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Thermodynamic and Kinetic Studies of the Complexes $W(CO)_3(PCy_3)_2(L)$ ($L = H_2$, N_2, $NCCH_3$, Pyridine, $P(OMe)_3$, CO)

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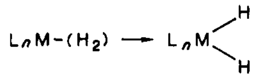
The complexes $W(CO)_3(PCy_3)_2(L)$ have been studied by solution calorimetry. The enthalpies of binding (kcal/mol) of ligands to $W(PCy_3)_2(CO)_3$ in toluene solution are as follows: H_2, −9.9, N_2, −13.5; $NCCH_3$, −15.1; pyridine, −18.9; $P(OMe)_3$, −26.5; CO, −30.4. Similar values are obtained in tetrahydrofuran solution. These data imply bond strengths much lower than expected from gas-phase studies. The origin of this discrepancy is attributed to the presence of the W···H–C "agostic" interaction. This is estimated to be on the order of 10 ± 6 kcal/mol. In order to investigate the role of the "agostic" interaction in the energetics of this complex, the kinetics of reaction of $W(CO)_3[P(C_6H_{11})_3]_2(py)$ and $W(CO)_3[P(C_6D_{11})_3]_2(py)$ with $P(OMe)_3$ in toluene were studied. A kinetic isotope effect, $k_H/k_D = 1.20 \pm 0.05$, was observed, and verifies the importance of the "agostic" bond in ligand substitution for this complex. A mechanism is proposed that involves concerted replacement of coordinated pyridine by the three-center W···H–C bond.

Introduction

Activation of hydrogen is one of the fundamental steps in a number of catalytic processes. The recent discovery of coordination of molecular hydrogen in complexes such as $W(CO)_3(PCy_3)_2(H_2)$[1] is of special interest since it was the first complex shown to bind H_2 in an arrested form of oxidative addition. Since then several new molecular hydrogen complexes, including complexes previously considered to be hydrides, have been discovered or reformulated.[1c,2] Theoretical calculations have been performed on these compounds,[3] particularly with regard to the distinction between dihydride complexes and molecular hydrogen complexes, as shown in eq 1. The energy difference between these tautomers is probably small, since spectral changes have shown that in some cases an equilibrium exists between the molecular hydrogen form and the dihydride form.[1b,2c] No thermochemical data have been reported for the binding of molecular hydrogen in solution.[4] One goal of this work was to determine how H_2 compares as a ligand to more conventional two-electron donors.



(1)

In addition to binding molecular hydrogen, the unsaturated precursor $W(CO)_3(PCy_3)_2$ binds a selective "menu" of ligands.[5] For example, ammonia and primary amines will coordinate to the complex, but secondary and tertiary amines will not. As part of a program of solution thermochemistry we have measured heats of binding of a variety of ligands to group VI complexes.[6] These data were

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[1] (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000. (c) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

[2] (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. (c) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (d) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548. (e) Arliguie, T.; Chaudret, B.; Devillers, J.; Poilblanc, R. *C. R. Acad. Sci., Ser. 2* **1987**, *305*, 1523. (f) Heinekey, D. M.; Payne, N. G.; Schulte, G. K. *J. Am. Chem. Soc.* **1988**, *110*, 2303. (g) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 598. (h) Fontaine, X. L. R.; Fowles, E. H.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1988**, 482.

[3] (a) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705. (b) Burdett, J. K.; Phillips, J. R.; Pourian, M.; Turner, J. J.; Upmacis, R. *Inorg. Chem.* **1987**, *26*, 3054. (c) Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B.; Sefta, F. *J. Am. Chem. Soc.* **1986**, *108*, 6587.

[4] The enthalpy of dissociation from the solid complex has been determined to be on the order of 12 kcal/mol: Zilm, K. W., private communication.

[5] (a) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294. (b) Kubas, G. J. *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds., Elsevier: New York, 1986; Vol. 3, p 254.

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all for relatively strain-free environments. There are few examples in the literature of examination of the thermodynamics of binding of ligands in a sterically demanding environment. Data for such complexes may provide a basis for theoretical understanding of the forces involved in ligand binding.

Finally, the title complex is of interest since it has been shown to contain a three-center C–H···W "agostic" bond. A number of complexes have been shown to display this type of bonding for both intra- and intermolecular binding. For example, photolysis of $Cr(CO)_6$ has been shown to produce $Cr(CO)_5$(heptane) as shown in reaction 2. The

$$Cr(CO)_6 \xrightarrow[\text{heptane}]{h\nu} Cr(CO)_5(\text{heptane}) \qquad (2)$$

energy of the Cr···H–C interaction has been measured by photoacoustic calorimetry to be on the order of 10 kcal/mol.[7] In the same way that formation of a molecular hydrogen complex can be viewed as the first step toward oxidative addition of hydrogen, these "agostic" bonds can be viewed as the first step toward alkane activation.[8] In order to assess the role of the three center W···H–C bond in this system, we report kinetic studies on ligand substitution for $W(CO)_3[P(C_6H_{11})_3]_2(py)$ and its deuterium substituted analogue $W(CO)_3[P(C_6D_{11})_3]_2(py)$. The combination of thermochemical and kinetic data give a good picture of the reaction energetics in these complexes.

Experimental Section

General Data. Manipulations of organometallic complexes were carried out under an atmosphere of argon, nitrogen, or hydrogen using standard Schlenk tube techniques or in a Vacuum/Atmospheres glovebox. Tetrahydrofuran and toluene were purified by distillation from sodium benzophenone ketyl under an argon atmosphere. The complexes $W(CO)_3(PCy_3)_2(L)$ were prepared as described in the literature.[5] The phosphine $P(C_6D_{11})_3$ (98.5% D) was purchased from MSD Isotopes, Montreal, Canada (custom synthesis), and used to prepare $W(CO)_3(P(C_6D_{11})_3)_2(H_2)$ which was then converted to $W(CO)_3(P(C_6D_{11})_3)_2(py)$.

