Effect of Ancillary Ligation on the Relative Bond Disruption Enthalpies of Ru−H and Ru−Cl Bonds in $Cp(PR_3)_2RuX$ ($PR_3 = PMe_3, PMe_2Ph, PMePh_2, PPh_3$; X = H, Cl)

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Received May 18, 2000

The ruthenium chloride and hydride complexes $Cp(PR_3)_2RuH$ {X = Cl; $PR_3 = PMe_3$ (**1**), PMe_2Ph (**2**), $PMePh_2$ (**3**), PPh_3 (**4**); X = H; $PR_3 = PMe_3$ (**5**), PMe_2Ph (**6**), $PMePh_2$ (**7**), PPh_3 (**8**)} were studied by spectroscopy and solution calorimetry. The structures of **2** and **3** are reported and complete the structural characterization of the series **1**−**4**. In this series, the Ru−Cl distance (2.449 ± 0.007 Å) remains constant, while the Ru−PR_3 distance increases in the order **1** < **2** < **3** < **4**. The ruthenium hydrides **5**−**8** were prepared from the reaction of the corresponding ruthenium chloride with KOMe in methanol. Spectroscopic data on hydrides **5**−**8** indicated that the ruthenium hydride interaction decreases in the order **5** > **6** > **7** > **8**. Enthalpies of reaction for the hydride/chloride metatheses of **5**−**8** with chlorocarbons ($CHCl_3$ or CCl_4) were studied by solution calorimetry and allowed for the determination of Ru−Cl bond disruption enthalpies (BDEs) relative to the corresponding Ru−H BDEs. [BDE(Ru−Cl) − BDE(Ru−H)] values covered a 6 kcal/mol range with an average of 21.4 ± 2.5 kcal/mol. The magnitude of [BDE(Ru−Cl) − BDE(Ru−H)] correlated with the number of methyl groups on the phosphine and was dependent on the electronic and steric properties of the phosphine.

Introduction

Transition metal hydrides are involved in many stoichiometric and catalytic processes.[1−3] Thus, knowledge of the bond strength between hydrogen and a transition metal system is important to gain a fundamental understanding of these processes. Recently, we reported the formation of ruthenium silyl complexes from the reaction of ruthenium hydrides with chlorosilanes[4,5] and the $RuCl_2(PPh_3)_3$-catalyzed hydrosilylation of phenylacetylene.[6] In both of these processes, the making and/or breaking of Ru−H, Ru−Cl, and Ru−Si bonds was observed to be dependent on the substituents attached to ruthenium and silicon. As part of our ongoing interest in substituent effects, the ruthenium complexes $Cp(PR_3)_2RuX$ ($PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$, PPh_3; X = H, Cl) were studied. This paper presents thermochemical data on the hydride/chloride metathesis reaction, as well as spectroscopic and structural data, to evaluate the effect of ancillary ligation on the Ru−H and Ru−Cl bonds.

Results and Discussion

Structures of $Cp(PR_3)_2RuCl$ ($PR_3 = PMe_2Ph$ (2), $PMePh_2$ (3)). The crystal structures of $Cp(PMe_2Ph)_2RuCl$ (**2**) and $Cp(PMePh_2)_2RuCl$ (**3**) have been determined by X-ray diffraction at 295 K. Perspective views of **2** and **3** are shown in Figures 1 and 2, respectively. The geometry of **2** and **3** can be described in terms of a “three-legged piano stool”, with the legs comprising the phosphine and chloride ligands. The structures of **2** and **3**, in combination with the reported structures of $Cp(PMe_3)_2RuCl$ (**1**)[7] and $Cp(PPh_3)_2RuCl$ (**4**),[7] complete the crystallographic characterization of this class of complexes. Pertinent interatomic distances and angles for ruthenium chloride complexes **1**−**4** are presented in Table 1.

A comparison of the structural data for ruthenium chloride complexes **1**−**4** indicated that these complexes were surprisingly similar. There was essentially no change in the Ru−Cl (2.449 ± 0.007 Å) and the Ru−Cp (1.849 ± 0.002 Å) distances over the range of phosphine ligands. A similar insensitivity in the Ru−Cl (2.453 ±

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[1] *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH Publishers: New York, 1992; p 399.

[2] Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis,* 2nd ed.; John Wiley & Sons: New York, 1992; p 342.

[3] *Comprehensive Handbook on Hydrosilylation*; Marciniec, B., Ed.; Pergamon Press: New York, 1992.

[4] Lemke, F. R. *J. Am. Chem. Soc.* **1994**, *116*, 11183−11184.

[5] Lemke, F. R.; Galat, K. J.; Youngs, W. J. *Organometallics* **1999**, *18*, 1419−1429.

[6] Yardy, N. M.; Lemke, F. R. *Main Group Chem.* **2000**, in press.

[7] Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1398−1405.

