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Organoruthenium Thermochemistry. Enthalpies of Reaction of Cp′Ru(COD)Cl (Cp′ = η^5-C_5H_5 and η^5-C_5Me_5) with Tertiary Phosphite Ligands

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The enthalpies of reaction of Cp′Ru(COD)Cl (Cp′ = η^5-C_5H_5 (Cp), η^5-C_5Me_5 (Cp*); COD = cyclooctadiene) with a series of monodentate phosphite ligands, leading to the formation of Cp′Ru(P(OR)$_3$)$_2$Cl, have been measured by anaerobic solution calorimetry in THF at 30 °C. The overall relative order of stability established for the preceding complexes is as follows: for the CpRu(P(OR)$_3$)$_2$Cl series, P(O-o-MeC_6H_4)$_3$ < P(OC_6H_5)$_3$ < P(O^{i}Pr)$_3$ < P(OCH_2)$_3$CEt < P(OMe)$_3$; for the Cp*Ru(P(OR)$_3$)$_2$Cl series, P(O-o-MeC_6H_4)$_3$ < P(OC_6H_5)$_3$ < P(OCH_2)$_3$CEt < P(O^{i}Pr)$_3$ < P(OMe)$_3$. Single-crystal diffraction studies were carried out on two members of the Cp*Ru(P(OR)$_3$)$_2$Cl series, P(OR)$_3$ = P(OMe)$_3$ and P(OR)$_3$ = P(OCH_2)$_3$CEt (TMPP). Comparisons with other organometallic systems and insight into factors influencing the Ru−P(OR)$_3$ bond disruption enthalpies are discussed.

Introduction

Thermochemical studies performed on organometallic systems have gained recognition as an area of research that could provide important insights into reactivity and bonding patterns.[1−3] Tertiary phosphine ligands constitute a family of transition-metal ancillary modifiers which have proven useful as catalyst stereoelectronic fine tuning tools.[4−6] An area in which we have most recently focused our research efforts is phosphine stereoelectronic influences on metal−phosphine bond enthalpy terms.[7,8]

$$\text{Cp*Ru(COD)Cl(soln)} + \text{2PR3(soln)} \xrightarrow[30\ ^\circ\text{C}]{\text{THF}} \text{Cp*Ru(PR}_3)_2\text{Cl(soln)} + \text{COD(soln)} \quad (1)$$

$$\text{CpRu(COD)Cl(soln)} + 2\text{PR}_3\text{(soln)} \xrightarrow[30\ ^\circ\text{C}]{\text{THF}} \text{CpRu(PR}_3)_2\text{Cl(soln)} + \text{COD(soln)} \quad (2)$$

$$\text{(BDA)Fe(CO)}_3\text{(soln)} + 2\text{PR}_3\text{(soln)} \xrightarrow[50\ ^\circ\text{C}]{\text{THF}} trans\text{-(PR}_3)_2\text{Fe(CO)}_3\text{(soln)} + \text{BDA(soln)} \quad (3)$$

$$\text{Cp} = \text{C}_5\text{H}_5;\ \text{Cp*} = \text{C}_5\text{Me}_5;\ \text{BDA} = \text{PhCH{=}CHCOMe};\ \text{PR}_3 = \text{tertiary phosphine}$$

These fundamental thermodynamic parameters remain largely understudied for large portion of the Periodic Table.[9] Considering the large number of catalytic processes mediated by phosphine-based organometallic systems (ranging from hydrogenation of olefins to ring opening metathesis polymerization),[5] the limited num-

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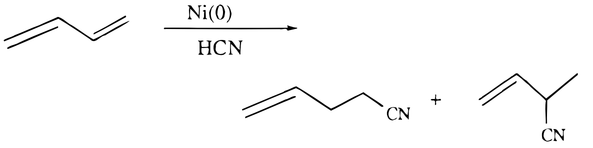
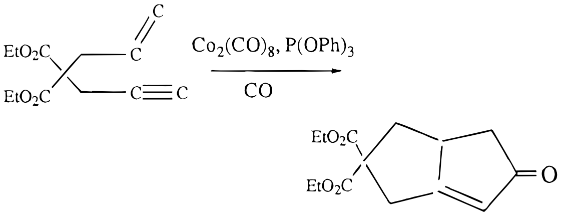
ber of thermochemical studies performed on these systems is remarkable.

A related family of catalyst modifiers is comprised of tertiary phosphite ligands. These have been utilized as ancillary ligation in the nickel catalyzed (Lewis acid promoted) hydrocyanation of dienes:[10] The active nickel phosphite catalyst subsequently isomerizes the minor branched isomer to the major desired monoolefin which undergoes a second addition of HCN to yield adiponitrile.[11]



(4)

A recent example of the use of phosphite as catalyst modifier was reported by Jeong and co-workers in their development of a practical catalytic Pauson−Khand reaction employing triphenyl phosphite as a coligand for the conversion of enynes to bicyclic pentenones.[12] Substitution reactions are at the heart of such catalytic transformations since creation of vacant coordination sites oftentimes requires liberation of one or more ligands from the coordination sphere of the metal.[4] The relative bond strengths or enthalpies associated with such ligand displacement processes are of fundamental importance to catalysis. It is therefore surprising to discover that little thermodynamic information is available concerning metal−phosphite complexes. Tolman and co-workers have investigated, by solution calorimetry, substitution reactions of phosphite ligands binding to a Ni(0) system:[13]



(5)

$$\mathrm{Ni(COD)_2(soln)} + 4\mathrm{PR_3(soln)} \rightarrow \mathrm{Ni(PR_3)_4(soln)} + 2\mathrm{COD(soln)} \tag{6}$$

PR_3	$-\Delta H$ (kcal/mol)
$P(OMe)_3$	51
$P(OEt)_3$	48
$P(OPh)_3$	39

The DuPont group has in this contribution presented the largest tabulation of relative metal−phosphite bond enthalpy terms within a single system. This paucity of information is again rather surprising considering the industrial interest in processes such as hydroformylation where phosphite ligands have been employed and demonstrated to affect product selectivity.[14] Most recently, chiral phosphites have been synthesized for use in asymmetric catalysis,[15] yet many fundamental questions remain unanswered in the area of metal−phosphite thermodynamics. The present contribution provides insight into the thermochemistry of ligand substitution of a variety of phosphite ligands within a similar coordination environment thereby affording a relative stability scale for ruthenium−phosphite complexes.