Calorimetric Measurements. Calorimetric measurements were made by using the Guild solution calorimeter or Setaram Calvet calorimeter described previously.[6] A typical procedure is described below for reaction of $W(CO)_3(PCy_3)_2(H_2)$ and $P(OMe)_3$ in toluene. All other measurmements were made by using techniques similar to this or to those described previously. A clean 500-mL Schlenk tube was taken into the glovebox and filled with 3.0 g of (cycloheptatriene)$W(CO)_3$, 6.0 g of PCy_3, and about 300 mL of freshly distilled toluene. The vessel was closed and taken outside the glovebox to a Schlenk manifold with hydrogen as the insert gas (caution: all manipulations under hydrogen atmosphere were done in a hood and in an environment designed to minimize the danger of explosions).

The solution (which had begun to turn purple due to formation of $W(CO)_3(PCy_3)_2$) was exposed to hydrogen and stirred for 2 h. During this time the color changed to yellow-brown and some precipitate formed. An additional 200 mL of toluene was added under hydrogen flow and the solution filtered under hydrogen into the calorimeter. An infrared spectrum of the calorimeter solution showed only peaks due to $W(CO)_3(PCy_3)_2(H_2)$ and a small amount of $W(CO)_4(PCy_3)_2$. The latter does not interfere with the calorimetry since it is inert under the reaction conditions. A slight excess pressure of hydrogen (1.1–1.3 atm) was maintained during the calorimetry. The color of the filtered solution under hydrogen was clear yellow, indicating no $W(CO)_3(PCy_3)_2$, which is an intense purple. Trimethyl phosphite (0.050 mL) was added by a thermostated Hamilton syringe. Electrical calibrations were run before and after addition of the phosphite. The value of -16.2 ± 0.5 kcal/mol is the average of six separate measurements. At the end of the calorimetry, 1.0 mL of $P(OM_3)_3$ was added to complete the reaction. Since the solution was saturated with H_2, the net thermochemical reaction involves loss of H_2 as a gas. An infrared spectrum of the solution showed $W(CO)_3(PCy_3)_2(P(OMe)_3)$, and only a small amount of $W(CO)_4(PCy_3)_2$. Prior to cleaning the calorimeter, 0.050 mL of $P(OMe)_3$ was added and showed no detectable heat of mixing. The enthalpies of all reactions measured refer to reaction of the complexes in solution. Heats of solution or dilution of the liquid or gaseous ligands are not included: however, these are generally small compared to experimental errors.

Table I. Heats of Reaction of $W(CO)_3(PCy_3)_2(L)$ Complexes with Various Ligands

complex	ligand	solvent[a]	$-H_{rxn}$[b]
$W(CO)_3(PCy_3)_2$	H_3CCN	toluene	15.1 (0.5)
$W(CO)_3(PCy_3)_2$	H_3CCN	THF	15.5 (0.6)
$W(CO)_3(PCy_3)_2$	pyridine	toluene	18.9 (0.4)
$W(CO)_3(PCy_3)_2$	pyridine	THF	19.2 (0.8)
$W(CO)_3(PCy_3)_2$	$P(OMe)_3$	toluene	26.5 (1.5)
$W(CO)_3(PCy_3)_2$	$P(OMe)_3$	THF	25.1 (1.3)
$W(CO)_3(PCy_3)_2(H_2)$	pyridine	toluene	9.5 (0.5)
$W(CO)_3(PCy_3)_2(H_2)$	pyridine	THF	10.0 (0.5)
$W(CO)_3(PCy_3)_2(H_2)$	$P(OM_3)_3$	toluene	16.2 (0.5)
$W(CO)_3(PCy_3)_2(H_2)$	$P(OM_3)_3$	THF	15.6 (0.4)
$W(CO)_3(PCy_3)_2(H_2)$	CO	toluene	20.5 (0.7)
$W(CO)_3(PCy_3)_2(H_2)$	CO	THF	22.8 (1.0)
$W(CO)_3(PCy_3)_2(N_2)$	$P(OMe)_3$	toluene	13.0 (1.0)

Kinetic Measurements. Kinetic measurements were made in a thermostated UV–vis cell using a Cary 17 spectrophotometer. Solutions of $W(CO)_3(PCy_3)_2(py)$ in toluene were prepared in the glovebox and measured amount of pyridine was added to the solution. The UV–vis cell was loaded in the glovebox and transferred to the spectrophotometer. After temperature equilibration, the reaction was initiated by adding trimethyl phosphite and followed by monitoring the decay in absorbance at 545.5 nm due to $W(CO)_3(PCy_3)_2(py)$. This procedure was followed for the measurements in toluene at 5, 15, 25, and 35 °C. Measurements that followed the buildup of $W(CO)_3(PCy_3)_2(P(OMe)_3)$ by either IR or UV–vis yielded identical rate constants at 25 °C. Individual values of k_{obsd} calculated under the pseudo-first-order conditions showed straight lines over 3–5 half-lives. All measurements are the average of from two to six separate experiments.

Results

A. Calorimetry. Thermochemical results are based on reactions 3–5. These reactions are rapid and quantitative at room temperature. Enthalpies of reaction measured

$$W(CO)_3(PCy_3)_2 + L \xrightarrow{Ar} W(CO)_3(PCy_3)_2(L) \qquad (3)$$

$$W(CO)_3(PCy_3)_2(H_2) + L \xrightarrow{H_2} W(CO)_3(PCy_3)_2(L) + H_2 \qquad (4)$$

$$W(CO)_3(PCy_3)_2(N_2) + L \xrightarrow{N_2} W(CO)_3(PCy_3)_2(L) + N_2 \qquad (5)$$

in toluene and tetrahydrofuran are collected in Table I. Any differences in the heats of reaction in the two solvents are masked by the experimental error in the measurements. The agreement between the values in the two solvents is reasonable since these covalent complexes would not be expected to show a large solvent dependence.