10.1021/om000420x CCC: $19.00
Publication on Web 10/12/2000

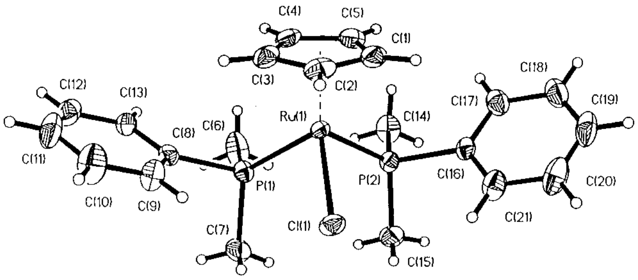


Figure 1. Perspective view of the molecular structure of one of the independent molecules of $Cp(PMe_2Ph)_2RuCl$ (**2**) with atom labels provided for all unique non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 30% probability. In this molecule, the C(8)–P(1)···P(2)–C(16) torsion angle was 24.9°. In the other independent molecule in the unit cell, one PMe_2Ph group was rotated about the Ru–P bond by ~150°, so the corresponding C(8)–P(1)···P(2)–C(16) torsion angle was 175.2°.

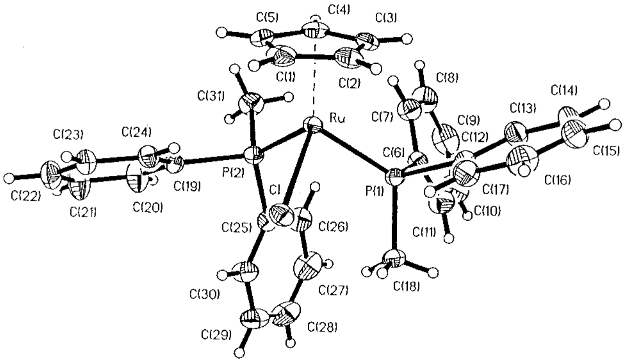


Figure 2. Perspective view of the molecular structure of $Cp(PMePh_2)_2RuCl$ (**3**) with atom labels provided for all unique non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 30% probability.

Table 1. Selected Interatomic Distances (Å) and Bond Angles (deg) for $Cp(PR_3)_2RuCl$ Complexes 1–4

	$1^{a,b}$	2^{a}	3	4^{b}	av^{c}
Ru–Cl	2.451(6) 2.440(5)	2.455(2) 2.436(2)	2.456(1)	2.453(2)	2.449(7)
Ru–P1	2.273(5) 2.280(6)	2.292(2) 2.283(2)	2.295(1)	2.337(1)	2.293(18)
Ru–P2	2.275(6) 2.273(6)	2.277(2) 2.288(2)	2.302(1)	2.335(1)	2.292(19)
Ru–Cp^{d}	1.850 1.849	1.846 1.852	1.849	1.847	1.849(2)
P1–Ru–P2	94.7(2) 95.0(2)	94.47(6) 96.14(6)	95.58(3)	103.99(4)	96.6(29)
P1–Ru–Cl	89.7(2) 90.6(2)	90.83(6) 91.34(6)	89.23(3)	89.05(3)	90.1(7)
P2–Ru–Cl	90.1(2) 88.9(2)	90.70(5) 86.40(5)	92.22(3)	90.41(4)	89.8(16)
Cp-Ru-P1^{d}	122.7 123.8	125.2 126.1	124.6	121.5	124.0(13)
Cp-Ru-P2^{d}	126.3 124.7	123.8 124.3	123.5	121.4	124.0(13)
Cp-Ru-Cl^{d}	123.3 124.0	122.4 121.9	122.5	122.5	122.8(6)

[a] Two independent molecules per unit cell. [b] Structural data from ref 7. [c] Average interatomic distances and angles for **1**–**4**. Values in parentheses represent the 95% confidence limits in the last digits. [d] Cp refers to the centroid of the cyclopentadienyl ring.

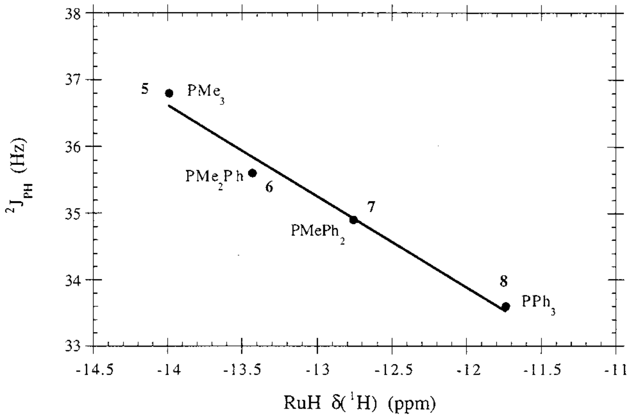
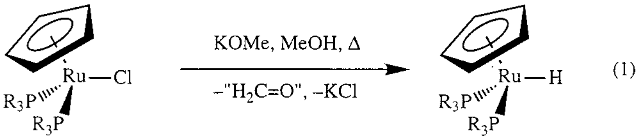


Figure 3. $^2J_{PH}$ versus the RuH ^{1}H NMR chemical shift for ruthenium hydride complexes $Cp(PR_3)_2RuH$ (**5**–**8**): slope = −1.37 ± 0.13 Hz per ppm, $R = 0.991$.