Experimental Section

General Considerations. All manipulations involving organoruthenium complexes were performed under inert atmospheres of argon or nitrogen using standard high-vacuum or Schlenk tube techniques or in a Vacuum/Atmospheres glovebox containing less than 1 ppm oxygen and water. Ligands were purchased from Strem Chemicals and used as received. Solvents were dried and distilled under dinitrogen before use by employing the following drying agents:[16] tetrahydrofuran (THF) (Na dispersion) and CH_3CN (P_2O_5). Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. NMR spectra were recorded using a Varian Gemini 300 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[17] or the enthalpy of solution of KCl in water.[18] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[19] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

Synthesis. The compounds Cp′Ru(COD)Cl [Cp′ = C_5Me_5 (Cp*),[20] C_5H_5 (Cp)[21]] were synthesized according to the reported literature procedure. The identity of the $CpRu(P(OR)_3)_2Cl$ ($P(OR)_3$ = $P(OMe)_3$,[22] $P(OPh)_3$,[23] $P(O^iPr)_3$[22a]) and $Cp^*Ru(P(OR)_3)_2Cl$ ($P(OR)_3$ = $P(OMe)_3$,[7b] $P(OPh)_3$[7b]) complexes was ascertained by comparison with literature NMR spectroscopic data. Experimental synthetic procedures, leading to the isolation of five unreported complexes, are described below.

$Cp^*Ru(P(OCH_2)_3CEt)_2Cl$. A round bottom flask was charged with 208 mg (0.55 mmol) of Cp*Ru(COD)Cl and 0.184 mg (1.13 mmol) of trimethylolpropane phosphite. A 20 mL volume of THF was vacuum transferred onto the solids at −78 °C, and the solution was allowed to reach room temperature where it was reacted for 1 h. The product slowly precipitates out of solution. The solid microcrystalline material was filtered and the filtrate evacuated to dryness. The residue was dried under vacuum for 3 h and recrystallized from THF by slowing cooling a saturated solution to −78 °C to afford yellow

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Table 1. Enthalpies of Substitution (kcal/mol) in the Following Reaction:

$$\mathrm{Cp^*Ru(COD)Cl_{(soln)}} + \mathrm{2L(soln)} \xrightarrow[30\ °\mathrm{C}]{\mathrm{THF}} \mathrm{Cp^*Ru(L)_2Cl(soln)} + \mathrm{COD(soln)}$$

L	complex	$-\Delta H_{rxn}$[a]
$AsEt_3$	$Cp^*Ru(AsEt_3)_2Cl$	15.0(0.2)[b]
PPh_3	$Cp^*Ru(PPh_3)_2Cl$	18.1(0.2)[b]
$P(p\text{-}CF_3C_6H_4)_3$	$Cp^*Ru(P(p\text{-}CF_3C_6H_4)_3)_2Cl$	20.7(0.2)[c]
$P(NC_4H_4)Ph_2$	$Cp^*Ru[P(NC_4H_4)Ph_2]_2Cl$	20.7(0.4)[d]
$P(NC_4H_4)_3$	$Cp^*Ru[P(NC_4H_4)_3]_2Cl$	21.5(0.4)[d]
$P(p\text{-}ClC_6H_4)_3$	$Cp^*Ru(P(p\text{-}ClC_6H_4)_3)_2Cl$	21.7(0.4)[c]
$P(p\text{-}CH_3OC_6H_4)_3$	$Cp^*Ru(P(p\text{-}CH_3OC_6H_4)_3)_2Cl$	21.8(0.4)[c]
$P(p\text{-}FC_6H_4)_3$	$Cp^*Ru(P(p\text{-}FC_6H_4)_3)_2Cl$	22.0(0.5)[c]
$P(NC_4H_4)_2Ph$	$Cp^*Ru[P(NC_4H_4)_2Ph]_2Cl$	22.1(0.4)[d]
$P(NC_4H_8)_3$	$Cp^*Ru[P(NC_4H_8)_3]_2Cl$	23.8(0.4)[d]
P^nBu_3	$Cp^*Ru(P^nBu_3)_2Cl$	26.0(0.2)[b]
$P(O\text{-}o\text{-}MeC_6H_4)_3$	$Cp^*Ru(P(O\text{-}o\text{-}MeC_6H_4)_3)_2Cl$	26.0(0.2)[e]
PEt_3	$Cp^*Ru(PEt_3)_2Cl$	27.2(0.2)[b]
PPh_2Me	$Cp^*Ru(PPh_2Me)_2Cl$	29.4(0.2)[b]
$P(OPh)_3$	$Cp^*Ru(P(OPh)_3)_2Cl$	31.2(0.2)[b]
$P(OCH_2)_3CEt$	$Cp^*Ru(P(OCH_2)_3CEt)_2Cl$	31.6(0.2)[e]
$PPhMe_2$	$Cp^*Ru(PPhMe_2)_2Cl$	31.8(0.3)[b]
PMe_3	$Cp^*Ru(PMe_3)_2Cl$	32.2(0.4)[b]
$P(O^iPr)_3$	$Cp^*Ru(P(O^iPr)_3)_2Cl$	32.7(0.3)[e]
$P(OMe)_3$	$Cp^*Ru(P(OMe)_3)_2Cl$	37.5(0.4)[b]

[a] Enthalpy values are reported with 95% confidence limits. [b] Taken from ref 7b. [c] Taken from ref 7i. [d] Taken from ref 7j. [e] This work.

needle-shaped crystals. The product (176 mg, 56% yield) was finally isolated by cold filtration. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.79 (t, 6H, $-CH_3$), 1.14 (q, 4H, $-CH_2CH_3$), 1.71 (s, 15H, Cp*), 4.18 (s, 12H, $-CH_2-O$). Anal. Calcd for $C_{22}H_{37}ClRuP_2O_6$: C, 44.29; H, 6.26. Found: C, 44.37; H, 6.34.