The data in Table I can be used to calculate a relative order of stability for these complexes. For example, subtraction of eq 6 from eq 7 leads directly to eq 8. The

$$W(CO)_3(PCy_3)_2 + py \rightarrow W(CO)_3(PCy_3)_2(py) \qquad (6)$$

$$\Delta H = -18.9 \pm 0.4 \text{ (toluene)}$$
$$-19.2 \pm 0.8 \text{ (THF)}$$

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[6] (a) Nolan, S. P.; de la Vega, R. L.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529. (b) Mukerjee, S. L.; Gonzalez, A. A.; Zhang, K.; Chou, S. J.; Hoff, C. D., unpublished results.

[7] Yang, G. K.; Peters, K. S.; Vaida, V. *Chem. Phys. Lett.* **1986**, *125*, 566.

[8] Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

$$W(CO)_3(PCy_3)_2 + P(OMe)_3 \rightarrow W(CO)_3(PCy_3)_2(P(OMe)_3) \quad (7)$$

$$\Delta H = -26.5 \pm 1.5 \text{ (toluene)}$$
$$-25.1 \pm 1.3 \text{ (THF)}$$

$$W(CO)_3(PCy_3)_2(py) + P(OMe)_3 \rightarrow W(CO)_3(PCy_3)_2(P(OMe)_3) + py \quad (8)$$

$$\Delta H = -7.6 \pm 1.9 \text{ (toluene)}$$
$$-5.9 \pm 2.1 \text{ (THF)}$$

enthalpy of reaction 8 calculated in this way can be compared to data based on reactions of the hydrogen complex $W(CO)_3(PCy_3)_2(H_2)$ and provides a partial check on the data. Thus subtraction of eq 9 from eq 10 also leads to

$$W(CO)_3(PCy_3)_2(H_2) + py \rightarrow W(CO)_3(PCy_3)_2(py) + H_2 \quad (9)$$

$$\Delta H = -9.5 \pm 0.5 \text{ (toluene)}$$
$$-10.0 \pm 0.5 \text{ (THF)}$$

$$W(CO)_3(PCy_3)_2(H_2) + P(OMe_3) \rightarrow W(CO)_3(PCy_3)_2(P(OMe)_3) + H_2 \quad (10)$$

$$\Delta H = -16.2 \pm 0.5 \text{ (toluene)}$$
$$-15.6 + 0.4 \text{ (THF)}$$

reaction 8. The enthalpies of reaction calculated in this way, −6.7 ± 1.0 in toluene and −5.6 ± 0.9 in THF, are in excellent agreement with the values determined based on eq 6 and 7 discussed above.

The enthalpy of coordination of dihydrogen, as shown in reaction 11, is calculated from data obtained by using

$$W(CO)_3(PCy_3)_2 + H_2 \rightarrow W(CO)_3(PCy_3)_2(H_2) \quad (11)$$

the same ligand in reactions of $W(CO)_3(PCy_3)_2$ and $W(CO)_3(PCy_3)_2(H_2)$. Thus subtraction of eq 9 from eq 6 leads directly to values for the enthalpy of eq 11 of −9.4 ± 0.9 kcal/mol in toluene solution. In a similar way, subtraction of eq 10 from eq 7 yields values of −10.3 ± 2.0 kcal/mol in toluene solution. The values in THF solution are calculated to be −9.2 ± 1.3 and −9.5 ± 1.7 kcal/mol. It is clear that the data have good internal consistency. In a similar fashion the enthalpy of binding of N_2 is calculated to be −13.5 ± 2.5 kcal/mol in toluene solution. The enthalpies (kcal/mol) of ligand addition shown in Figure 1 have been rounded off and show stabilities relative to $W(CO)_3(PCy_3)_2$: H_2, 10; N_2, 13; $NCCH_3$, 15; py, 19; $P(OMe)_3$, 26; CO, 30 kcal/mol. These data refer to reaction of the complexes in solution and does not include heats of solution or dilution of the ligands (either gases or liquids). For the systems studied here these are generally small compared to experimental errors in the measurements.

B. Kinetics. Preliminary study of the kinetics of reaction 8 showed it to be surprisingly fast in both THF and toluene. Kinetic data were collected in toluene solution at 5, 15, 25, and 35 °C and are shown in Table II. These data are consistent with the mechanism shown in eq 12. A steady-state treatment of this yields eq 13. For the

$$W(CO)_3(PCy_3)_2(py) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} W(CO)_3(PCy_3)_2 + py \xrightarrow[P(OMe)_3]{k_2} W(CO)_3(PCy_3)_2(P(OMe)_3) \quad (12)$$

$$\text{rate} = \frac{k_1k_2[(PCy_3)_2W(CO)_3(py)][P(OMe)_3]}{k_{-1}[py] + k_2[P(OMe)_3]} \quad (13)$$

pseudo-first-order reaction conditions ([py] and $[P(OMe)_3]$ ≫ $[W(CO)_3(PCy_3)_2(py)]$) plots of ln [complex] versus time were linear over 5 half-lives and yielded the observed first-order rate constant k_{obsd} (eq 14). Plots of $1/k_{obsd}$

$$k_{obsd} = \frac{k_1k_2[P(OMe)_3]}{k_{-1}[py] + k_2[P(OMe)_3]} \quad (14)$$

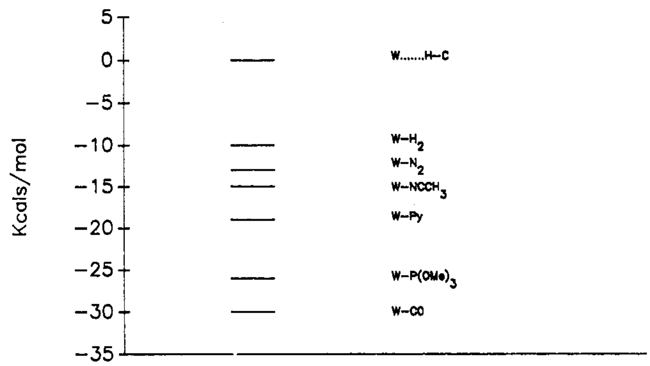

Figure 1. Enthalpies of addition (kcal/mol) of ligands to $W(CO)_3(PCy_3)_2$.

