that gave ^1H decoupling but eliminated NOE effects on ^{31}P intensities was utilized. The 15 s delay time gave equivalent signal intensities for isomers of equal concentration. Each spectrum was integrated four times by following standard procedures,[19] and the average value was used in subsequent calculations. The nonlinear least-squares fitting function in Psi Plot for Windows was used to fit the analytical solutions of the kinetics equations to the data for the molybdenum complexes. Samples were protected from light throughout the kinetic runs. Adventitious catalytic species were considered but ruled out. The molybdenum complex isomerizations were approached from both directions (starting with pure **3Mo** and with pure **4Mo)** to give the same equilibrium position and the same rate constants. The tungsten complexes give nearly the same results in both chloroform[2] and toluene, and the isomerization of **1W** and **2W** has been reproduced many times.

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