Cp*Ru(P(O^{i}Pr)$_3$)$_2$Cl. A round bottom flask was charged with 200 mg (0.53 mmol) of Cp*Ru(COD)Cl and 240 μL (1.26 mmol) of Triisopropyl phosphite. A 30 mL volume of THF was vacuum transferred onto the mixture at −78 °C, and the solution was allowed to reach room temperature where it was reacted for 1 h. The solution was filtered, and the filtrate was evacuated to dryness. The residue was washed with a small amount of hexane and dried in vacuum to afford 232 mg (65%) of the product. ^{1}H-NMR (300 MHz, THF-d_8): 1.27−1.33 (q, 36H, $-CH_3$), 1.63 (s, 15H, Cp*), 4.82 (sp, 6H, −CH). Anal. Calcd for $C_{28}H_{57}ClRuP_2O_6$: C, 48.82; H, 8.35. Found: C, 48.87; H, 8.47.

Cp*Ru(P(O-*o*-MeC$_6$H$_4$)$_3$)$_2$Cl. A round bottom flask was charged with 150 mg (0.40 mmol) of Cp*Ru(COD)Cl and 240 μL (1.14 mmol) of tri-*o*-tolylphosphite. A 25 mL volume THF was vacuum transferred onto the mixture at −78 °C, and the solution was allowed to reach room temperature where it was allowed to react for 3 h. The solution was filtered, and the solvent was evacuated to dryness. The residue was dried in vacuum for 3 h and recrystallized from hexane at −20 °C to afford crystals. The product (156 mg, 42% yield) was finally isolated by cold filtration. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.50 (t, 15H, Cp*), 2.09 (s, 18H, Me), 6.76−7.45 (m, 24H, $-C_6H_4$). Anal. Calcd for: $C_{52}H_{57}ClRuP_2O_6$: C, 63.96; H, 5.88. Found: C, 64.08; H, 5.82.

CpRu(P(OCH$_2$)$_3$CEt)$_2$Cl. A round bottom flask was charged with 150 mg (0.48 mmol) of CpRu(COD)Cl and 157 mg (0.97 mmol) of trimethylolpropane phosphite. A 30 mL volume THF was vacuum transferred onto the solids at −78 °C, and the solution was allowed to reach room temperature where it was allowed to react for 3 h. The solution was filtered, and the filtrate was evacuated to dryness. The residue was washed with a small amount of hexane and dried in vacuum to afford 206 mg (81% yield) of the product. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.81 (t, 6H, $-CH_3$), 1.17 (q, 4H, $-C-CH_2$), 4.24 (s, 12H, $-CH_2-O$), 4.89 (s, 5H, Cp). Anal. Calcd for $C_{17}H_{27}ClRuP_2O_6$: C, 38.78; H, 5.17. Found: C, 38.92; H, 5.27.

Table 2. Enthalpies of Substitution (kcal/mol) in the Following Reaction:

$$\mathrm{CpRu(COD)Cl(soln)} + \mathrm{2L(soln)} \xrightarrow[30\ °\mathrm{C}]{\mathrm{THF}} \mathrm{CpRu(L)_2Cl(soln)} + \mathrm{COD(soln)}$$

L	complex	$-\Delta H_{rxn}$[a]
$AsEt_3$	$CpRu(AsEt_3)_2Cl$	19.4(0.2)[b]
PPh_3	$CpRu(PPh_3)_2Cl$	22.9(0.4)[b]
$P(p\text{-}CH_3C_6H_4)_3$	$CpRu(P(p\text{-}CH_3C_6H_4)_3)_2Cl$	23.7(0.3)[c]
$P(p\text{-}ClC_6H_4)_3$	$CpRu(P(p\text{-}ClC_6H_4)_3)_2Cl$	24.0(0.2)[c]
$P(p\text{-}FC_6H_4)_3$	$CpRu(P(p\text{-}FC_6H_4)_3)_2Cl$	24.2(0.2)[c]
$P(p\text{-}CF_3C_6H_4)_3$	$CpRu(P(p\text{-}CF_3C_6H_4)_3)_2Cl$	24.4(0.2)[c]
$P(p\text{-}CHOC_6H_4)_3$	$CpRu(P(p\text{-}CH_3OC_6H_4)_3)_2Cl$	24.6(0.3)[c]
$P(NC_4H_4)_2Ph$	$CpRu[P(NC_4H_4)_2Ph]_2Cl$	25.3(0.1)[d]
$P(NC_4H_4)_3$	$CpRu[P(NC_4H_4)_3]_2Cl$	25.8(0.3)[d]
$P(NC_4H_4)Ph_2$	$CpRu[P(NC_4H_4)Ph_2]_2Cl$	26.2(0.3)[d]
$P(NC_4H_8)_3$	$CpRu[P(NC_4H_8)_3]_2Cl$	27.2(0.3)[d]
PPh_2Me	$CpRu(PPh_2Me)_2Cl$	32.8(0.2)[b]
$P(O\text{-}o\text{-}MeC_6H_4)_3$	$CpRu(P(O\text{-}o\text{-}MeC_6H_4)_3)_2Cl$	33.2(0.2)[e]
$P(OPh)_3$	$CpRu(P(OPh)_3)_2Cl$	34.1(0.4)[b]
PEt_3	$CpRu(PEt_3)_2Cl$	34.5(0.2)[b]
P^nBu_3	$CpRu(P^nBu_3)_2Cl$	35.4(0.2)[b]
$P(O^iPr)_3$	$CpRu(P(O^iPr)_3)_2Cl$	35.9(0.3)[e]
$P(OCH_2)_3CEt$	$CpRu(P(OCH_2)_3CEt)_2Cl$	35.9(0.4)[e]
$PPhMe_2$	$CpRu(PPhMe_2)_2Cl$	35.9(0.2)[b]
PMe_3	$CpRu(PMe_3)_2Cl$	38.4(0.4)[b]
$P(OMe)_3$	$CpRu(P(OMe)_3)_2Cl$	41.8(0.2)[b]

[a] Enthalpy values are reported with 95% confidence limits. [b] Taken from ref 7f. [c] Taken from ref 7i. [d] Taken from ref 7j. [e] This work.