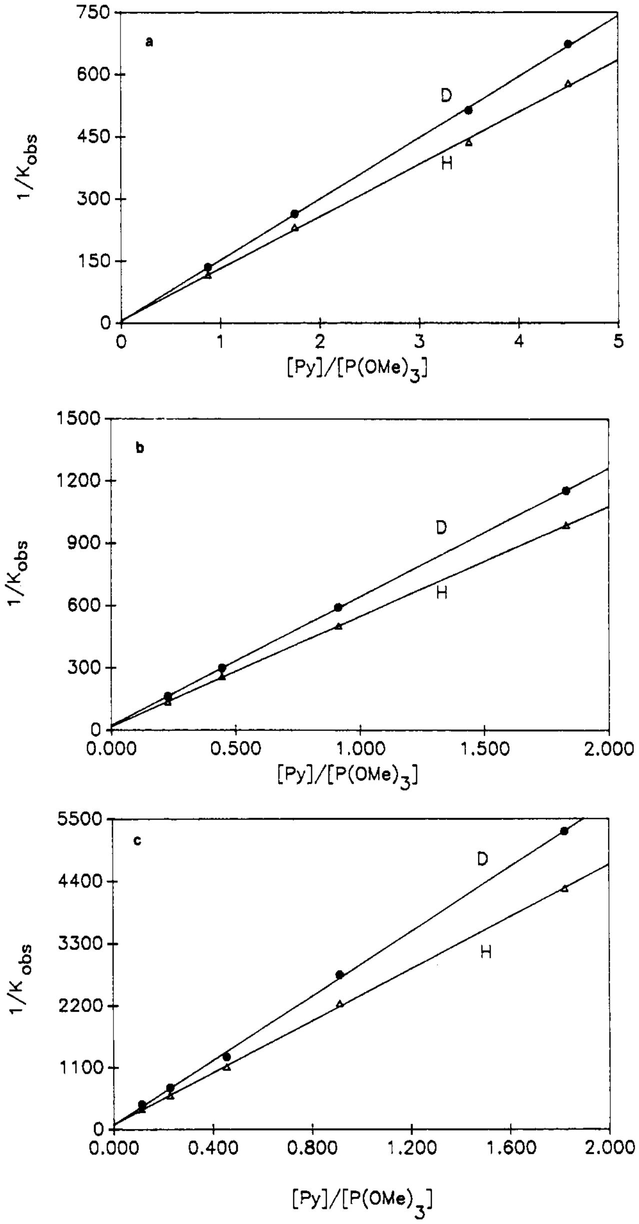

Figure 2. Plots of $1/k_{obsd}$ versus $[py]/[P(OMe)_3]$ at (a) 25, (b) 15, and (c) 5 °C (H = $W(CO)_3(P(C_6H_{11})_3)_2(py)$; D = $W(CO)_3(P(C_6D_{11})_3)_2(py)$).

Table II. Kinetic Data[a] for the Reaction $W(CO)_3(PCy_3)_2(py) + P(OMe)_3 \Rightarrow W(CO)_3(PCy_3)_2(P(OMe)_3) + py$

temp, °C	complex[b]	$[P(OMe)_3]/[py]$	10^3k_{obsd}, s^{-1}
35	H	0.905	35.3
	D	0.905	30.3
	H	1.810	16.8
	D	1.810	14.5
25	H	1.143	8.67
	D	1.143	7.40
	H	0.571	4.32
	D	0.571	3.79
	H	0.286	2.30
	D	0.286	1.95
	H	0.222	1.73
	D	0.222	1.49
15	H	4.386	7.30
	D	4.386	6.13
	H	2.198	3.88
	D	2.198	3.36
	H	1.095	2.00
	D	1.095	1.69
	H	0.546	1.013
	D	0.546	0.866
5	H	8.772	2.81
	D	8.772	2.24
	H	4.386	1.66
	D	4.386	1.35
	H	2.199	0.904
	D	2.199	0.777
	H	1.095	0.447
	D	1.095	0.364
	H	0.546	0.234
	D	0.546	0.190

[a] In toluene solution, see Experimental Section for details. [b] H = $W(CO)_3[P(C_6H_{11})_3]_2(py)$; D = $W(CO)_3[P(C_6D_{11})_3]_2(py)$.

versus $[py]/[P(OMe)_3]$ should be linear with a slope of k_1k_2/k_{-1} and intercept of $1/k_1$ as described by eq 15.

$$1/k_{obsd} = \frac{k_{-1}[py]}{k_1k_2[P(OMe)_3]} + 1/k_1 \qquad (15)$$

Kinetic data for this reaction are collected in Table II, and graphs of this type are shown in Figure 2. Data were also collected for the perdeuterated complex shown in eq 16.

$$W(CO)_3(P(C_6D_{11})_3)_2(py) + P(OMe)_3 \rightarrow (P(C_6D_{11})_3)_2W(CO)_3(P(OMe)_3) + py \qquad (16)$$

A kinetic isotope effect $k_{obsd\text{-}H}/k_{obsd\text{-}D} = 1.20 \pm 0.04$ is apparent, and confirms the importance of the agostic bond in the mechanism of the reaction.

