ORGANOMETALLICS

Note

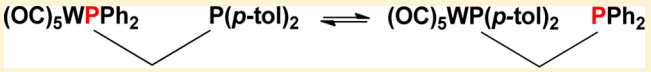
pubs.acs.org/Organometallics

Intramolecular Exchange of Coordinated and Dangling Phosphine Groups in Pentacarbonyl[(diphenylphosphino)-(di-*p*-tolylphosphino)methane]tungsten(0)

Richard L. Keiter,*[†] Deliang Chen,[†] Geoffrey A. Holloway,[†] Ellen A. Keiter,[†] Yi Zang,[†] M. Todd Huml,[†] Jonathan Filley,[†] and Douglas E. Brandt[‡]

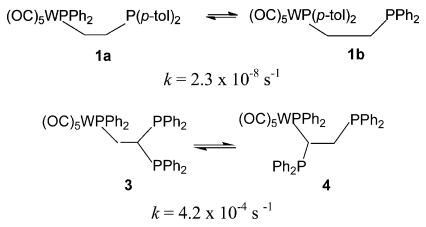
[†]Department of Chemistry and [‡]Department of Physics, Eastern Illinois University, Charleston, Illinois 61920, United States

ABSTRACT: Equilibrium constants and rates have been determined for the isomerization of the linkage isomers $(OC)_5W[\kappa^1\text{-}PPh_2CH_2P(p\text{-tolyl})_2]$ (**5**) and $(OC)_5W[\kappa^1\text{-}P(p\text{-tolyl})_2CH_2PPh_2]$ (**6**). It is proposed that this intramolecular exchange involves a nucleophilic attack of the pendant phosphine on a cis carbonyl group, followed by ring opening and a 1,2-shift.



Previous work has shown that the complexes $(OC)_5W[\kappa^1\text{-}PPh_2CH_2CH_2P(p\text{-tol})_2]$ (**1**) and $(OC)_5W[\kappa^1\text{-}PPh_2CH_2\text{-}CH(PPh_2)_2]$ (**3**) exchange pendant and coordinated phosphines in solution, forming linkage isomers that exist in equilibrium. The rate of isomerization for **3**, however, is about 10^4 times faster than that for **1** in $CDCl_3$ at 55 °C (Scheme 1).[1]

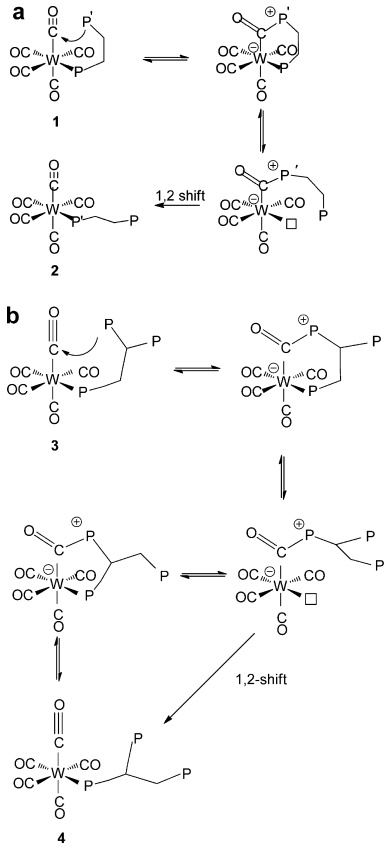
Scheme 1



Reaction schemes based on thermodynamic and kinetic results have been proposed to account for the relative rates (Scheme 2).[2] In both part a and part b of Scheme 2, the reactions are initiated by attack of the pendant phosphine nucleophile on a cis carbonyl carbon, which leads to the formation of a six-membered ring. Ring opening allows for a 1,2-shift in both mechanisms, but the shift is unfavorable in Scheme 2b relative to the formation of a five-membered ring which can then open to give the new isomer **4** directly.