CpRu(P(O-*o*-MeC$_6$H$_4$)$_3$)$_2$Cl. A round bottom flask was charged with 150 mg (0.48 mmol) of CpRu(COD)Cl and 290 μL (1.38 mmol) of tri-*o*-tolyl phosphite. A 30 mL volume of THF was vacuum transferred onto the mixture at −78 °C, and the solution was allowed to reach room temperature where it was reacted for 3 h. The solution was filtered and was concentrated to one-tenth of its original volume; to this, 15 mL of hexane was vacuum transferred, and the solution was stirred to afford a yellow product, which was filtered off, washed with cold hexane, and dried under high vacuum to afford 352 mg (80% yield) of the product. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.97 (s, 18H, Me), 4.22 (s, 5H, Cp), 6.93−7.42 (m, 24H, $-C_6H_4$). Anal. Calcd for $C_{47}H_{47}ClRuP_2O_6$: C, 62.28; H, 5.23. Found: C, 62.38; H, 5.35.

^{1}H NMR Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount (±0.1 mg) of the organoruthenium complex was placed in a Wilmad screw-capped NMR tube fitted with a septum, and THF-d_8 was subsequently added. The solution was titrated with a solution of the ligand of interest by injecting the latter in aliquots through the septum with a microsyringe, followed by vigorous shaking. The reactions were monitored by ^{1}H NMR spectroscopy, and the reactions were found to be rapid, clean, and quantitative under experimental calorimetric (temperature and concentration) conditions necessary for accurate and meaningful calorimetric results. These conditions were satisfied for all organoruthenium reactions investigated.

Solution Calorimetry. Calorimetric Measurement of Reaction between Cp*Ru(COD)Cl (1) and Trimethylolpropane Phosphite (P(OCH$_2$)$_3$CEt). 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*Ru(COD)Cl was accurately weighed into the lower vessel, which was closed and sealed with 1.5 mL of mercury. A 4 mL volume of a stock solution of $P(OCH_2)_3CEt$ [1 g of $P(OCH_2)_3CEt$ in 25 mL of THF] 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 organoruthenium complex was added to the lower vessel.

Table 3. Summary of Crystallographic Data

	$Cp^*Ru[P(OMe)_3]_2Cl$ (**2**)	$Cp^*Ru(P(OCH_2)_3CEt)_2Cl$ (**3**)
empirical formula	$C_{16}H_{33}O_6P_2ClRu$	$C_{22}H_{37}O_6P_2ClRu$
fw	519.93	590.08
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
unit cell dimens		
a, Å	8.510(2)	14.764(9)
b, Å	9.540(2)	21.859(8)
c, Å	15.223(3)	10.884(6)
α, deg	97.27(1)	90
β, deg	95.27(1)	106.13(9)
γ, deg	111.70(1)	90
V, $Å^3$	1126.1	3374(5)
Z, molecule/cell	2	4
d(calcd), g/cm^3	1.533	1.173
μ(Mo), cm^{-1}	9.68	6.54
monochromator	highly ordered graphite cryst	highly ordered graphite cryst
temp, K	208	105(5)
abs corr	empirical (ψ-scan method)	empirical (ψ-scan method)
diffractometer	Syntex R3	Enraf-Nonius CAD 4
scan type	$\theta-2\theta$	$\theta-2\theta$
data collcd	$0 \leq h \leq 11, -12 \leq k \leq 12, -19 \leq l \leq 19$	$-14 \leq h \leq 14, -21 \leq k \leq 0, 0 \leq l \leq 10$
2θ range, deg	4.7–55.0	4.0–40.0
no. of collcd reflns	5519	4617
no. of unique relfns	3521	3130
R_F (all data), %	4.0	19.5
R_F (obsd data), %	4.0	7.8
R_{wF} (all Data), %	3.7	20.3
goodness of fit	1.16	1.37
no. of variables	235	153

After the calorimeter had reached thermal equilibrium at 30.0 °C (about 2 h), the calorimeter was inverted thereby allowing the reactants to mix. After the reaction had reached completion and the calorimeter had once again reached thermal equilibrium (ca. 2 h), the vessels were removed from the calorimeter. Conversion to $Cp^*Ru(P(OCH_2)_3CEt)_2Cl$ was found to be quantitative under these reaction conditions. Control reactions with Hg and no phosphine show no reaction. The enthalpy of reaction, −26.7 ± 0.2 kcal/mol, represents the average of five individual calorimetric determinations. The final enthalpy value listed in Table 1 (−31.6 ± 0.2 kcal/mol) represents the enthalpy of ligand substitution with all species in solution. The enthalpy of solution of **1** (4.9 ±0.1 kcal/mol) has therefore been subtracted from the −26.7 kcal/mol value. This methodology represents a typical procedure involving all organometallic compounds and all reactions investigated in the present study.

Calorimetric Measurement of Enthalpy of Solution of Cp*Ru(COD)Cl (1) in THF. In order to consider all species in solution, the enthalpies of solution of **1** had to be directly measured. This was performed by using a similar procedure as the one described above with the exception that no ligand was added to the reaction cell. This enthalpy of solution represents the average of five individual determinations and is worth 4.9 ± 0.1 kcal/mol.

Structure Determination of $Cp^*Ru(P(OMe)_3)_2Cl$ (2). A yellow plate crystal, grown from slow evaporation of a 1:5 solution of THF/hexane, having approximate dimensions 0.26 × 0.10 × 0.33 mm was selected and mounted in a capillary tube and mounted on the goniostat of a Syntex R3 automated X-ray diffractometer. Data were collected using Mo Kα radiation at 208 K. Cell dimensions were determined by least squares refinement of the measured setting angles of 44 reflections with 24° < 2θ < 40°. The structure was solved using direct methods (MULTAN) and refined by full-matrix least-squares techniques. Crystal data for **2** are summarized in Table 2, and selected bond distances and angles are listed in Table 3. Figure 1 gives an ORTEP drawing of this molecule.