It is clear from the graphical treatment of the data that whereas the slope of the line can be evaluated accurately at all three temperatures, only at 5 °C is it possible to evaluate the intercept, $1/k_1$, to any significant accuracy. Determination of $1/k_1$ in this way allows determination of k_{-1}/k_2, since from the slope of the line the value for k_{-1}/k_2k_1 is known. The factor k_2/k_{-1} is important since it measures the selectivity of the $W(CO)_3(PCy_3)_2$ for $P(OMe)_3$ as compared to py. Calculated rate constant data are collected in Table III. Of particular note is the high value of k_1, reflecting a $t_{1/2} = 100$ s for exchange at 5 °C, and the low value of k_2/k_{-1}, 0.06 ± 0.02. The majority of coordinatively unsaturated organometallic complexes shows selectivity factors near 1.0.[9]

Kinetic data can be used to calculate the overall activation energy using the Arrhenius equation

$$\ln [k_1k_2/k_{-1}] = -\Delta H^{\ddagger}_{total}/RT + \text{constant} \qquad (17)$$

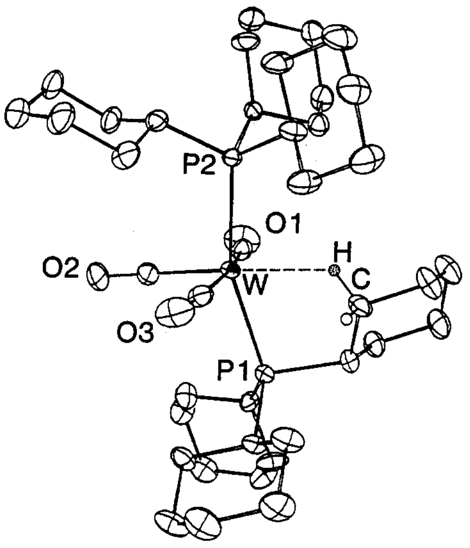

Figure 3. ORTEP drawing of $W(CO)_3(PCy_3)_2$ (**5**).

The $\ln [k_1k_2/k_{-1}]$ term can be broken down to $[\ln k_1 + \ln k_2 - \ln k_{-1}]$, and so it is clear that the activation energy calculated in this obeys eq 18. The total activation enthalpies calculated in this way are 23.9 ± 1.0 and 24.4 ± 1.2 kcal/mol for the hydrogen- and deuterium-substituted complexes, respectively.

$$\Delta H^{\ddagger}_{total} = \Delta H^{\ddagger}_1 + [\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1}] \qquad (18)$$

A reasonable estimate for the value of $[\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1}]$ can be made from the kinetic data at 5 °C. The value of k_2/k_{-1} is calculated to be 0.06 ± 0.02 and 0.035 ± 0.02 for the hydrogen- and deuterium-substituted complexes, respectively. The overall activation energy difference, $[\Delta G^{\ddagger}_2 - \Delta G^{\ddagger}_{-1}]$, is calculated to be 1.7 ± 0.4 kcal/mol. Since the data for k_2/k_{-1} are uncertain at the higher temperatures, it is not possible to separate this into enthalpies and entropies of activation. *Assuming* that the difference is due entirely to enthalpy of activation, and $\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1} = 1.7$ kcal/mol, we consider the enthalpy of activation for the k_1 step to be 22.2 ± 3.0 kcal/mol. The error limit has been increased to allow for the situation that the entire free energy of activation difference *could* be due entirely to entropy differences.

Discussion

A long-range goal in our work is determining the energetics of ligand exchange and interconversion in organometallic complexes. In this paper we report initial thermodynamic and kinetic studies of the complexes $W(CO)_3(PCy_3)_2(L)$. The steric crowding in this system is evident even in the parent complex $W(CO)_3(PCy_3)_2$. The crystal structure shown in Figure 3 clearly displays the bulky nature of the axial phosphine ligands and the presence of the W···H–C three-center "agostic" bond which fills the sixth coordination site at tungsten.[5] Ligand addition reactions such as that shown in eq 19 should actually be viewed as ligand displacement reactions in which the relatively weak W···H–C bond is displaced by a stronger ligand. An additional feature of real interest in these complexes is that they bind both hydrogen and nitrogen reversibly. Despite a number of qualitative observations there is little thermodynamic data for the binding of these important ligands.

$$W(CO)_3(PCy_3)_2 + L \rightarrow W(CO)_3(PCy_3)_2(L) \qquad (19)$$

Thermochemical data for enthalpies of addition of ligands $W(CO)_3(PCy_3)_2$ are shown in Figure 1. As discussed above, the enthalpies of these reactions are similar in

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(9) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113.
(10) Lewis, K. E.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 4650.

Table III. Calculated Rate Constants[a] for the Reaction
$W(CO)_3(PCy_3)_2(py) + P(OMe)_3 \rightarrow W(CO)_3(PCy_3)_2(P(OMe)_3) + py$

temp, °C	compd[e]	k_1k_2/k_{-1}[b]	k_1[c]	k_2/k_{-1}[d]	$k_{obsd}(H)/K_{obsd}(D)$[e]
5	H	0.436 (0.04)	0.007 (0.002)	0.06 (0.02)	1.24
	D	0.352 (0.08)	0.010 (0.004)	0.035 (0.02)	
15	H	1.88 (0.02)			1.17
	D	1.61 (0.03)			
25	H	7.95 (0.11)			1.17
	D	6.77 (0.06)			
35	H	30.7 (1.4)			1.12
	D	27.5 (2.0)			

[a] H = $W(CO)_3[P(C_6H_{11})_3]_2(py)$; D = $W(CO)_3[P(C_6D_{11})_3]_2(py)$. [b] Rate constants calculated from data in Table II, × 10^3 s^{-1}. [c] First-order rate constant, s^{-1}, calculated from intercept in Figure 2. Only for 5 °C could accurate value be obtained. [d] Ratio calculated from k_1 and k_1k_2/k_{-1}. [e] Ratio of k_1k_2/k_{-1} for H and D complexes.

toluene and THF. A surprising result is the relatively low heat of binding of carbon monoxide. Gas-phase laser photolysis studies have indicated the W–CO bond in $W(CO)_6$ to be 46 kcal/mol[10]

$$W(CO)_6 \rightarrow W(CO)_5 + CO \qquad (20)$$
$$\Delta H = +46 \text{ kcal/mol}$$

This is to be compared to the value that we have obtained for the phosphine-substituted complex:

$$W(CO)_4(PCy_3)_2 \rightarrow W(CO)_3(PCy_3)_2 + CO \qquad (21)$$
$$\Delta H = +30 \text{ kcal/mol}$$

