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Enthalpies of Reaction of [(*p*-cymene)$OsCl_2$]$_2$ with Monodentate Tertiary Phosphine Ligands. Importance of Steric and Electronic Ligand Factors in an Osmium(II) System

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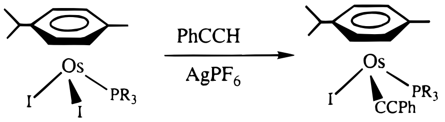
The enthalpies of reaction of [$OsCl_2$(*p*-cymene)]$_2$ (**1**) (*p*-cymene = η^6-$CH_3C_6H_4CH(CH_3)_2$) with a series of monodentate phosphines (PR_3), leading to the formation of $OsCl_2$(*p*-cymene)(PR_3) complexes, have been measured by anaerobic calorimetry in CH_2Cl_2 at 30 °C. These reactions are rapid and quantitative. The overall relative order of stability established is as follows: $PPh(NC_4H_4)_2 < P(NC_4H_4)_3 < P(p\text{-}CF_3C_6H_4)_3 < PPh_2(NC_4H_4) < PPh_3 < P(p\text{-}ClC_6H_4)_3 < P(p\text{-}CH_3C_6H_4)_3 < P(p\text{-}FC_6H_4)_3 < PCy_3 < PBz_3 < P^iPr_3 < P(p\text{-}CH_3OC_6H_4)_3 < P(NC_4H_8)_3 < PPh_2Me < PPhMe_2 < PEt_3 < PMe_3$. A quantitative analysis of ligand effects for the present data helps clarify the exact steric versus electronic ligand contributions to the enthalpy of reaction in this system. Both steric and electronic factors appear to play an important role in dictating the magnitude of the enthalpy of reaction. The data are compared to the previously studied $RuCl_2$(*p*-cymene)(PR_3) system.

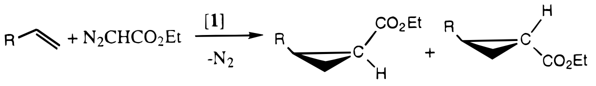
Introduction

Fewer synthetic and reactivity studies have been performed on organoosmium systems when compared to the extensive amount of work performed on organoruthenium systems.[1,2] Notable exceptions are the work of Roper,[3] Caulton,[4] and Esteruelas[5] on osmium-phosphine/carbonyl systems. Girolami[6] has recently prepared an attractive synthon, [Cp*$OsBr_2$]$_2$, enabling access to the reaction chemistry of the Cp*Os moiety.[7] The osmium systems bearing arene ligands that have been synthesized by Maitlis[8] and Werner[9] have led to a number of synthetic and physical studies. The latter system has displayed interesting C−H bond activation behavior in low-temperature matrixes[10] and is capable of supporting various ancillary ligands.[11] Metal polyhydrides incorporating the arene−Os fragment have been synthesized and characterized.[12] Synthetic and spectroscopic studies have been performed on the (*p*-cymene)$OsX_2(PR_3)$ (X = halide and alkyl) complexes by von Philipsborn (eq 1).[13]



(1)

Demonceau has recently demonstrated that [(*p*-cymene)$OsCl_2$]$_2$ (**1**) is an active precatalyst in the cyclopropanation of olefins (eq 2).[14,15]



(2)

The catalytic behavior of **1** proved a marked improvement over the use of its ruthenium congener, [(*p*-cymene)$RuCl_2$]$_2$.

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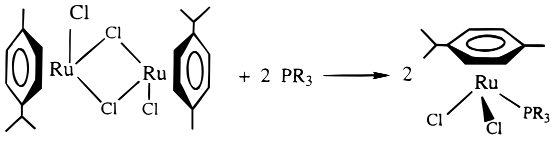
We have previously reported on the solution calorimetry of ligand addition to the ruthenium analogue of **1** (eq 3).[16]



(3)

PR$_3$ = Tertiary Phosphine

To probe the effects of ligand substitution on descending a chemical group, we now wish to expand on our solution thermochemical studies of organometallic complexes[17] by focusing on quantitatively addressing the binding ability of a series of phosphine ligands to the (*p*-cymene)OsCl$_2$ fragment.