0.002 Å) distance was observed in the structures of the related $Cp^*(PR_3)_2RuCl$ complexes,[8] and it is interesting to note that changing the Cp group to the more electron-donating Cp* group had no effect on the Ru–Cl distance. The average P–Ru–Cl angle remained constant (90.0 ± 0.8°) even though the number of phenyl groups and the steric demand of the phosphines significantly increased from **1** (with PMe_3, $\theta = 118°$) to **4** (with PPh_3, $\theta = 145°$).[9] The P1–Ru–P2 angle was essentially constant in complexes **1**–**3** (95.2 ± 0.6°) but increased dramatically in the PPh_3 complex **4** (103.99°); an opposite trend was observed in the average Cp–Ru–P angles (124.5 ± 0.7° for **1**–**3** versus 121.5 ± 0.1° for **4**). The most significant structural change was observed in the Ru–P distance, which gradually increased with the number of phenyl groups on phosphorus: **1** (2.28 Å) < **2** (2.29 Å) < **3** (2.30 Å) < **4** (2.34 Å). Overall, the coordination environment around the ruthenium center was not significantly affected by changes in the substituents on phosphorus.

Ruthenium Hydride Complexes. Ruthenium hydrides **5**–**8** were prepared in high yields by a modification of the β-hydride elimination method involving the reaction of ruthenium chlorides **1**–**4** with KOMe in refluxing MeOH (eq 1).[10] Hydrides **6** and **7** were new compounds and were characterized by elemental analysis as well as NMR (^{1}H and ^{31}P) and IR spectroscopies. In the ^{1}H NMR spectra (CD_2Cl_2), the hydride resonances for **5**–**8** were observed as characteristic triplets ($^2J_{PH}$ = 33–37 Hz) over the −11.5 to −14 ppm region.



(1)

PR$_3$	PMe$_3$	PMe$_2$Ph	PMePh$_2$	PPh$_3$
Cl	1	2	3	4
H	5	6	7	8

A linear inverse relationship was observed between $^2J_{PH}$ and RuH ^{1}H chemical shift (Figure 3). The hydride resonances moved upfield and the magnitude of $^2J_{PH}$ increased as the number of methyl groups on the

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[8] Smith, D. C., Jr.; Haar, C. M.; Luo, L.; Li, C.; Cucullu, M. E.; Mahler, C. H.; Nolan, S. P.; Marshall, W. J.; Jones, N. L.; Fagan, P. J. *Organometallics* **1999**, *18*, 2357–2361.

[9] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

[10] Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980–3987.

Table 2. Hydride/Chloride Metathesis Reaction Enthalpies and Relative BDE(Ru−H) Values (kcal/mol) for Cp(PR$_3$)$_2$RuH

$$Cp(PR_3)_2RuH_{(soln)} + R-Cl_{(soln)} \xrightarrow[30\ °C]{CH_2Cl_2} Cp(PR_3)_2RuCl_{(soln)} + R-H_{(soln)}$$

PR$_3$	R−Cl	$-\Delta H_{rxn}$[a]	BDE(R−Cl) − BDE(R−H)[b]	BDE(Ru−Cl) − BDE(Ru−H)[c]	χ_d[d]	θ[e]
PMe$_3$	HCl$_2$C−Cl	45.7(0.3)	−21.3(0.1)	24.4(0.3)	8.55	118
PMe$_2$Ph	HCl$_2$C−Cl	43.8(0.4)	−21.3(0.1)	22.5(0.4)	10.60	122
PMePh$_2$	HCl$_2$C−Cl	41.2(0.2)	−21.3(0.1)	19.9(0.2)	12.10	136
PPh$_3$	Cl$_3$C−Cl	43.7(0.3)	−24.8 (0.1)	18.9(0.3)	13.25	145

[a] Corrected for the enthalpy of solution of the corresponding ruthenium hydride in CH$_2$Cl$_2$. [b] [BDE(R−Cl) − BDE(R−H)] values derived from ΔH_f° gas-phase data for RH, RCl, H$^•$, and Cl$^•$ taken from ref 33. [c] [BDE(Ru−Cl) − BDE(Ru−H)] = $-\Delta H_{rxn}$ + [BDE(R−Cl) − BDE(R−H)]. [d] PR$_3$ σ-donicity from ref 15. [e] PR$_3$ cone angle from ref 9.