The exchanging phosphorus atoms in both processes are separated by two carbon atoms. Complex **4** also has an uncoordinated phosphine that is separated from the ligated site by one carbon. Because these two phosphines are symmetry equivalent, their exchange with the metal cannot be determined directly by ^{31}P NMR. We have now synthesized two complexes with nonequivalent exchanging phosphines: $(OC)_5W[\kappa^1\text{-}PPh_2CH_2P(p\text{-tol})_2]$ (**5**) and its linkage isomer **6**. The Ph_2P and $(p\text{-tol})_2P$ groups are isosteric but nonequivalent and have ^{31}P chemical shifts that differ by 2 ppm, allowing the ratio of the two isomers in solution to be determined. To further assess the mechanistic models presented in Scheme 2, we have investigated the kinetics and thermodynamics of isomerization for these complexes (Scheme 3).

Scheme 2



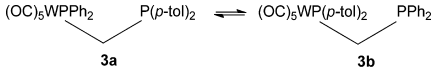
RESULTS AND DISCUSSION

Syntheses. Two approaches were used to synthesize $Ph_2PCH_2P(p\text{-tol})_2$ (**7**), a ligand not previously reported. Following the work of Langhans, Ph_2PCH_2Cl was obtained

Received: February 6, 2012
Published: June 12, 2012

   dx.doi.org/10.1021/om300092x | *Organometallics* 2012, 31, 4619−4622

Scheme 3



from a two-phase reaction[3] and its subsequent reaction with $LiP(p\text{-tol})_2$ gave **7**.

$$Ph_2PH + CH_2Cl_2 + KOH \rightarrow Ph_2PCH_2Cl + KCl + H_2O \quad (1)$$

$$Ph_2PCH_2Cl + LiP(p\text{-tol})_2 \rightarrow \mathbf{7} + LiCl \quad (2)$$

Alternatively, **7** was prepared from $Ph_2PCH_2SiMe_3$[4] and $(p\text{-tol})_2PCl$.

$$Ph_2PCH_2SiMe_3 + (p\text{-tol})_2PCl \rightarrow Me_3SiCl + \mathbf{7} \quad (3)$$

The first approach uses less expensive reactants and mild reaction conditions and requires only two steps. It works best when carried out with a large excess of CH_2Cl_2 (also the solvent) at temperatures below 10 °C. The second approach leads to a higher yield (82%) than the first (40%), but a disadvantage of this reaction is that several steps are required to prepare the starting materials. Reaction of **7** with $(OC)_5WNH_2Ph$ gave a mixture of **5** and **6**. As **5** is less soluble than **6**, it was possible to isolate pure **5** by slow crystallization.

$$(OC)_5WNH_2Ph + \mathbf{7} \rightarrow \mathbf{5} + \mathbf{6} + PhNH_2 \quad (4)$$

Complexes **5** and **6** have identical elemental analyses and nearly identical IR spectra. To distinguish one isomer from the other with certainty by ^{31}P NMR, $(OC)_5W[\kappa^1\text{-}P(p\text{-tol})_2CH_2P(p\text{-tol})_2]$ (**8**) and the known $(OC)_5W[\kappa^1\text{-}PPh_2CH_2PPh_2)]$ were prepared and their chemical shifts were compared with those of the new isomers.

Efforts to obtain **5** selectively from the reaction of $(OC)_5WPPh_2CH_2X$ (X = Cl (**9**), Br (**10**)) with $LiP(p\text{-tol})_2$ were unsuccessful. Presumably, the steric requirements of the reactants make an S_N2 reaction unfavorable. The precursors **9** and **10** were obtained selectively from the reaction of $(OC)_5WNH_2Ph$ with PPh_2CH_2X or from the nonselective reaction of $Li[(OC)_5WPPh_2]$ with CH_2X_2. The latter reaction also gave $(OC)_5WPPh_2Me$,[5] possibly forming from a competing metalation reaction in which $(OC)_5WPPh_2CH_2Li$ is protonated in the workup.

Thermodynamics and Kinetics. The **5** ⇌ **6** isomerization was followed at 25, 40, and 55 °C by ^{31}P NMR. Each isomer gives rise to two first-order doublets resulting from phosphorus−phosphorus coupling of the nonequivalent phosphorus atoms. The nonoverlapping signals of the PPh_2 and $P(p\text{-tol})_2$ groups allowed isomer ratios to be obtained via integration. Tungsten−phosphorus satellites were observed for the coordinated phosphines. There was no evidence for chelation of **5** or **6** in any of the isomerization runs, consistent with the previously reported stability of $(OC)_5W(\kappa^1\text{-}PPh_2CH_2PPh_2)$.[6] In fact, a $CDCl_3$ solution of **5** and **6** showed no spectroscopic or visual evidence for degradation over a 2 year period.