At first sight it is tempting to ascribe this difference completely to the formation of the agostic W···H–C bond which must be on the order of 16 kcal/mol. This would be in keeping with the value of 10 kcal/mol for the $Cr(CO)_5$(heptane) bond[7] and the fact that the order of bond strengths in group VI is generally W > Mo > Cr.[6] A second factor to be considered is that even in the absence of an "agostic" interaction, there is no reason to expect the W–CO bond to be of the same strength in $W(CO)_4(PCy_3)_2$ as in $W(CO)_6$. Despite a lot of work in this area it is not clear to the authors which W–CO bond would be expected to be stronger.[11]

Spectroscopic measurements were not successful in determining the exchange energy between the agostic and nonagostic complexes.[12a] In the absence of this information we *estimate*[12b] the agostic bond strength as 10 ± 6 kcal/mol. Thus the enthalpies of addition shown in Figure 1, relative to the agostic bond, probably reflect "absolute" bond strengths about 10 kcal/mol higher, if the product did not have a W···H–C bond. Certainly the value of 30 kcal/mol for the W–CO bond seems to be very low and out of keeping with the gas-phase data.[10]

A kinetic estimate for the $W–NCCH_3$ bond strength has recently been reported[13] for the complex shown in eq 22.

$$W(CO)_3(dppm)(NCCH_3) \rightarrow W(CO)_3(dppm) + CH_3CN \qquad (22)$$
$$\Delta H^{\ddagger} = +23.5 \text{ kcal/mol}$$
$$dppm = Ph_2PCH_2PPh_2$$

While there are several important differences[14] between this complex and $W(CO)_3(PCy_3)_2(NCCH_3)$, it may represent a better model for bond strength estimates than $W(CO)_5(NCCH_3)$. The activation energy for this process can be compared to the enthalpy of reaction 23 calculated from calorimetric data. The difference (= 8 kcal/mol)

$$W(CO)_3(PCy_3)_2(NCCH_3) \rightarrow W(CO)_3(PCy_3)_2 + CH_3CN \qquad (23)$$
$$\Delta H = +15.3 \text{ kcal/mol}$$

could be due primarily to the formation of the agostic bond in $W(CO)_3(PCy_3)_2$.[14] The estimate of 10 ± 6 kcal/mol for the agostic interaction appears reasonable. The remainder of the discussion will deal primarily with relative bond strengths in this system since they are known to greater accuracy.

The order of bond strengths in Table I [$H_2 < N_2 < NCCH_3 <$ py $< P(OMe_3) <$ CO] is in keeping with synthetic observations. The free energy of binding is determined by the sum of the enthalpy and entropy components. The entropy of binding can be estimated to be on the order of 35 ± 10 eu for this reaction,[15] leading to a $T\Delta S$ term on the order of 10 ± 3 kcal/mol opposing uptake of ligand. Adopting this value would lead to approximate free energies of binding for H_2, N_2, and $NCCH_3$ of 0, –3, and –5 kcal/mol. On a synthetic basis the hydrogen and nitrogen complexes were classified[1] as "reversible" and the acetonitrile complex as "irreversible". While none of these

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(11) Logical arguments can be presented from both sides of the question of whether the W–CO bond would be stronger or weaker in $W(CO)_6$ as compared to $W(CO)_4(PR_3)_2$ if there was no agostic bond formed. Thus loss of CO is more difficult from the phosphine-substituted complexes by either thermal or photochemical methods. In addition there is a lowering of the CO stretching frequency in the phosphine complexes due to the increased back-bonding. This would imply a stronger W–CO bond in the phosphine-substituted complex. On the other hand, the coordinatively unsaturated fragment $W(CO)_3(PR_3)_2$ might be more stable than $W(CO)_5$. That is, increased donation from the basic phosphine ligands might partially compensate for the loss of the CO. Experimental determination of this will require either determination of the exact value of the agostic interaction or investigation of a system not containing this bond. Work in this direction is in progress. At the present time it seems unlikely that the difference in bond strengths exceeds our assignment of uncertainty of ±6 kcal/mol.

(12) (a) Attempts to determine the barrier for interconversion of the one agostic hydrogen with the other 23 equivalent hydrogen atoms by NMR spectroscopy were unsuccessful at temperatures as low as –70 °C. Since the splitting between the signals is not known, this cannot be used to provide an estimate for the energy barrier. It is clear from FT-IR studies (Gonzalez, A. A.; Hoff, C. D., unpublished results) that the agostic bond is retained in solution. Additional work to try to define this is in progress. (b) The estimate 10 ± 6 kcal/mol for the agostic interaction was based on the bond strength of 10 kcal/mol for $Cr(CO)_5$(heptane).[7] This value is also in keeping with other literature values.[8] The error limit is assigned arbitrarily, but it seems reasonable to assume that this bond is in the wide range of 4–16 kcal/mol implied by this estimate. The upper limit value corresponds to the full difference in enthalpy of carbonyl dissociation as shown in eq 20 and 21. The fact that the bond is retained in solution,[12a] coupled with the fact that entropic factors probably disfavor constraint of the cyclohexyl group to the bonded conformation,[15] makes it unlikely that it is weaker than the lower estimate of 4 kcal/mol.

(13) Darensbourg, D. J.; Zalewski, D. J.; Plepys, C.; Campana, C. *Inorg. Chem.* **1987**, *26*, 3727.

(14) The biggest difference is that $W(CO)_3(dppm)(CH_3CN)$ is the *fac* isomer and $W(CO)_3(PCy_3)_2(CH_3CN)$ is *mer*. In addition to being bulkier, PCy_3 should be a stronger sigma donor than dppm. Finally, it must be considered possible that the intermediate $W(CO)_3(dppm)$ also contains an agostic bond, since it is known that $Mo(CO)(dppe)_2$ does [Sato, M.; Tatsumi, T.; Kodama, T.; Hidai, M.; Uchida, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 4447].