phosphine increased. A similar inverse relationship was observed between $^2J_{PH}$ and NiH ^{1}H chemical shift in the complexes *trans*-HNi(X)(PCy$_3$)$_2$ (X = Ph, Me, I, Br, Cl, etc.).[11] The upfield chemical shifts indicated greater electronic shielding of the hydrogen (the hydrogen is "buried" in the ruthenium's electron cloud), which suggested stronger ruthenium−hydrogen interaction. In **5**−**8**, stronger ruthenium−hydrogen interaction was also supported by increased communication between phosphorus and hydrogen in the form of larger $^2J_{PH}$ values: **5** (36.8 Hz) > **6** (35.6 Hz) > **7** (34.9 Hz) > **8** (33.6 Hz).

Hydride/Chloride Metathesis Studies. Halogenating agents have been used in organometallic thermochemistry to determine metal−hydride and metal−halide bond disruption enthalpy (BDE) values and trends.[12−14] In the present study, we have found that ruthenium hydrides **5**−**7** readily underwent hydride/chloride metathesis with CHCl$_3$ (eq 2). Hydride **8**, on the other hand, did not readily react with CHCl$_3$, but rapid hydride/chloride metathesis was observed with CCl$_4$ (eq 3). This set of hydride/chloride metathesis reactions provided direct solution calorimetric access to enthalpy of reactions which allowed for determination of ruthenium−chloride BDE values relative to the corresponding ruthenium−hydride BDE, [BDE(Ru−Cl) − BDE(Ru−H)].

$$Cp(PR_3)_2RuH + CHCl_3 \xrightarrow[30\ °C]{CH_2Cl_2} Cp(PR_3)_2RuCl + CH_2Cl_2 \qquad (2)$$

$$PR_3 = PMe_3, PMe_2Ph, PMePh_2$$

$$Cp(PPh_3)_2RuH + CCl_4 \xrightarrow[30\ °C]{CH_2Cl_2} Cp(PPh_3)_2RuCl + CHCl_3 \qquad (3)$$

Enthalpies of reaction with the appropriate chlorinating agents are reported in Table 2. All reported enthalpies of reaction were solution phase values and took into account the enthalpy of solution of the appropriate ruthenium hydride complex. The reactions described in eqs 2−3 were examined by NMR spectroscopy prior to performing the calorimetric experiments and were determined to be rapid and quantitative under calorimetric conditions. All reactions investigated led to unique products under the calorimetric conditions as determined by NMR spectroscopy.

The hydride/chloride metathesis reaction of hydrides **5**−**7** with CHCl$_3$ (eq 2) became more exothermic (i.e., $-\Delta H_{rxn}$ increased) as the number of methyl groups on phosphorus increased: **7** (41.2 kcal/mol) < **6** (43.8 kcal/mol) < **5** (45.7 kcal/mol). This trend in the enthalpies of reaction was attributed to the change in electronic properties of the phosphine ligands and paralleled the σ-donor ability[15] of the phosphine ligands (PMePh$_2$ < PMe$_2$Ph < PMe$_3$). The greater σ-donor and poorer π-acceptor ability of PPh$_3$ compared to CO also explained why the hydride/chloride metathesis reaction of hydride **8** with CCl$_4$ (eq 3, $\Delta H = -43.7$ kcal/mol) was more exothermic than the hydride/chloride metathesis reaction of Cp*(CO)$_2$RuH with CCl$_4$ (eq 4).[14]

$$Cp^*(CO)_2RuH + CCl_4 \xrightarrow[30\ °C]{THF} Cp^*(CO)_2RuCl + CHCl_3 \qquad (4)$$

$$\Delta H = -41.1 \pm 0.6 \text{ kcal/mol}$$

BDE(Ru−Cl) was greater than BDE(Ru−H) for each chloride/hydride pair studied; consistent with previously investigated ruthenium,[14] molybdenum,[16,17] and iridium[18] systems. The [BDE(Ru−Cl) − BDE(Ru−H)] differences covered a 6 kcal/mol range with an average of 21.4 ± 2.5 kcal/mol. This [BDE(Ru−Cl) − BDE(Ru−H)] difference was significantly larger than the [BDE(Ru−Cl) − BDE(Ru−H)] differences observed for Cp*(CO)$_2$RuX (15.7 kcal/mol)[14] and Cp*(dppe)RuX (15.0 kcal/mol)[14] and reflects the greater σ-donicity of the monodentate phosphines PMe$_{3-n}$Ph$_n$ compared to CO and dppe.