The plot in Figure 1, which depicts the isomerization of **5** at 40 °C, shows a decrease in the concentration of **5** with time and a corresponding increase in the concentration of **6** until equilibrium is reached.

A plot of $\ln([\mathbf{5}] - [\mathbf{5}]_{eq})$ versus time (Figure 2) gave a straight line, as expected for first-order kinetics, and from its slope, $-(k_1 + k_{-1})$, and K both rate constants were determined.

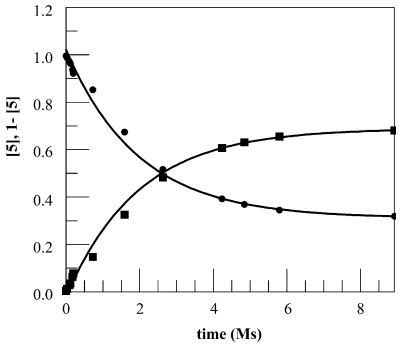


Figure 1. Isomerization of **5** at 40 °C.

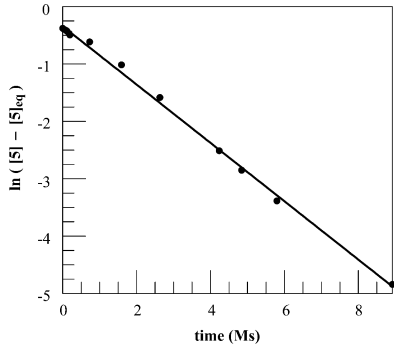


Figure 2. Plot of $\ln([\mathbf{5}] - [\mathbf{5}]_{eq})$ versus time at 40 °C.

Rate constants, half-lives to equilibrium, and equilibrium constants for the reaction are shown in Table 1. From the slope

Table 1. Rate Data and Equilibrium Constants for 5 ⇌ 6 in $CDCl_3$

T (K)	k_1 (s^{-1})	k_{-1} (s^{-1})	ln 2/(k_1 + k_{-1}) (days)	K
328	(2.40 ± 0.12) × 10^{-6}	(1.16 ± 0.12) × 10^{-6}	2.25	2.07
313	(3.50 ± 0.02) × 10^{-7}	(1.58 ± 0.02) × 10^{-7}	15.8	2.22
298	(3.17 ± 0.06) × 10^{-8}	(1.34 ± 0.06) × 10^{-8}	178	2.36

of ln K versus $1/T$, ΔH and ΔS for the forward reactions were found to be −3.35 ± 0.24 kJ/mol and −4.74 ± 0.76 J/(mol K), respectively. The reaction is thermodynamically favorable (**6** is more stable than **5**), but entropy favors the formation of **5**.

Application of the Eyring equation allowed determination of activation parameters. For the forward reaction, $\Delta H^{\ddagger}$ = 114.7 ± 4.2 kJ/mol and $\Delta S^{\ddagger}$ = −3.1 ± 14 J/(mol K), and for the reverse reaction, $\Delta H^{\ddagger}$ = 118.4 ± 4.1 kJ/mol and $\Delta S^{\ddagger}$ = 1.9 ± 13 J/(mol K). The enthalpies of activation are much lower than the estimated W−P bond strengths for similar complexes[7] and are consistent with a mechanism that includes a significant associative component.

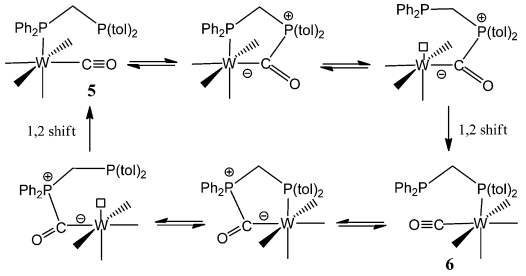
Our expectation that **5** would isomerize more slowly than **3** was realized. This expectation was based on the assumption that isomerizations of **5** and **1** follow analogous mechanistic pathways in which the rate-determining step is a 1,2-shift (Scheme 2). Both **5** and **1** are missing a second uncoordinated phosphine arm, which precludes the faster pathway available to **3**.