Experimental Section

General Considerations. All manipulations involving organometallic complexes were performed under inert atmospheres of argon or nitrogen using standard high-vacuum or Schlenk tube techniques or in an argon-filled glovebox containing less than 1 ppm oxygen and water. Solvents including deuterated solvents for NMR analysis were dried and distilled under nitrogen before use employing standard drying agents. For example, tetrahydrofuran was stored over sodium wire, distilled from sodium benzophenone ketyl, stored over Na/K alloy, and vacuum-transferred into flame-dried glassware prior to use. The P(NC$_4$H$_4$)$_3$, PPh(NC$_4$H$_4$)$_2$, PPh$_2$(NC$_4$H$_4$), and P(NC$_4$H$_8$)$_3$ phosphines were synthesized according to literature procedures.[18] Other phosphine or phosphite ligands were purchased from Strem Chemicals and used as received. 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 or Varian 400 MHz spectrometer. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[19] or the enthalpy of solution of KCl in water.[20] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[21] 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.

NMR Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount (±0.1 mg) of the organometallic complex was placed in a Wilmad screw-capped NMR tube fitted with a septum, and CD$_2$Cl$_2$ 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 or by ^{31}P NMR spectroscopy, and the reactions were found to be rapid, clean, and quantitative under experimental calorimetric conditions. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all organometallic reactions investigated.

Solution Calorimetry. Calorimetric Measurement for Reaction between [(*p*-cymene)OsCl$_2$]$_2$ and Trimethylphosphine. 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 [(*p*-cymene)OsCl$_2$]$_2$ was accurately weighed into the lower vessel; it was closed and sealed with 1.5 mL of mercury. Four milliliters of a stock solution of phosphine [1 g of PMe$_3$ in 25 mL of CH$_2$Cl$_2$] 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 organoosmium complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (about 2 h), the calorimeter was inverted, allowing the reagents to mix. After the calorimeter had once again reached thermal equilibrium, the vessels were removed from the calorimeter, taken into the glovebox, opened, and analyzed using ^{1}H NMR spectroscopy. Conversion to (*p*-cymene)OsCl$_2$(PMe$_3$) was found to be quantitative under these reaction conditions. The enthalpy of reaction, -52.9 ± 0.4 kcal/mol, represents the average of five individual calorimetric determinations. The enthalpy of solution of [(*p*-cymene)OsCl$_2$]$_2$ was then subtracted from this value to obtain a value of -61.6 ± 0.5 kcal/mol for all species in solution.

Calorimetric Measurement of Enthalpy of Solution of [(*p*-cymene)OsCl$_2$]$_2$ in CH$_2$Cl$_2$. To consider all species in solution, the enthalpy of solution of [(*p*-cymene)OsCl$_2$]$_2$ had to be directly measured. This was performed by using a procedure similar to that described above with the exception that no ligand was added to the reaction cell solution. This enthalpy of solution representing the average of five individual determinations is 8.8 ± 0.1 kcal/mol.

Syntheses. The compound [OsCl$_2$(*p*-cymene)]$_2$ (**1**) was synthesized according to the literature procedure.[22] The organoosmium complexes (*p*-cymene)OsCl$_2$(PPh$_3$) (**2**),[22] (*p*-cymene)OsCl$_2$(PPh$_2$Me) (**3**),[22] (*p*-cymene)OsCl$_2$(PPhMe$_2$) (**4**),[22] (*p*-cymene)OsCl$_2$(PBz$_3$) (**5**),[22] (*p*-cymene)OsCl$_2$(PCy$_3$) (**6**),[22] (*p*-cymene)OsCl$_2$(PMe$_3$) (**7**),[23] (*p*-cymene)OsCl$_2$(P(OPh)$_3$) (**8**),[23] (*p*-cymene)OsCl$_2$(P^{i}Pr$_3$) (**9**),[24] and (*p*-cymene)OsCl$_2$(P(OMe)$_3$) (**10**)[24] have been reported in the literature. The identity of all calorimetric products was determined by comparison with literature spectroscopic data. Experimental synthetic procedures leading to the isolation of previously unreported complexes are described below.