A definite trend in the [BDE(Ru−Cl) − BDE(Ru−H)] difference data was also observed. A plot of [BDE(Ru−Cl) − BDE(Ru−H)] as a function of the number of methyl groups in the chloride/hydride pairs exhibited a linear relationship (Figure 4). Replacing a phenyl group with a methyl group changed the electronic as well as the steric properties of the phosphines. A QALE[15] analysis was used to evaluate the dependence of [BDE(Ru−Cl) − BDE(Ru−H)] on the electronic (σ-donicity, χ_d) and steric (cone angle, θ) properties of the phosphines (eq 5). This analysis indicated that both the

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(11) Darensbourg, M. Y.; Ludwig, M.; Riordan, C. G. *Inorg. Chem.* **1989**, *28*, 1630−1634.

(12) Simões, J. A. M.; Beauchanp, J. L. *Chem. Rev.* **1990**, *90*, 629−688.

(13) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844−7853.

(14) Luo, L.; Li, C.; Cucullu, M. E.; Nolan, S. P. *Organometallics* **1995**, *14*, 1333−1338.

(15) Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1990**, *9*, 1758−1766.

(16) Nolan, S. P.; de la Vega, R. L.; Hoff, C. D. *J. Organomet. Chem.* **1986**, *315*, 187−199.

(17) Calado, J. C. G.; Dias, A. R.; Simões, J. A. M. *J. Organomet. Chem.* **1979**, *174*, 77−80.

(18) Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.; Newman, L. J.; Buchanan, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 3143−3145.

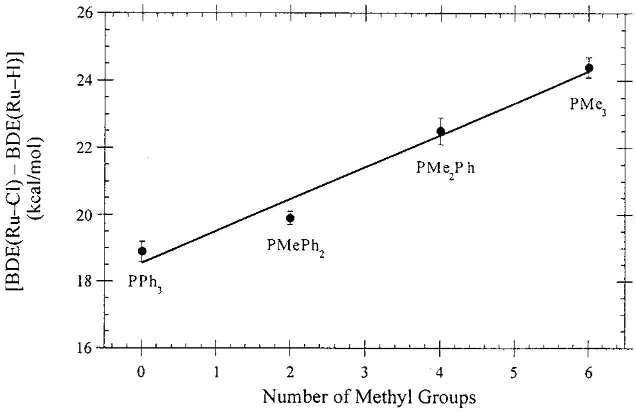

Figure 4. [BDE(Ru−Cl) − BDE(Ru−H)] versus number of methyl groups in the $Cp(PR_3)_2RuX$ complexes **1**−**8**: slope = 0.96 ± 0.11 kcal/mol per methyl group, $R = 0.987$.

steric and electronic contributions of the phosphines were significant in determining [BDE(Ru−Cl) − BDE(Ru−H)]. No apparent steric threshold was observed, and the magnitude of the electronic contribution was larger than the steric contribution in determining [BDE(Ru−Cl) − BDE(Ru−H)].

$$[\mathrm{BDE(Ru{-}Cl)} - \mathrm{BDE(Ru{-}H)}]\ (\text{in kcal/mol}) = -[0.84 \pm 0.40]\chi_d - [0.06 \pm 0.06]\theta + (39.15 \pm 4.39) \quad (5)$$

$$n = 4;\ R^2 = 0.973$$

The [BDE(Ru−Cl) − BDE(Ru−H)] data in Table 2 and Figure 4 were consistent with three scenarios. (1) Based on the constancy of the Ru−Cl bond lengths, absolute BDE(Ru−Cl) may be constant regardless of the $PMe_{3-n}Ph_n$ ligation. Absolute BDE(Ru−H) would then decrease with increasing number of phosphine methyl groups, a trend inconsistent with the $^2J_{PH}$ data and the σ-donicity of the phosphines. (2) On the other hand, absolute BDE(Ru−H) may be constant regardless of $PMe_{3-n}Ph_n$ ligation, consistent with the observation that BDE(Cr−H) did not change when PPh_3 was replaced with PEt_3 in $Cp(CO)_2(PR_3)CrH$ complexes.[19] Absolute BDE(Ru−Cl) would then increase with the number of phosphine methyl groups, a trend inconsistent with the Ru−Cl bond length data. (3) Alternatively, absolute values of both BDE(Ru−Cl) and BDE(Ru−H) may increase with the number of phosphine methyl groups, but with BDE(Ru−Cl) increasing at a faster rate than BDE(Ru−H).

Which scenario was active in **1**−**8** could not be determined at this point due to a lack of absolute values for either BDE(Ru−H) or BDE(Ru−Cl) as a function of $PMe_{3-n}Ph_n$ ligation. BDE differences in solution were the only reliable information obtainable from the thermochemical experiments employed in this study. We know that the energy difference, [BDE(Ru−Cl) − BDE(Ru−H)], increases with the number of phosphine methyl groups, but we do not know at this time how the energy scales for the $Cp(PR_3)_2Ru$ moieties relate to each other.