However, the isomerization of **5** at 328 K is 100 times faster than that of **1**. To account for this difference, a more detailed look at the mechanism is required (Schemes 4 and 2a). Specifically,

dx.doi.org/10.1021/om300092x | Organometallics 2012, 31, 4619−4622

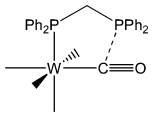
consideration of the solution conformations of **5** and **1** is instructive.

Scheme 4



The crystal structure of $(OC)_5W(\kappa^1\text{-}PPh_2CH_2PPh_2)$, which is isosteric with **5**, has been determined.[8] It reveals that the pendant phosphine points toward the $W(CO)_4$ equatorial plane of the molecule with a phosphorus−carbonyl carbon separation of 3.42 Å (Scheme 5), which is about the sum of the van der Waals

Scheme 5

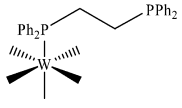


radii (3.5 Å).[9] Spectroscopic evidence previously reported suggests that this conformation largely persists in solution.[1b,2] The pendant arm is not localized on a particular carbonyl group but rather can be viewed as moving about the equatorial carbonyl plane. The phosphorus lone pair of the pendant phosphine is thus poised for nucleophilic attack on the nearby carbonyl carbon, thereby creating a five-membered ring and increasing the electron density at the tungsten atom. This leads to a weakening of the W−P bond and increases the probability of dissociation, which in turn allows a 1,2-shift.

In the ^{13}C NMR spectra for the complexes of this study, long-range phosphorus−carbon coupling is observed between the pendant phosphine and the cis carbonyls of **5** ($^4J_{PC}$ = 3.2 Hz) and **6** ($^4J_{PC}$ = 2.9 Hz), as reported for $(OC)_5W(\kappa^1\text{-}PPh_2CH_2PPh_2)$ ($^4J_{PC}$ = 3.0 Hz), but it is not observed for **1**. No coupling is observed to the trans carbonyl for any of the complexes. The long-range coupling is thought to have a significant "through-space" contribution and is consistent with the close approach of the short phosphine arm to the equatorial carbonyl plane.[2,8]

Unlike isomers **5** and **6**, the most favorable conformation for **1** is one in which the pendant phosphine is oriented away from the carbonyl plane (Scheme 6).[10] As a consequence, it is less

Scheme 6



probable that the dangling phosphine in **1** will interact with the carbonyl group to form a ring and, therefore, less likely that there will be a 1,2-shift. In other words, the equilibria for the forward reactions are shifted further to the right for **5** than for **1**, thereby increasing the probability of a 1,2-shift. Thus, k for the isomerization of **5** is larger than for **1**. This difference could also be viewed as resulting from the greater rotational degrees of freedom in **1**, which would decrease the probability of collision between its pendant phosphine and an equatorial carbonyl.

That a pendant group of a coordinated ligand in group 6 metal carbonyl complexes may influence substitution reaction rates is not a new idea. Examples involving the distal oxygen and sulfur atoms of acetate, carboxylate, and thiolate ligands have been reported.[11]

The difference in the W−P bond dissociation energies in **1** and **5** may make a small contribution to the faster isomerization rate observed for **5**. The pK_a's of $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2PCH_2CH_2PPh_2$ (dppe) are 3.86 and 3.81, respectively, showing that dppe is slightly more basic (toward protons) than is dppm.[12] While this does not tell us anything about the π capacities of the two ligands, it does suggest that there is likely to be too little difference in W−P bond strengths to account for the large difference in rates.