Structure Determination of $Cp^*Ru(P(OCH_2)_3CEt)_2Cl$ (3). Considerable difficulty was encountered in obtaining a crystal with sufficient dimensions to allow a structure determination. The largest crystal of **3** obtained was a needle-shaped crystal grown from a tetrahydrofuran/hexane solution, having approximate dimensions of 0.02 × 0.05 × 0.50 mm. The crystal was attached to a glass fiber, mounted on an Enraf-Nonius CAD 4 automated X-ray diffractometer, and cooled to 105(5) K with a stream of cold N_2 gas. Cell dimensions were determined using Mo Kα radiation by least-squares refinement of the measured setting angles of 25 reflections with 24° < 2θ < 40°. The structure was solved using direct methods (MULTAN) and refined by full-matrix least-squares techniques. Because of the small size of the crystal, only 970 reflections (31%) had intensities greater than $3\sigma_I$. This required that the refinement model be restricted to isotropic temperature factors for the oxygen and carbon atoms. Hydrogen atom positions were calculated and included as fixed contributions with isotropic thermal parameters. The best refinement was obtained when all reflections were included in the refinement. Inclusion of the weak intensities inflates the R_F and R_{wF} agreement factors, although the agreement factor for the observed data is still reasonable (R_w = 7.8%). Crystal data for **3** are summarized in Table 2, and selected bond distances

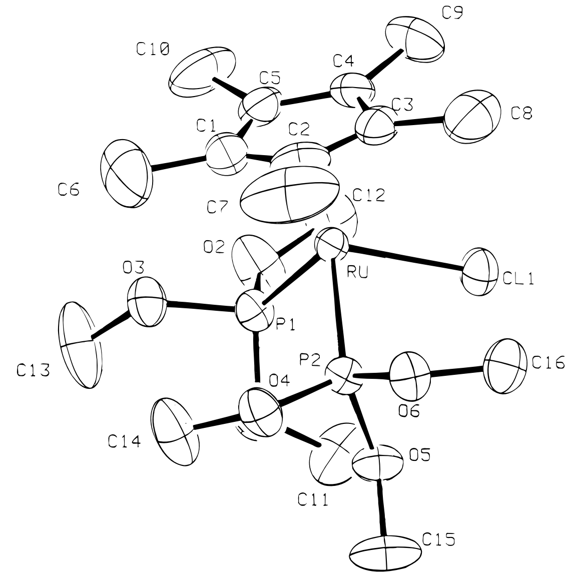

Figure 1. ORTEP diagram of $Cp^*Ru(P(OMe)_3)_2Cl$ (**2**) with ellipsoids drawn at 30% probability.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for Cp*Ru(P(OMe)$_3$)$_2$Cl (2)

	Bond Lengths[a]		
Ru−P(1)	2.232(1)	P(1)−O(1)	1.597(3)
Ru−P(2)	2.232(1)	P(1)−O(2)	1.613(3)
Ru−Cl	2.440(1)	P(1)−O(3)	1.588(3)
Ru−C(1)	2.203(4)	P(2)−O(4)	1.604(3)
Ru−C(2)	2.229(5)	P(2)−O(5)	1.599(3)
Ru−C(3)	2.232(4)	P(2)−O(6)	1.610(3)
Ru−C(4)	2.250(4)	Ru−Cp*(c)	1.878(5)
Ru−C(5)	2.247(4)		
	Bond Angles[a]		
Cl(1)−Ru−P(1)	94.46(4)	P(2)−Ru−C(1)	110.7(1)
Cl(1)−Ru−P(2)	90.84(4)	P(2)−Ru−C(2)	92.6(1)
Cl(1)−Ru−C(1)	152.4(1)	P(2)−Ru−C(3)	110.5(1)
Cl(1)−Ru−C(2)	127.8(2)	P(2)−Ru−C(4)	147.5(1)
Cl(1)−Ru−C(3)	94.4(1)	P(2)−Ru−C(5)	147.9(1)
Cl(1)−Ru−C(4)	90.7(1)	Ru(1)−P(1)−O(1)	124.7(1)
Cl(1)−Ru−C(5)	119.8(1)	Ru(1)−P(1)−O(2)	119.3(1)
P(1)−Ru−P(2)	92.84(4)	Ru(1)−P(1)−O(3)	110.9(1)
P(1)−Ru−C(1)	101.3(1)	Ru(1)−P(2)−O(4)	120.1(1)
P(1)−Ru−C(2)	137.3(2)	Ru(1)−P(2)−O(5)	115.7(1)
P(1)−Ru−C(3)	154.9(1)	Ru(1)−P(2)−O(6)	117.4(1)
P(1)−Ru−C(4)	119.4(1)	P(1)−Ru−Cp*	124.65(2)
P(1)−Ru−C(5)	93.7(1)	P(2)−Ru−Cp*	125.58(2)
Cl−Ru−Cp*	119.58(2)		

[a] Numbers in parentheses are the estimated standard deviations.

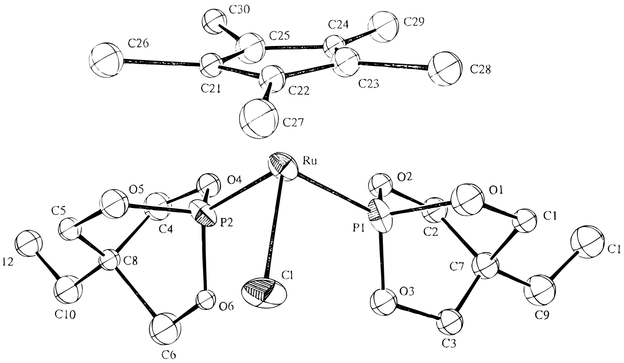

Figure 2. ORTEP diagram of Cp*Ru(P(OCH$_2$)$_3$CEt)$_2$Cl (**3**) with ellipsoids drawn at 30% probability.

and angles are listed in Table 4. Figure 2 gives an ORTEP drawing of this molecule.