(*p*-cymene)OsCl$_2$(P(pyrrolyl)$_3$) (11). A 50 mL flask was charged with 29 mg (0.126 mmol) of P(pyrrolyl)$_3$, 50 mg (0.063 mmol) of [OsCl$_2$(*p*-cymene)]$_2$, and 15 mL of CH$_2$Cl$_2$. The clear yellow solution was stirred at room temperature for 60 min, after which the solvent was removed under vacuum. The residue was washed with 10 mL of hexane, filtered, and dried under vacuum, affording 56 mg of the yellow product (yield: 86%). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, δ): 1.24 (d, 6H, 2CH$_3$, J = 6.9 Hz), 2.07 (s, 3H, −CH$_3$), 2.80 (m, 1H, −CH), 5.37 (d, 2H, −C$_6$H$_4$, J = 6), 5.65 (d, 2H, −C$_6$H$_4$, J = 6), 6.29 (m, 6H, pyrrolyl), 6.86 (m, 6H, pyrrolyl). ^{31}P NMR (121 MHz, CD$_2$Cl$_2$, δ): 47.5. Calcd for C$_{22}$H$_{26}$N$_3$Cl$_2$POs: C, 42.31; H, 4.20; N, 6.73. Found: C, 41.98; H, 4.02; N, 6.47.

(*p*-cymene)OsCl$_2$(PPh(pyrrolyl)$_2$) (12). In a manner analogous to the synthesis of **11**, complex **12** was isolated in 75% yield. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, δ): 1.15 (d, 6H, 2CH$_3$, J = 7.2 Hz), 2.02 (s, 3H, −CH$_3$), 2.70 (m, 1H, −CH), 5.34 (d, 2H, −C$_6$H$_4$, J = 6), 5.53 (d, 2H, −C$_6$H$_4$, J = 6), 6.27 (m, 4H, pyrrolyl), 7.00 (m, 4H, pyrrolyl), 7.47 (m, 5H, PPh).^{31}P NMR (121 MHz, CD$_2$Cl$_2$, δ): 46.4. Calcd for C$_{24}$H$_{27}$Cl$_2$N$_2$POs: C, 45.36; H, 4.28; N, 4.41. Found: C, 44.91; H, 4.12; N, 4.18.

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(*p*-cymene)OsCl$_2$(PPh$_2$(pyrrolyl)) (13). In a manner analogous to the synthesis of **11**, complex **13** was isolated as a yellow microcrystalline product in 88% yield. ^{1}H NMR (300 MHz, CD_2Cl_2, δ): 1.21 (d, 6H, 2CH_3, $J = 7.2$ Hz), 2.04 (s, 3H, $-CH_3$), 3.08 (m, 1H, $-CH$), 5.30 (d, 2H, $-C_6H_4$, $J = 6$), 5.51 (d, 2H, $-C_6H_4$, $J = 6$), 6.32 (m, 2H, pyrrolyl), 7.04 (m, 2H, pyrrolyl), 7.34−7.70 (br, 10H, phenyl).^{31}P NMR (121 MHz, CD_2Cl_2, δ): 29.7. Calcd for $C_{26}H_{28}Cl_2NPOs$: C, 48.30; H, 4.36; N, 2.17. Found: C, 48.40; H, 4.58; N, 2.34.

(*p*-cymene)OsCl$_2$(P(pyrrolidinyl)$_3$) (14). In a manner analgous to the synthesis of **11**, complex **14** was isolated as an orange microcrystalline product in 88% yield. ^{1}H NMR (300 MHz, CD_2Cl_2, δ): 1.27 (d, 6H, 2CH_3, $J = 6.9$ Hz), 1.75 (m, 12H, pyrrolidinyl), 2.26 (s, 3H, $-CH_3$), 2.82 (m, 1H, $-CH$), 3.21 (m, 12H, pyrrolidinyl), 5.37 (d, 2H, $-C_6H_4$, $J = 6$), 5.63 (d, 2H, $-C_6H_4$, $J = 6$).^{31}P NMR (121 MHz, CD_2Cl_2, δ): 44.2. Calcd for $C_{22}H_{38}Cl_2N_3POs$: C, 41.51; H, 6.02; N, 6.60. Found: C, 41.38; H, 6.20; N, 6.23.