■ CONCLUDING REMARKS

For many years it was not recognized that complexes of group 6 pentacarbonyls with monocoordinated polyphosphines undergo exchange of the coordinated and uncoordinated phosphine moieties. It was thought that such complexes could only serve as ligands toward Lewis acids or undergo chelation if heated or photolyzed. The discovery that **3** undergoes phosphine exchange much more quickly than expected led us to investigate reactions of this type in more detail.[7c,13] We have found that exchange is slowed when the coordinated and pendant phosphines are separated by one or two carbon atoms if a third phosphine arm is missing. Thus, **1** and **5** exhibit much slower phosphine exchange than does **3**. For one-armed diphosphine complexes, reactions proceed by nucleophilic attack on the carbon of M−CO, which leads to phosphine dissociation followed by a 1,2-shift. For the two-armed **3**, the 1,2-shift is avoided by formation of a new ring followed by dissociation of the phosphine from the M−CO group. Complex **5** isomerizes more quickly than **1** primarily because, in the predominant conformational arrangement in **5** (but not **1**), the pendant phosphine lies toward the carbonyl substrate, thereby facilitating nucleophilic attack. In summary, complexes **1**, **3**, and **5** all undergo phosphorus exchange more quickly than chelation at modest temperatures and the exchange rates vary considerably ($k = 10^{-4}$−10^{-8} s^{-1} at 55 °C), depending on the nature of the phosphine.

■ EXPERIMENTAL SECTION

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was dried with sodium metal in the presence of benzophenone and was freshly distilled under N_2 before use. All other solvents were used without further purification. The starting materials $P(p\text{-}tol)_3$,[14] $LiP(p\text{-}tol)_2$,[15] $(p\text{-}tol)_2PCl$,[16] Ph_2PCH_2Cl,[3] $Ph_2PCH_2SiMe_3$,[4] $(OC)_5WNH_2Ph$,[17] $(p\text{-}tol)_2PCH_2P(p\text{-}tol)_2$,[18] and $Li[W(CO)_5PPh_2]$[19] were prepared by literature methods. Phosphorus-31 NMR spectra (referenced to 85% phosphoric acid) and carbon-13 NMR spectra (referenced to TMS) of $CDCl_3$ solutions were recorded with a GE QE-300 NMR spectrometer; all spectra were proton-decoupled. Chemical shifts are quoted in ppm and coupling constants in Hz. Infrared spectra of $CHCl_3$ solutions were recorded with a Nicolet 20 DXB FT-IR spectrometer, and results are reported as cm^{-1}. Elemental analyses were performed at the University of Illinois Microanalytical Laboratory in Urbana, IL.

(Diphenylphosphino)(di-*p*-tolylphosphino)methane, $Ph_2PCH_2P(p\text{-}tol)_2$ (7). (a) To a freshly prepared solution of

dx.doi.org/10.1021/om300092x | *Organometallics* 2012, 31, 4619−4622

Ph_2PCH_2Cl (9.2 mmol in 60 mL of THF) was slowly added a red solution of $LiP(p\text{-tol})_2$ (12.5 mmol in 25 mL of THF). The red color disappeared rapidly at first and then more slowly until at 19 mL the red color persisted. The solution was stirred for 20 h and the THF removed by vacuum. Treatment of the resulting oil with ethanol gave a white solid (1.50 g, 40%).

(b) A solution prepared from $Ph_2PCH_2SiMe_3$ (5.5 mmol) and $(p\text{-tol})_2PCl$ (4.9 mmol) was slowly heated to 150 °C over 4 h. The volatile Me_3SiCl was removed by vacuum and the remaining solid crystallized from ethanol (1.9 g, 82%). ^{31}P NMR: AB quartet, δ −22.1, −23.8; $^2J_{PP}$ = 126.7.