Results

A facile entryway into the thermochemistry of Cp′Ru(PR$_3$)$_2$Cl (Cp′ = η^5-C$_5$H$_5$ and η^5-C$_5$Me$_5$) complexes is made possible by the rapid and quantitative reaction of Cp′Ru(COD)Cl (**1**) with the phosphite ligand.[7e−g]

$$\mathrm{Cp'Ru(COD)Cl(s)} + 2\mathrm{PR_3(soln)} \xrightarrow[30\ ^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{Cp'Ru(PR_3)_2Cl(soln)} + \mathrm{COD(soln)} \quad (7)$$

$$\mathrm{Cp'} = \mathrm{C_5H_5},\ \mathrm{C_5Me_5};\ \mathrm{PR_3} = \text{tertiary phosphite}$$

This type of phosphine/phosphite binding reaction appears general and was found to be rapid and quantitative for all ligands calorimetrically investigated at 30.0 °C in tetrahydrofuran. A similar use of this entryway has been employed in previous calorimetric studies involving ligand substitution reaction. A compilation of phosphine/phosphite ligands with their respective enthalpies of reaction, in solution, is presented in Tables 1 and 2.

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for Cp*Ru(P(OCH$_2$)$_3$CEt)$_2$Cl (3)

	Bond Lengths[a]		
Ru−Cl	2.402(7)	Ru−P(1)	2.250(9)
Ru−P(2)	2.212(9)	Ru−Cp*	1.84(2)
Ru−C(ave)	2.17(1)	P(1)−O(2)	1.65(2)
P(1)−O(3)	1.59(4)	P(1)−O(1)	1.59(2)
P(2)−O(4)	1.45(2)	P(2)−O(5)	1.64(3)
P(2)−O(6)	1.57(2)	O(1)−C(1)	1.47(3)
O(1)−C(2)	1.45(3)	O(3)−C(3)	1.51(3)
O(4)−C(4)	1.50(3)	O(5)−C(5)	1.49(3)
O(6)−C(6)	1.35(4)	C(1)−C(7)	1.63(5)
C(2)−C(7)	1.63(4)	C(3)−C(7)	1.38(4)
C(4)−C(8)	1.49(3)	C(5)−C(8)	1.36(3)
C(7)−C(9)	1.58(4)	C(8)−C(10)	1.59(4)
C(9)−C(11)	1.58(5)	C(10)−C(12)	1.39(5)
	Bond Angles[a]		
Cl−Ru−P(1)	93.8(3)	Cl−Ru−P(2)	88.6(3)
P(1)−Ru−P(2)	91.1(3)	Ru−P(1)−O(1)	115.2(9)
Ru−P(1)−O(2)	115.2(7)	Ru−P(1)−O(3)	120.1(8)
O(1)−P(1)−O(2)	101(1)	O(1)−P(1)−O(3)	104(2)
O(2)−P(1)−O(3)	100(1)	Ru−P(2)−O(4)	119.8(7)
Ru−P(2)−O(5)	114.4(8)	Ru−P(2)−O(6)	118.1(8)
O(4)−P(2)−O(5)	103(2)	O(4)−P(2)−O(6)	99(2)
O(5)−P(2)−O(6)	100(1)	O(1)−C(1)−C(7)	109(3)
O(2)−C(2)−C(7)	108(2)	O(3)−C(3)−C(7)	115(2)
O(4)−C(4)−C(8)	108(2)	O(5)−C(5)−C(8)	114(2)
C(1)−C(7)−C(9)	111(2)	C(5)−C(8)−C(10)	114(2)
Cl−Ru−Cp*	121.8(9)	P(1)−Ru−Cp*	124.2(9)
P(2)−Ru−Cp*	127.3(9)		

[a] Numbers in parentheses are the estimated standard deviations.

Single-crystal structural studies were carried out on two of the phosphite complexes, Cp*Ru(P(OMe)$_3$)$_2$Cl (**2**) and Cp*Ru(P(OCH$_2$)$_2$CEt)$_2$Cl (**3**) (Cp* = C$_5$Me$_5$). Crystallographic data and important bond distances and angles are presented in Tables 3−5. ORTEP drawings of the two complexes are presented in Figures 1 and 2.

Discussion

The donicity of phosphite ligands, just as phosphines, can be regarded as comprised of an electronic and a steric parameter.[24,25] A number of groups have considered them significantly different from phosphines in view of the π involvement possible through the oxygen p orbitals. They have been characterized by Tolman[24] in a similar fashion as phosphines with appropriate cone angle and electronic parameters. In earlier contributions, phosphites have been investigated by solution calorimetry in both organoiron and organoruthenium systems.[7b,8a] These investigations on phosphite binding focused on P(OMe)$_3$ and P(OPh)$_3$. Such thermochemical investigations, using these two phosphite ligands, have also been performed by Tolman and Manzer in a platinum system:[26]

$$trans\text{-}[\mathrm{CH_3Pt(PMe_2Ph)_2(thf)}]^+ + \mathrm{P(OR)_3} \rightarrow trans\text{-}[\mathrm{CH_3Pt(PMe_2Ph)_2(P(OR)_3)}]^+ + \mathrm{thf} \quad (8)$$

$$\mathrm{P(OR)_3} = \mathrm{P(OMe)_3},\ \mathrm{P(OPh)_3}$$

Here a difference in enthalpy of reaction between the two phosphite ligands examined is 5 kcal/mol favoring

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(24) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

(25) (a) White, D.; Coville. N. J. *Adv. Organomet. Chem.* **1994**, *36*, 95−158. (b) Müller, T. E.; Mingos, D. M. P. *Transition Met. Chem.* **1995**, *20*, 533−539.

(26) Manzer, L. E.; Tolman, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1955−1956.