Experimental Section

General Procedures. All manipulations of oxygen- or water-sensitive compounds were carried out either under an atmosphere of argon by using Schlenk or vacuum-line techniques or under an argon atmosphere in a MBraun drybox.[20] ^{1}H NMR (400 and 250 MHz) spectra were recorded on a Varian VXR 400S and a Brüker AC-250 spectrometer, respectively. The ^{1}H chemical shifts were referenced to the residual proton peak of the solvent ($CDHCl_2$, δ 5.32). IR spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer. Elemental analyses were carried out by Oneida Research Services. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80), which was periodically calibrated using the TRIS reaction[21] or the enthalpy of solution of KCl in water.[22] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[23,24] and typical procedures are described below. Only materials of high purity, as indicated by IR and NMR spectroscopies, were used in the calorimetric experiments.

Materials. $Cp(PR_3)_2RuCl$ ($PR_3 = PMe_3$,[7,25] PMe_2Ph,[26] $PMePh_2$,[26] PPh_3),[27] $Cp(PMe_3)_2RuH$,[10] and $Cp(PPh_3)_2RuH$[28] were prepared according to literature procedures. All solvents were transferred under vacuum. Hexane was distilled from sodium/benzophenone and stored over $[Cp_2TiCl]_2ZnCl_2$.[29] Dichloromethane was distilled from and stored over CaH_2. Methanol was dried and stored over Mg. Dichloromethane-d_2 was dried over P_2O_5 and stored over CaH_2. KOMe was prepared by reacting solid K with excess MeOH in Et_2O, collecting the solid by filtration, and drying the white solid under vacuum.

$Cp(PMePh_2)_2RuH$ (3). This method was adapted from the literature preparation of $Cp(PMe_3)_2RuH$.[10] MeOH (30 mL) was added by vacuum transfer to a flask charged with $Cp(PMePh_2)_2RuCl$ (1.0 g, 1.66 mmol) and KOMe (500 mg, 7.13 mmol). The orange reaction mixture was heated to reflux for 4−5 h, after which time the now yellow reaction mixture was evaporated to dryness under vacuum. The reaction residue was extracted with Et_2O, until the extracts were colorless, and filtered through Celite. The yellow filtrate was evaporated to dryness under vacuum to give $Cp(PMePh_2)_2RuH$ as a pale yellow solid (794 mg, 79%; typical yields were 75−85%). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.32 (m, 20H, Ph), 4.34 (s, 5H, Cp), 1.52 (filled-in-doublet, $^2J_{PH} + {}^4J_{PH} = 7.9$ Hz, 6H, PMe), −12.76 (t, $^2J_{PH} = 34.9$ Hz, 1H, RuH). $^{31}P\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 31.23 (s). IR (CH_2Cl_2): ν(Ru−H) 1896 (br) cm^{-1}. Anal. Calcd for $C_{31}H_{32}P_2Ru$: C, 65.60; H, 5.68. Found: C, 65.47; H, 5.38.

$Cp(PMe_2Ph)_2RuH$(2). $Cp(PMe_2Ph)_2RuH$ was prepared from the reaction of $Cp(PMe_2Ph)_2RuCl$ (1.0 g, 2.1 mmol) with KOMe (0.70 g, 10.0 mmol) in MeOH as described above for $Cp(PMePh_2)_2RuH$. $Cp(PMe_2Ph)_2RuH$ was further purified by sublimation at 100 °C (<0.01 mmHg) to yield 752 mg (82%) of bright yellow, microcrystalline solid. Typical yields were 75−85%. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 7.43 (m, 10H, Ph), 4.57 (s, 5H, Cp), 1.42 (filled-in-doublet, $^2J_{PH} + {}^4J_{PH} = 7.9$ Hz, 12H,

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[19] Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D.; Roper, G. C. *J. Am. Chem. Soc.* **1990**, *112*, 5657−5658.

[20] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

[21] Ojelund, G.; Wadsö, I. *Acta Chem. Scand.* **1968**, *22*, 1691−1699.

[22] Kilday, M. V. *Res. Natl. Bur. Stand. (U.S.)* **1980**, *85*, 467−481.

[23] Nolan, S. P.; Hoff, C. D.; Landrum, J. T. *J. Organomet. Chem.* **1985**, *282*, 357−362.

[24] Mukerjee, S. L.; Nolan, S. P.; Hoff, C. D.; de la Vega, R. *Inorg. Chem.* **1988**, *27*, 81−85.

[25] Treichel, P. M.; Komar, D. A. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 205−218.

[26] Lomprey, J. R.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518−5523.

[27] Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 78−84.

[28] Davies, S. G.; Moon, S. D.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1278−1279.

[29] Sekutowski, D. G.; Stucky, G. D. *Inorg. Chem.* **1975**, *14*, 2192−2199.