Pentacarbonyl[(diphenylphosphino)(di-*p*-tolylphosphino)-methane]tungsten(0), $(OC)_5W[\kappa^1\text{-}PPh_2CH_2P(p\text{-tol})_2]$ (5) and $(OC)_5W[\kappa^1\text{-}P(p\text{-tol})_2CH_2PPh_2]$ (6). To a solution of $(OC)_5WNH_2Ph$ (0.83 g, 2.2 mmol in 30 mL of CH_2Cl_2) was added $Ph_2PCH_2P(p\text{-tol})_2$ (0.90 g, 2.2 mmol in 30 mL of CH_2Cl_2). The solution was stirred for 24 h, and the solvent was removed by vacuum. The resulting solid was dissolved in 10 mL of a 1:1 solution of CH_2Cl_2 and CH_3OH and placed in a freezer at −15 °C, where a white solid precipitated consisting of **5** and **6** (1.2 g, 82%). IR: ν_{CO} 2070 (m), 1980 (w), 1939 (s). The overlapping signals for the two isomers were slightly broadened and were not resolved. ^{31}P NMR: **5**, δ_{PPh_2} 10.1, $\delta_{P(tol)_2}$ −26.1, $^2J_{PP}$ = 104.9, J_{WP} = 245.0; **6**, δ_{PPh_2} −23.9, $\delta_{P(tol)_2}$ 8.0, $^2J_{PP}$ = 104.0, J_{WP} = 244.4. ^{13}C NMR (CO): **5**, δ_{cis} 205.6 (dd, $^2J_{PC}$ = 7.1, $^4J_{PC}$ = 2.9), δ_{trans} 208.0 (d, $^2J_{PC}$ = 21.7); **6**, δ_{cis} 205.7 (dd, $^2J_{PC}$ = 7.0, $^4J_{PC}$ = 3.2), δ_{trans} 208.2 (d, $^2J_{PC}$ = 21.9). Pure white crystals of **5** were obtained by dissolving the isomer mixture in CH_2Cl_2, adding a layer of CH_3OH, and refrigerating for 3 weeks. Mp: 168−170 °C dec. IR: ν_{CO} 2071 (m), 1981 (w), 1940 (s). Anal. Calcd for $C_{32}H_{26}O_5P_2W$: C, 52.20; H, 3.60; P, 8.41. Found: C, 51.99; H, 3.44; P, 8.80.

Pentacarbonyl[bis(di-*p*-tolylphosphino)methane]tungsten-(0), $(OC)_5W[\kappa^1\text{-}P(p\text{-tol})_2CH_2P(p\text{-tol})_2]$ (8). This compound was prepared in 58.8% yield from $(OC)_5WNH_2Ph$ and $(p\text{-tol})_2PCH_2P(p\text{-tol})_2$ by the same method used for **5** and **6**. IR: ν_{CO} 2070 (m), 1979 (w), 1938 (s). ^{31}P NMR: δ_{PW} 7.89, δ_P −25.7, $^2J_{PP}$ = 102.8, J_{WP} = 243.4. Anal. Calcd for $C_{34}H_{30}O_5P_2W$: C, 53.42; H, 3.96; P, 8.10. Found: C, 53.19; H, 3.80; P, 7.65.

[(Chloromethyl)diphenylphosphine]pentacarbonyltungsten(0), $(OC)_5WPPh_2CH_2Cl$ (9). (a) This compound was obtained from the reaction of $(OC)_5WNH_2Ph$ (1.0 g, 2.4 mmol) with Ph_2PCH_2Cl (0.56 g, 2.4 mmol) in toluene (25 mL). Addition of an equal volume of methanol followed by refrigeration led to 0.64 g of crystalline product (45%). IR: ν_{CO} 2074 (m), 1984 (w), 1942(s). ^{31}P NMR: δ_P 20.7, J_{WP} = 246.3. Anal. Calcd for $C_{18}H_{12}O_5PWCl$: C, 38.71; H, 2.17; P, 5.55. Found: C, 38.30; H, 1.70; P, 5.40.

(b) **9** was also formed from the reaction of $Li[(OC)_5WPPh_2]$ with CH_2Cl_2. Similarly, $(OC)_5WPPh_2CH_2Br$ (**10**) was obtained. IR: ν_{CO} 2073 (m), 1982 (w), 1943 (s). ^{31}P NMR: δ_P 19.4, J_{WP} = 245.8. However, in the preparation of both the chloride and bromide complexes by this method, $(OC)_5WPPh_2Me$[5] was formed as a side product (25%). ^{31}P NMR: δ_P −3.27, J_{WP} = 237.0.

Reaction Rates and Equilibrium Constants. Into an NMR tube was placed 30 mg of pure **5** or a mixture of **5** and **6**, dissolved in 0.5 mL of $CDCl_3$. The tube was vacuum-sealed and placed into a constant-temperature bath. ^{31}P NMR spectra were recorded periodically for each of three temperatures: 25, 40, and 55 °C. The NMR probe was brought to the appropriate temperature before each spectrum was collected. The ratio of the two isomers was determined by integration of the phosphorus signals.[1a] Equilibrium was assumed to have been reached when the ratio no longer changed with time.