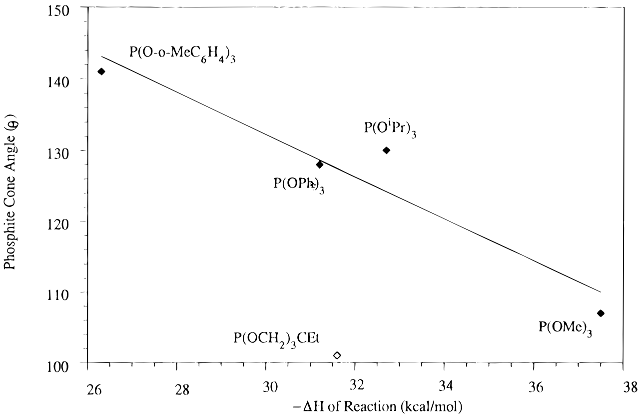

Figure 3. Phosphine cone angle (deg) vs enthalpies of reaction (kcal/mol) for the $CpRu(PR_3)_2Cl$ system (slope = −2.95; $R = 0.96$).

the trimethyl phosphite. Hoff and co-workers have mapped out the thermochemical surface of a number of organo group 6 complexes incorporating trimethyl and triphenyl phosphites as ligands.[27]

$$\text{(arene)Mo(CO)}_3 + 3\text{P(OR)}_3 \rightarrow (\text{P(OR)}_3)_3\text{Mo(CO)}_3 + \text{arene} \quad (9)$$

$$\text{(norbornadiene)Mo(CO)}_4 + 2\text{P(OR)}_3 \rightarrow (\text{P(OR)}_3)2\text{Mo(CO)}_4 + \text{NBD} \quad (10)$$

$$\text{P(OR)}_3 = \text{P(OMe)}_3,\ \text{P(OPh)}_3$$

The enthalpy difference between the two phosphites is 3.7 and 2.8 kcal/mol (per Mo−P bond) more exothermic for trimethyl phosphite, for eqs 8 and 9, respectively. In the present systems, this enthalpy difference is 3.2 and 3.8 kcal/mol for the Cp*- and Cp-based systems. These differences are comparable to the previously measured differences in the Pt and Mo systems.

It has previously been established that phosphine cone angle (steric demand) dominated contributions to the enthalpies of reaction in the two ruthenium systems discussed here.[7f] The data presented in this contribution allow for a test of this relationship with phosphite ligands. Simple one-parameter relationships are established for the phosphite ligands investigated, and these are presented in Figures 3 and 4. Both relationship exhibit fairly linear correlation, if the caged phosphite, $P(OCH_2)_3CEt$, is excluded from the treatment. Ernst and co-workers[28] have previously remarked on the low steric demand/compact nature of this caged phosphite to an early transition metal-containing moiety. The cage phosphite possesses a cone angle of 101°, a value reported by Tolman.[23] This compares with cone angles of 107° ($P(OMe)_3$), 128° ($P(OPh)_3$), 130° ($P(O^iPr)_3$), and 141° ($P(O\text{-}o\text{-}MeC_6H_4)_3$).[24] Coville and White have recently reported a solid cone angle for this series of 82, 113, 135, 138, and 147°, respectively.[25a] Using either approach, the cage phosphite is the least sterically demanding phosphite examined and falls in the middle of the series in terms of binding affinity to ruthenium. The compact nature of the ligand accounts for the deviation observed in Figures 3 and 4. A steric threshold of 135°, the point at which phosphine steric demands affect the overall donicity of the ligand, has previously been calculated from QALE analysis of phosphine data.[7f] This alone would explain the relative importance (and good linear fit of these data points) for phosphites possessing cone angles larger than 135° (($P(OPh)_3$), $P(O^iPr)_3$, ($P(O\text{-}o\text{-}MeC_6H_4)_3$). The exception is trimethyl phosphite with a solid angle between triphenyl phosphite and the cage phosphite, yet closer to the triphenyl phosphite. It appears that the corrected cone angle value proposed by Ernst [28](128°) fits the observed trend. For trimethyl phosphite, in this system, ligand sterics dominate any contribution to the enthalpy of ligand substitution. Ernst has previously proposed the inclusion of such caged phosphite ligands as an internal check on the steric parameters within a series.[28] Here, this caveat is considered but the steric threshold of the QALE analysis is much higher than the cage phosphite cone angle which translates into this member of the series being an anomaly rather than a verification.

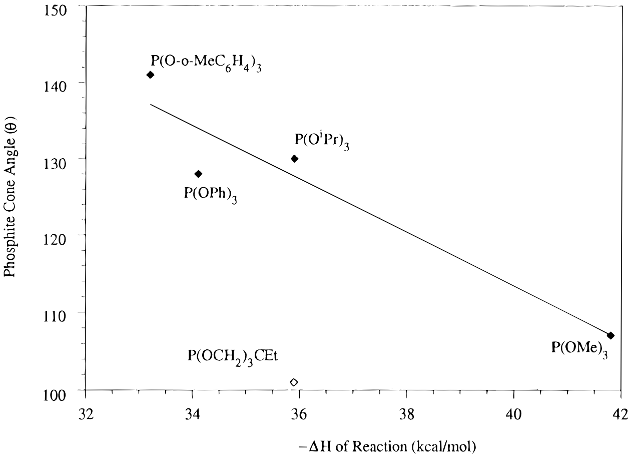

Figure 4. Phosphine cone angle (deg) vs enthalpies of reaction (kcal/mol) for the $Cp^*Ru(PR_3)_2Cl$ system (slope = −3.50; $R = 0.95$).

In Ernst's bis(pentadienyl)titanium system, the enthalpy difference between $P(OMe)_3$ and $P(OCH_2)_3CEt$ is 4.9 kcal/mol.[28]

$$\text{Ti(2,4-C}_7\text{H}_{11})_2 + \text{P(OR)}_3 \rightarrow \text{Ti(2,4-C}_7\text{H}_{11})_2\text{P(OR)}_3 \quad (11)$$

$$\text{P(OR)}_3 = \text{P(OMe)}_3,\ \text{P(OCH}_2)_3\text{CEt}$$

In the present systems, this difference (on a per Ru−P bond basis) is 3.0 kcal/mol in both the Cp and Cp* systems. This smaller difference for the ruthenium systems may be attributed to the relatively smaller importance of electronic effects in the ruthenium cases compared to the titanium complexes where important bonding involvement of the oxygen lone pair has been proposed. The difference between first- and second-row metals is also to be considered. The first-row Ti−P distance (2.472 Å)[28] is longer that the second-row Ru−P distance (2.232Å) for P = $P(OMe)_3$ and $P((OCH_2)CC_2H_5$, suggesting the relative greater importance of sterics in the second-row metal system.

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[27] (a) Nolan, S. P.; de la Vega, R. L.; Hoff., C. D. *Organometallics* **1986**, *5*, 2529−2537. (b) Mukerjee, S. L.; Nolan, S. P.; Hoff, C. D.; de la Vega, R. L. *Inorg. Chem.* **1988**, *27*, 81−85.