(*p*-cymene)OsCl$_2$(PEt$_3$) (15). In a manner analogous to the synthesis of **11**, complex **15** was isolated as a yellow microcrystalline product in 86% yield. ^{1}H NMR (300 MHz, CD_2Cl_2, δ): 1.07 (m, 9H, $P-CH_2CH_3$), 1.24 (d, 6H, 2CH_3, $J = 6.9$ Hz), 2.00 (m, 6H, PCH_2CH_3), 2.15 (s, 3H, $-CH_3$), 2.66 (m, 1H, $-CH$), 5.58 (m, 4H, $-C_6H_4$).^{31}P NMR (121 MHz, CD_2Cl_2, δ): −19.9. Calcd for $C_{16}H_{29}Cl_2POs$: C, 37.43; H, 5.69. Found: C, 37.30; H, 5.66.

(*p*-cymene)OsCl$_2$(P(*p*-ClC$_6$H$_4$)$_3$) (16). In a manner analogous to the synthesis of **11**, complex **16** was isolated as a yellow microcrystalline product in 94% yield. ^{1}H NMR (300 MHz, CD_2Cl_2, δ): 1.16 (d, 6 H, 2CH_3, $J = 6.9$ Hz), 1.94 (s, 3H, $-CH_3$), 2.68 (m, 1H, $-CH$), 4.15 (d, 2H, $-C_6H_4$, $J = 5.4$), 5.42 (d, 2H, $-C_6H_4$, $J = 6.0$), 7.36 (m, 6H, PPh), 7.62 (m, 6H, PPh). ^{31}P NMR (121 MHz, CD_2Cl_2, δ): −13.0. Calcd for $C_{28}H_{26}Cl_5POs$: C, 44.20; H, 3.44. Found: C, 43.91; H, 3.27.

(*p*-cymene)OsCl$_2$(P(*p*-CH$_3$OC$_6$H$_4$)$_3$) (17). In a manner analogous to the synthesis of **11**, complex **17** was isolated as a yellow microcrystalline product in 93% yield. ^{1}H NMR (300 MHz, CD_2Cl_2, δ): 1.16 (d, 6 H, 2 CH_3, $J = 7.2$ Hz), 1.94 (s, 3 H, $-CH_3$), 2.68 (m, 1H, $-CH$), 3.80 (s, 3H, OCH_3), 5.14 (d, 2H, $-C_6H_4$, $J = 5.7$), 5.40 (d, 2H, $-C_6H_4$, $J = 6.0$), 6.87 (m, 6H, PPh), 7.59 (m, 6H, PPh). ^{31}P NMR (121 MHz, CD_2Cl_2, δ): −15.3. Calcd for $C_{31}H_{35}OsCl_2PO_3Os$: C, 49.80; H, 4.72. Found: C, 50.13; H, 4.60.

(*p*-cymene)OsCl$_2$(P(*p*-CF$_3$C$_6$H$_4$)$_3$) (18). In a manner analogous to the synthesis of **11**, complex **18** was isolated as a yellow microcrystalline product in 92% yield. ^{1}H NMR (300 MHz, CD_2Cl_2, δ): 1.12 (d, 6 H, 2CH_3, $J = 6.6$ Hz), 1.96 (s, $-CH_3$), 2.63 (m, 1H, $-CH$), 5.20 (d, 2H, $-C_6H_4$, $J = 5.7$), 5.41 (d, 2H, $-C_6H_4$, $J = 5.7$), 7.67 (m, 6H, PPh, $J = 9.2$), 7.88 (m, 6H, PPh). ^{31}P NMR (121 MHz, CD_2Cl_2, δ): −12.3. Calcd for $C_{31}H_{26}Cl_2PF_9Os$: C, 43.21; H, 3.04. Found: C, 43.03; H, 2.81.