Table 3. X-ray Crystallographic Data for $CpRu(PMe_2Ph)_2Cl$ (2) and $CpRu(PMePh_2)_2Cl$ (3)

	2	**3**
empirical formula	$C_{21}H_{27}ClP_2Ru$	$C_{31}H_{31}ClP_2Ru$
cryst dimens, mm	0.12 × 0.32 × 0.62	0.20 × 0.36 × 0.60
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
a, Å	16.106(1)	9.244(1)
b, Å	14.220(1)	15.079(2)
c, Å	37.378(4)	19.991(2)
α, deg	90	90
β, deg	90	94.377(8)
γ, deg	90	90
volume, Å^3	8560.8(1.3)	2778.3(5)
Z	16	4
fw, amu	477.89	602.02
calc density, g/cm^3	1.483	1.439
μ, cm^{-1}	10.09	7.94
F(000)	3904	1232
temperature, K	295 ± 2	295 ± 2
scan type	ω, variable	ω, variable
scan rate, deg/min	4.0−20.0	4.0−10.0
2θ, deg	5.0−50.0	3.4−50.0
2θ, centered reflns	10−25	14−25
reflns sampled	$h\ (-1 \leq h \leq 19)$	$h\ (-1 \leq h \leq 10)$
	$k\ (-1 \leq k \leq 16)$	$k\ (-1 \leq k \leq 17)$
	$l\ (-44 \leq l \leq 1)$	$l\ (-23 \leq l \leq 23)$
no. of reflns collected	9040	6322
no. of unique data	7515 ($R_{int} = 0.0402$)	4871 ($R_{int} = 0.0175$)
no. of data, $I > 2\sigma(I)$	4679	3837
R indices, $I > 2\sigma(I)$	R1 = 0.0456; wR2 = 0.0746	R1 = 0.0285; wR2 = 0.0569
R indices, all data	R1 = 0.1011; wR2 = 0.0927	R1 = 0.0470; wR2 = 0.0641
σ_1, GOF	1.001	1.039
weighting, *a* and *b*	0.0280, 0.0000	0.0262, 0.2493
no. of variables	460	319
max. diff peak and hole	0.438, −0.402	0.338, −0.265

PMe), −13.43 (t, $^2J_{PH} = 35.6$ Hz, 1H, RuH). $^{31}P\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 29.04 (s). IR (CH_2Cl_2): ν(Ru−H) 1904 (br) cm^{-1}. Anal. Calcd for $C_{21}H_{28}P_2Ru$: C, 56.88; H, 6.36. Found: C, 56.66; H, 6.02.

Ruthenium Hydride/Chloride Metathesis: ^{1}H NMR Studies. The H/Cl metathesis reactions were examined by ^{1}H NMR spectroscopy prior to every set of calorimetric experiments. An excess of chlorocarbon ($CHCl_3$ or CCl_4) was added to a CD_2Cl_2 solution of a ruthenium hydride. After vigorous mixing, the reactions were monitored by ^{1}H NMR spectroscopy and were found to be rapid and quantitative, conditions necessary for accurate and meaningful calorimetric results. These criteria were satisfied for all of the hydride/chloride metathesis reactions investigated.

Ruthenium Hydride/Chloride Metathesis: Calorimetric Measurements. The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20−30 mg sample of recrystallized $Cp(PPh_3)_2RuH$ was accurately weighed into the lower vessel, and it was closed and sealed with 1.5 mL of mercury. Four milliliters of a stock solution of CCl_4 [5 mL in 25 mL of CH_2Cl_2] was added, and the remainder of the cell was assembled, removed from the glovebox, and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no ruthenium hydride complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (about 2 h), the reaction was initiated by inverting the calorimeter. At the end of the reaction (1−2 h), the vessels were removed from the calorimeter, taken into the glovebox, and opened, and an NMR tube was filled under inert atmosphere. An NMR spectrum of each product was recorded using this procedure. Conversion to $Cp(PPh_3)_2RuCl$ was found to be quantitative under these reaction conditions. The enthalpy of reaction, −36.9 ± 0.1 kcal/mol, represents the average of five individual calorimetric determinations. This methodology represents a typical procedure involving all organometallic compounds and all reactions investigated in the present study.

Calorimetric Determination of the Enthalpy of Solution for the Ruthenium Hydrides in CH_2Cl_2. To consider all species in solution, the enthalpy of solution for the ruthenium hydrides had to be directly measured. The calorimeter cells were loaded in the exact fashion as in the example described above with the exception that no CCl_4 was introduced into the reaction cell. The measured enthalpy of solution for $Cp(PPh_3)_2RuH$ is 6.7 ± 0.2 kcal/mol and represents seven separate determinations. To ensure that no decomposition had occurred during the thermal equilibration at 30 °C, a CH_2Cl_2 solution of $Cp(PPh_3)_2RuH$ was maintained at 30 °C for 3 h; the solvent was then removed and the residue examined by NMR spectroscopy. No decomposition of the ruthenium hydrides in CH_2Cl_2 was observed during this time.