[28] (a) Stahl, L.; Trakarnpruk, W.; Freeman, J. W.; Arif, A. M.; Ernst, R. D. *Inorg. Chem.* **1995**, *34*, 1810−1814. (b) Ernst, R. D.; Freeman, J. W.; Stahl, L.; Wilson, D. R.; Arif, A. M.; Nuber, B.; Ziegler, M. L. *J. Am. Chem. Soc.* **1995**, *117*, 5075−5081.

Comparison between the Cp- and Cp*-based systems also affords a look into the effects of ancillary ligation electronic contribution to the enthalpy of reaction. The Cp values are, on average, 4.4 kcal/mol more exothermic than the corresponding Cp* values for the phosphine ligands previously investigated. This was previously explained in terms of increased metal basicity in the Cp*-based system which corresponded to lower enthalpies of binding of a basic ligand.[7f,29] This difference in electronic properties at the metal center gauges a change in metal basicity. Sowa and Angelici have investigated a series of iridium complexes and have observed a difference in enthalpies of protonation of 5.7 kcal/mol between CpIr(COD) and Cp*Ir(COD) complexes.[30] Hoff and co-workers have first demonstrated this difference in metal basicity between Cp and Cp* in their thermochemical investigations of organomolybdenum complexes.[19a] In comparison of the enthalpy values for the phosphite series in the two systems, a similar difference (4.3 kcal/mol) is observed, with some minor exchange of stability position. This may be due to the difference in the electronic density at the metal on going from Cp to Cp* but also may include a steric component since the Cp* is more sterically demanding than its unmethylated congener. A dramatic example of this steric pressure in the Cp* system is illustrated by examining the enthalpy differences between $P(OPh)_3$ and $P(O\text{-}o\text{-}MeC_6H_4)_3$, which are 1.1 kcal/mol for Cp and 5.2 kcal/mol for Cp*. This is a significant telling sign of buildup of steric pressure in the Cp* system.

In an effort to compare structural and thermochemical features of members of the metal−phosphite series, single crystals of two complexes bearing the $Cp^*Ru(P(OR_2)_3)_2Cl$ composition were examined by X-ray diffraction technique. ORTEP drawings of $Cp^*Ru(P(OMe)_3)_2Cl$ (**2**) and $Cp^*Ru(P(OCH_2)_3CEt)_2Cl$ (**3**) are presented in Figures 1 and 2, respectively. The principal features structural of these two complexes are the similar ruthenium−phosphine average distances of 2.232(1) and 2.231(9) Å for **1** and **2**, respectively. Furthermore, similar P−O bond distances (1.60 Å) are present in the two complexes. A significant difference exists however when comparing the P−Ru−P angles of **2** and **3**, which are 92.84(4)° and 91.1(3)°, respectively. This difference illustrates the smaller steric requirement imposed by the caged-phosphite ligand. The two complexes cannot be directly compared in terms of ruthenium−phosphite bond length/bond strength in view of significant reorganization energy, apparent in a significant difference of Ru−Cl (2.440(1) vs 2.402(7) Å) and Ru−Cp*(centroid) (1.878(5) vs 1.84(2) Å) distances.

The relative stability order determined by solution calorimetry can be explained quite succinctly in terms of sterics and electronic contributions. At the low end of the enthalpic scale measured are sterically demanding and poorer donor phosphite ligands ($P(O\text{-}o\text{-}MeC_6H_4)_3$ and $P(OC_6H_5)_3$) and then comes $P(O^iPr)_3$, which is a better donor in view of the presence of alkyl substituents on the phosphorus oxygen. It should be noted that the steric hindrance contributed by isopropyl groups in the phosphite case ($\theta = 130°$)[24] is diminished as opposed to the phosphine congener ($\theta = 160°$)[24] since the alkyl group is significantly removed from the vicinity of the metal. On the most stable end of the series are the $P(OCH_2)_3CEt$ and $P(OMe)_3$ ligands. These two have significant similarities, but in both systems investigated the $Ru-P(OMe)_3$ bond is more stable. This can be explained in terms of the constriction brought about in the caged system. This might be a direct observation of restricted bonding involvement of the phosphite oxygen. In the caged and the trimethyl phosphite systems, the O−P−O angle average differs in the two complexes by 3 Å. This difference may be sufficient to decrease the oxygen lone pair involvement in the phosphite donor/acceptor ability by the observed 3 kcal/mol (per bond). A similar trend is observed in the $Cp^*Ru(P(OR_2)_3)_2Cl$ system with the exception of an exchange in stability between the $P(OCH_2)_3CEt$ and $P(O^iPr)_3$ complexes. This may be due again to the restricted position of the phosphite oxygens in the caged complex. Observation of the small variation in this parameter in the structures of **2** (1.60(3) Å) and **3** (1.58(2) Å) is inconclusive.

Conclusion

The labile nature of the COD ligand in CpRu(COD)Cl and Cp*Ru(COD)Cl was used to gain access into the thermochemistry of ligand substitution for tertiary phosphite ligands. The enthalpy trend can be explained in terms of overwhelming steric contribution to the enthalpy of reaction, with the notable exception of the caged-phosphite which deviates from this trend in view of its small steric parameter. The increased exothermicity displayed by the $CpRu(PR_3)_2Cl$ system over its Cp* parent is taken as a gauge of the increased metal basicity on going from Cp to Cp*. Structural studies have been performed on two members of this ruthenium−phosphite series, and principal features are discussed in terms of phosphite steric factor. Further thermochemical and structural studies are in progress in order to examine the binding ability of this ligand class to this and other metal centers.

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Supporting Information Available: Listings of atomic coordinates, *B* values, selected distances and angles, anisotropic thermal displacement parameters, and hydrogen bond distances for **2** and **3** (14 pages). Ordering information is given on any current masthead page.

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(29) It should be noted here that the difference mentioned is not between absolute bond disruption enthalpies. The Cp vs Cp* effect will also be present in the Ru−COD bond enthalpy.

(30) (a) Sowa, J. R., Jr.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2537−2544. (b) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267−7274.