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Table IV. Enthalpies of Substitution

$$W(CO)_3(CH_3CN)_3 + 3L \rightarrow W(CO)_3L_3 + CH_3CN \quad (A)$$

$$W(CO)_3(PCy_3)_2(CH_3CN) + L \rightarrow W(CO)_3(PCy_3)_2L + CH_3CN \quad (B)$$

ligand	ΔH_A[a]	$^1/_3\Delta H_A$[b]	ΔH_B[c]
CH_3CN	0	0	0
pyridine	−10.9	−3.6	−3.8
$P(OMe_3)_3$	−35.0	−11.6	−11.4
CO	−43.7	−14.6	−15.3

[a] All data in kcal/mol in toluene solution. Data in this column taken from: Gonzalez, A. A.; Mukerjee, S. L.; Nolan, S. P.; Hoff, C. D.; manuscript in preparation. [b] For comparison on a per mole basis. [c] Data calculated from Table I.

complexes could be classified as "irreversible" in a thermodynamic sense, the additional few kilocalories stabilization of acetonitrile may make a large practical difference in the observed stability of the acetonitrile complex. It should also be noted that in this system N_2 readily displaces H_2, also in keeping with the calorimetric results. In terms of functioning as a two-electron donor ligand, it is clear the H_2 is one of the weakest ligands known. In this system, only the agostic W···H–R bond can be viewed as being weaker and still strong enough to form a stable bond.

The measured heat of binding of molecular hydrogen is in surprising agreement with theoretical calculations. The bonding involves donation of electrons from the σ bond of H_2 to an empty metal d orbital and also back-donation from a filled metal orbital to the σ^* of H_2, much as in olefin or CO binding. The enthalpy of addition of H_2 to a model fragment, $W(CO)_3(PH_3)_2$, has been calculated to be 17 kcal/mol.[3a] This does not include allowance for the agostic bond in $W(CO)_3(PCy_3)_2$. Using our estimate of 10 ± 6 kcal/mol for this interaction leads to prediction of the enthalpy of binding of H_2 to a fragment without an agostic bond of 20 ± 7 kcal/mol. The agreement between theory and experiment is quite good in this case.

The data for addition of hydrogen can be used to estimate the values of single W–H bond strengths. There must be only a small enthalpic difference between the tautomers shown in eq 24 since spectroscopic studies[16a] have shown that the molecular hydrogen complex exists in equilibrium with the dihydride. Adopting the value

$$W(CO)_3(PR_3)_2(H_2) \rightarrow W(CO)_3(PR_3)_2(H)_2 \quad (24)$$

for the agostic interaction of 10 ± 6 kcal/mol would lead to average single W–H bond strength estimates of 62 ± 3 kcal/mol.[16b] This is considerably lower than other estimates of the W–H bond strength of 72.9 kcal/mol (Cp_2WH_2[17]) and 80.7 kcal/mol ($CpW(CO)_3H$[18]). There is good reason to believe the W–H bond is considerably stronger in $Cp_2W(H)_2$ than in $W(CO)_3(PCy_3)_2(H)_2$. Hydrogen is readily removed from the W(0) complex $(PCy_3)_2W(CO)_3(H_2)$ by simple evacuation.[1] The W(IV) complex Cp_2WH_2 can be purified by sublimation.[19] It is clear from these observations that oxidation state and

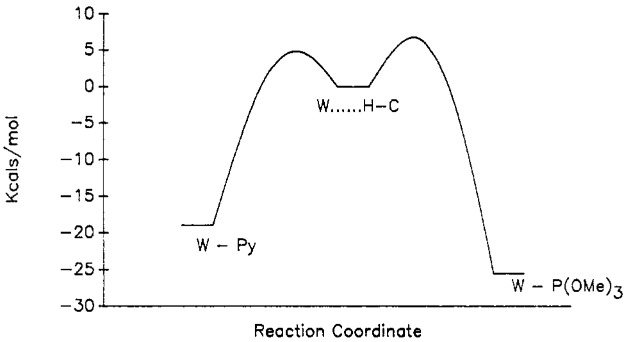

Figure 4. Potential energy diagram (enthalpy of reaction) for reaction of $W(CO)_3(PCy_3)_2(py)$ with $P(OMe)_3$.

ancillary ligands play a strong role in determining metal–hydrogen bond strength.

While it is difficult to assign "absolute" bond strengths in this system due to uncertainty about the strength of the agostic bond, relative W–L bond strengths are known to greater accuracy and provide a basis for comparison to other systems. We have recently measured the enthalpy of reaction 25 for a wide range of ligands. This allows

$$(\text{cycloheptatriene})W(CO)_3 + 3L \rightarrow L_3W(CO)_3 + \text{CHPT} \quad (25)$$

calculation of the enthalpies of ligand replacement shown in reaction 26. One-third the enthalpy of substitution of

$$L_3W(CO)_3 + 3L' \rightarrow L'_3W(CO)_3 + 3L \quad (26)$$

reaction 26 (since three moles of ligand are substituted) can be compared to the corresponding enthalpy of substitution in eq 27. These data are collected in Table IV,

$$W(CO)_3(PCy_3)_2(L) + L' \rightarrow W(CO)_3(PCy_3)_2(L') + L \quad (27)$$

using CH_3CN for comparison purposes since it is the weakest ligand for which data is available. It was expected that relatively bulky ligands such as py and $P(OMe)_3$ would show strain energies when compared to $NCCH_3$ and CO which should have much smaller cone angles.[20] Instead, there is remarkable agreement between the two systems. This work would seem to imply, as recently concluded by Bercaw and Bryndza,[21] that steric factors are unimportant in determining the M–X bond strength. That conclusion must breakdown at some point. The $W(CO)_3(PCy_3)_2$ and related systems provide an ideal system to test this,[22] and additional work in this regard is in progress.

Our initial investigation of the kinetics of reaction 28 was prompted out of practical interests. It was desired

$$W(CO)_3(PCy_3)_2(py) + P(OMe)_3 \rightarrow W(CO)_3(PCy_3)_2(P(OMe)_3) + py \quad (28)$$

to check our thermochemical results by measuring directly the heat of this reaction.[23] Since the pyridine ligand is strongly bound, we expected this reaction to be prohibitively slow for calorimetric measurements. To our surprise the reaction, in the absence of added pyridine, occurred almost immediately upon adding $P(OMe)_3$. Such a rapid reaction was not expected for an "irreversible" complex.