X-ray Crystal Structure Determinations of $Cp(PMe_2Ph)_2RuCl$ (2) and $Cp(PMePh_2)_2RuCl$ (3). Crystals suitable for X-ray diffraction analysis were grown by vapor diffusion of hexanes into saturated CH_2Cl_2 solutions of $Cp(PMe_2Ph)_2RuCl$ and $Cp(PMePh_2)_2RuCl$. The same general procedures were followed for the structural analyses of $Cp(PMe_2Ph)_2RuCl$ and $Cp(PMePh_2)_2RuCl$. A suitable crystal of each compound was sealed under a nitrogen atmosphere in a glass capillary tube and then optically aligned on the goniostat of a Siemens P4 automated X-ray diffractometer. The reflections that were used for the determination of the cell parameters were located and indexed by the automatic peak search routine XSCANS.[30] For $CpRu(PMePh_2)_2Cl$, the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$ (No. 14, C_{2h}),[5] whereas for $CpRu(PMe_2Ph)_2Cl$ the systematic absences were compatible with the centrosymmetric orthorhombic space group *Pbca* (No. 61, D_{2h})[15] with two independent molecules in the asymmetric unit. The refined lattice parameters and orientation matrix were calculated from a nonlinear least-squares fit of the orientation angles of at least 40 centered reflections at 22 °C. Pertinent crystallographic data are summarized in Table 3.

Intensity data were measured with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and variable ω scans. Background counts were measured at the beginning and at

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[30] XSCANS (version 2.0) is a diffractometer control system developed by Siemens Analytical X-ray Instruments, Madison, WI.

the end of each scan with the crystal and counter kept stationary. The intensities of three standard reflections were measured after every 100 reflections, and their combined intensity did not decrease during data collection. The data were corrected for Lorentz−polarization, and equivalent reflections were merged. For $CpRu(PMePh_2)_2Cl$, an empirical absorption correction (range of transmission coefficients: 0.890−0.977) based upon the PSI scans measured for eight reflections ($\chi \approx 90°$, $2\theta = 8-46°$) was applied to the diffraction data. For $CpRu(PMe_2Ph)_2Cl$, an empirical absorption correction (range of transmission coefficients: 0.821−0.984) based upon the PSI scans recorded for seven reflections ($\chi \approx 90°$, $2\theta = 8-40°$) was applied.

The positions of the non-hydrogen atoms were determined by a combination of direct methods and difference Fourier calculations, which were performed with algorithms provided by SHELXTL IRIS operating on a Silicon Graphics IRIS Indigo workstation. Idealized positions for the hydrogen atoms were included as fixed contributions using a riding model with isotropic temperature factors set at 1.2 times that of the adjacent carbon. The positions of the methyl hydrogens were optimized by a rigid rotating group refinement with idealized tetrahedral angles. Full-matrix least-squares refinement, based upon the minimization of $\sum w_i|F_o^2 - F_c^2|^2$, with $w_i^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$, was performed with SHELXL-93.[31] After convergence, the final discrepancy indices[32] for $CpRu(PMePh_2)_2Cl$ were R1 = 0.0285, wR2 = 0.0569 for 3837 reflections with $I > 2\sigma(I)$. The corresponding R-factors for $CpRu(PMe_2Ph)_2Cl$ were R1 = 0.0456, wR2 = 0.0746 for 4679 reflections with $I > 2\sigma(I)$.

Acknowledgment. F.R.L. acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, and Johnson Matthey for the generous loan of $RuCl_3 \cdot nH_2O$. S.P.N. acknowledges the financial support provided by the National Science Foundation (Grant No. CHE-9985213). J.L.P. acknowledges the financial support provided by the Chemical Instrumentation Program of the National Science Foundation (Grant No. CHE-9120098) to acquire a Siemens P4 X-ray diffractometer in the Department of Chemistry at West Virginia University.

Supporting Information Available: Tables of crystal data collection and refinement parameters, positional and anisotropic displacement parameters, and interatomic distances and angles for $Cp(PMe_2Ph)_2RuCl$ (**2**) and $Cp(PMePh_2)_2RuCl$ (**3**) and the perspective view of the other independent molecule in the unit cell of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[31] SHELXL-93 is a FORTRAN-77 program (Professor G. Sheldrick, Institut für Anorganische Chemie, University of Göttingen, D-37077, Göttingen, Germany) for single-crystal X-ray structural analyses.

[32] The R-factors were calculated from the expressions $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum(w_i(F_o^2 - F_c^2)^2]/\sum[w_i(F_o^2)^2)]^{1/2}$. The standard deviation of an observation of unit weight (GOF) is equal to $[\sum(w_i(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters that were varied during the last refinement cycle.

[33] Chase, M. W., Jr. *J. Phys. Chem. Ref. Data, Monograph 9* **1998**, 1−1951.