AUTHOR INFORMATION

Corresponding Author

*E-mail: rlkeiter@eiu.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Camille and Henry Dreyfus Foundation for a Scholar Fellow grant (SF-98-004) and the National Science Foundation (CHE-9708342) for support of this work.

REFERENCES

(1) (a) Keiter, R. L.; Benson, J. W.; Keiter, E. A.; Lin, W.; Jia, Z.; Olson, D. M.; Brandt, D. E.; Wheeler, J. L. *Organometallics* **1998**, *17*, 4291. (b) Keiter, R. L.; Benson, J. W.; Jia, Z.; Keiter, E. A.; Brandt, D. E. *Organometallics* **2000**, *19*, 4518.

(2) Keiter, R. L.; Ye, P.; Keiter, E. A.; Benson, J. W.; Lin, W.; Brandt, D. E.; Southern, J. S.; Rheingold, A. L.; Guzei, I.; Wheeler, K. A.; Cary, L. W. *Inorg. Chim. Acta* **2010**, *364*, 176.

(3) Langhans, K.-P.; Stelzer, O; Weferling, N. *Chem. Ber.* **1990**, *123*, 995.

(4) (a) Appel, R.; Geisler, K.; Scholer, H.-F. *Chem. Ber.* **1979**, *112*, 648. (b) Grim, S. O.; Barth, R. C. *J. Organomet. Chem.* **1975**, *94*, 327. (c) Campora, J.; Maya, C. M.; Matas, I.; Claasen, B.; Palma, P.; Alvarez, E. *Inorg. Chim. Acta* **2006**, *359*, 3191.

(5) McFarlane, H. C. E.; McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1976**, 1616.

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

(7) (a) Mukerjee, S. L.; Lang, R. F.; Ju., T.; Kiss, G.; Hoff, C. D.; Nolan, S. P. *Inorg. Chem.* **1992**, *31*, 4885. (b) Dias, P. B.; Minas da Pierdade, M. E.; Martinho Simões, J. A. *Coord. Chem. Rev.* **1994**, *135/136*, 737. (c) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*, 2nd ed.; Wiley-VCH: New York, 1997.

(8) Benson, J. W.; Keiter, R. L.; Keiter, E. A.; Rheingold, A. L.; Yap, G. P. A.; Mainz, V. V. *Organometallics* **1998**, *17*, 4275.

(9) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993.

(10) Keiter, R. L.; Rheingold, A. L.; Hamerski, J. J.; Castle, C. K. *Organometallics* **1983**, *2*, 1635.

(11) (a) Darensbourg, D. J.; Wiegreffe, H. P. *Inorg. Chem.* **1990**, *29*, 592. (b) Darensbourg, D. J.; Joyce, J. A.; Bischoff, C. J.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 1137. (c) Phelps, A. L.; Rampersad, M. V.; Fitch, S. B.; Darensbourg, M. Y.; Darensbourg, D. J. *Inorg. Chem.* **2006**, *45*, 119. (d) Jeffery, S. P.; Singleton, M. L.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **2007**, *46*, 179.

(12) Sowa, J. R.; Angelici, R. J. *Inorg. Chem.* **1991**, *30*, 3534.

(13) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*.

(14) Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716.

(15) (a) Grim, S. O.; Yankowsky, A. W. *J. Org. Chem.* **1977**, *18*, 1236. (b) Archer, L. J.; George, T. A. *Inorg. Chem.* **1979**, *18*, 2079.

(16) Montgomery, R. E.; Quin, L. D. *J. Org. Chem.* **1965**, *30*, 2293.

(17) Angelici, R. J.; Malone, M. D. *Inorg. Chem.* **1967**, *6*, 1731.

(18) Hao, L.; Jobe, I. R.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 2781.

(19) Maitra, K.; Wilson, W. L.; Jemin, M. M.; Yeung, C.; Rader, W. S.; Redwine, K. D.; Striplin, D. P.; Catalano, V. J.; Nelson, J. H. *Synth. React. Inorg. Met.-Org. Chem.* **1996**, *26*, 967.