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(16) (a) From variable-temperature NMR experiments it appears that the enthalpy of reaction 24 is on the order of +2 kcal/mol (Khalsa, G. R. K.; Unkefer, C. J.; Kubas, G. J.; Ryan, R. R. *Abstracts of Papers*, 3rd Chemical Congress of North America, Toronto, June 1988, Paper 291). (b) The W–H bond strength is estimated on the basis of the reaction with H_2 estimated to be exothermic by 20 kcal/mol if no agostic bond were formed. Since the H–H bond is broken (104 kcal/mol), then 2W–H must equal 124, and hence W–H = 62 kcal/mol.

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(22) The fact that steric factors must become important at some point in this system is illustrated by the fact that $W(CO)_3(PCy_3)_2$ will not bind a number of ligands such as tertiary amines or an additional mole of PCy_3. In the *fac*-$W(CO)_3L_3$ system these have high heats of binding.[6]

(23) Direct measurement has been performed, and it agrees within experimental error with the calculated value.

Since thermochemical data were available for this reaction, additional kinetic studies were indicated. Determination of the activation energy for reaction 28 would allow comparison of kinetic and thermodynamic bond strength estimates. An additional aspect of interest was the role of the M···H–C agostic bond in this process. Standard kinetic studies confirmed the mechanism outlined by eq 9. The kinetic isotope effect $k_H/k_D = 1.2$, showed that the reaction must involve interaction of the tungsten center with the cyclohexyl group of the phosphine. The activation parameters, when coupled with the thermochemical data, give some suggestion as to the mechanism of this reaction.

The reaction profile in Figure 4 combines the thermochemical data in Figure 1 with the enthalpy of activation of 24 kcal/mol for $\Delta H^{\ddagger}_1 + [\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1}]$ with an estimate of 2.0 kcal/mol for $[\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1}]$ based on the value of 0.06 for k_2/k_{-1}. It should be noted that the kinetic selectivity ($k_{-1}/k_2 = 17$) of the reactive intermediate $(PCy_3)_2W(CO)_3$ is high and that it favors the thermodynamically less stable pyridine complex. The selectivities of most such reaction intermediates have been shown to be small ($k_{-1}/k_2 = 1.0$).[9] The high kinetic selectivity in this system may reflect the fact that the intermediate is a stable complex. Since pyridine has a smaller cone angle[20] than $P(OMe)_3$, it is preferred kinetically despite a smaller heat of binding.

The major question regarding the mechanism of this substitution is whether replacement of coordinated pyridine is a concerted process. That is, is it an intramolecular associative reaction with the W···H–C ligand rotating into position and displacing the pyridine, or does the pyridine ligand dissociate followed by formation of the agostic bond. The activation energy is only about 3 kcal/mol larger than the ground-state energy difference as shown in Figure 4. If the agostic interaction does have a value on the order of 10 kcal/mol, then it must be at least partially formed during the expulsion of pyridine. The alternative interpretation is that the W···H–C interaction is very weak. In view of the thermochemical experiments that show a close correspondence between relative heats of substitution in this and related systems, it seems more likely that the mechanism is a concerted one.

Conclusion

Thermochemical data reported for addition of ligands to $W(CO)_3(PCy_3)_2$ showed binding of molecular hydrogen and nitrogen to be relatively weak, in keeping with the "reversible" nature of this addition. The value for addition of H_2 was in agreement with theoretical calculations done earlier.[4] For the ligands $NCCH_3$, py, $P(OMe)_3$, and CO, there was close correspondence of stability between the $W(CO)_3(PCy_3)_2(L)$ system and the $L_3W(CO)_3$ complexes. This was most likely due to the fact tht the ligands used were not bulky enough to induce large steric repulsions.[22] The enthalpy of addition of CO to $W(CO)_3(PCy_3)$ was unusually low, probably due to the fact that addition reactions involve cleaving the W···H–C agostic bond.

Kinetics of substitution for the complex $W(CO)_3(PCy_3)_2(py)$ also showed the importance of the agostic bond in these compounds. A kinetic isotope effect, $k_H/k_D = 1.2$, was observed when $W(CO)_3(P(C_6D_{11})_3)_2(py)$ was used in place of $W(CO)_3(P(C_6H_{11})_3)_2(py)$. The activation energy for dissociation of pyridine from this complex is 22 ± 3 kcal/mol, only 3 kcal/mol higher than the thermodynamic value for this dissociation. Since the agostic bond is estimated to be on the order of 10 kcal/mol, it is proposed that the reaction mechanism involves concerted displacement of the W–pyridine bond by the cyclohexyl group on the phosphine ligand. Additional kinetic and thermodynamic studies on these and related complexes are in progress.

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A Kinetic Investigation of Some Electronic Factors and Ligand Effects in the Heck Reaction with Allylic Alcohols

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The effect of several factors (salt, ligand, base, temperature, aryl iodide) on the initial reaction rate of the palladium-catalyzed arylation of pent-1-en-3-ol and but-3-en-2-ol was kinetically studied, and the activation parameters were calculated for the latter. It was shown that a tertiary amine not only neutralizes the hydrogen iodide formed in the reaction but also acts as a ligand of the palladium atom. The resulting catalytic species was very efficient, allowing the reaction to be carried out at low temperatures in good yields. A linear Hammett relationship ($\rho = -1.6$) was established with a series of para-substituted aryl iodides. All these results suggest that the rate-limiting step of the reaction is the oxidative addition of the halogenated compound to the palladium.

Introduction

The palladium-catalyzed arylation of double bonds[1] known as the Heck reaction[2] is generally applied to electron-deficient olefins.[3] With allylic alcohols, arylated ketones are obtained, but the reaction is rather sluggish.[4] There have been a number of studies aimed at both improving this reaction and determining its mechanism.[3]

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