(*p*-cymene)OsCl$_2$(P(*p*-FC$_6$H$_4$)$_3$) (19). In a manner analogous to the synthesis of **11**, complex **19** was isolated as a yellow microcrystalline product in 93% yield. ^{1}H NMR (300 MHz, CD_2Cl_2, δ): 1.16 (d, 6H, $-CH_3$, $J = 7.5$ Hz), 1.93 (s, 3 H, $-CH_3$), 2.68 (m, 1H, $-CH$), 5.16 (d, 2H, $-C_6H_4$, $J = 5.7$), 5.41 (d, 2H, $-C_6H_4$, $J = 5.7$), 7.09 (t, 6H, PPh), 7.78 (m, 6H, PPh). ^{31}P NMR (121 MHz, CD_2Cl_2, δ): −14.0. Calcd for $C_{28}H_{26}Cl_2PF_3Os$: C, 47.26; H, 3.68. Found: C, 47.36; H, 3.65.

(*p*-cymene)OsCl$_2$(P(*p*-CH$_3$C$_6$H$_4$)$_3$) (20). In a manner analogous to the synthesis of **11**, complex **20** was isolated as a yellow microcrystalline product in 90% yield. ^{1}H NMR (300 MHz, CD_2Cl_2, δ): 1.14 (d, 6 H, 2 CH_3, $J = 6.9$ Hz), 1.94 (s, 3 H, $-CH_3$), 2.35 (s, 3H, $-CH_3$), 3.66 (m, 1H, $-CH$), 5.13 (d, 2H, $-C_6H_4$, $J = 5.4$), 5.37 (d, 2H, $-C_6H_4$, $J = 5.4$), 7.16 (m, 6H, PPh), 7.50 (m, 6H, PPh). ^{31}P NMR (500 MHz, CD_2Cl_2, δ): −13.6. Calcd for $C_{31}H_{35}Cl_2PO_s$: C, 53.21; H, 5.04. Found: C, 53.54; H, 4.99.

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

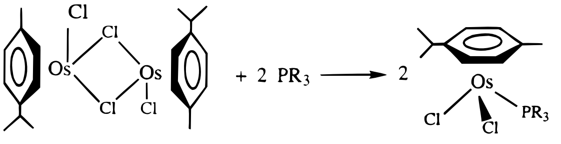
$$[OsCl_2(p\text{-cymene})]_2(soln) + 2PR_3(soln) \xrightarrow[30\ °C]{CH_2Cl_2} 2OsCl_2(p\text{-cymene})(PR_3)(soln)$$

L	complex	$-\Delta H_{rxn}$[a]
$PPh(NC_4H_4)_2$	$OsCl_2$(*p*-cymene)($PPh(NC_4H_4)_2$)	38.5(4)
$P(NC_4H_4)_3$	$OsCl_2$(*p*-cymene)($P(NC_4H_4)_3$)	39.1(1)
P(*p*-$CF_3C_6H_4)_3$	$OsCl_2$(*p*-cymene)(P(*p*-$CF_3C_6H_4)_3$)	40.9(3)
$PPh_2(NC_4H_4)$	$OsCl_2$(*p*-cymene)($PPh_2(NC_4H_4)$)	41.9(2)
PPh_3	$OsCl_2$(*p*-cymene)(PPh_3)	43.1(2)
P(p-$ClC_6H_4)_3$	$OsCl_2$(*p*-cymene)(P(*p*-$ClC_6H_4)_3$)	43.4(2)
P(p-$MeC_6H_4)_3$	$OsCl_2$(*p*-cymene)(P(*p*-$MeC_6H_4)_3$)	45.0(3)
P(p-$FC_6H_4)_3$	$OsCl_2$(*p*-cymene)(P(*p*-$FC_6H_4)_3$)	46.3(3)
PCy_3	$OsCl_2$(*p*-cymene)(PCy_3)	47.9(4)
PBz_3	$OsCl_2$(*p*-cymene)(PBz_3)	49.2(1)
P^iPr_3	$OsCl_2$(*p*-cymene)(P^iPr_3)	49.2(2)
P(p-$MeOC_6H_4)_3$	$OsCl_{2(}$*p*-cymene)(P(*p*-$MeOC_6H_4)_3$)	49.8(2)
$P(NC_4H_8)_3$	$OsCl_2$(*p*-cymene)($P(NC_4H_8)_3$)	51.5(5)
PPh_2Me	$OsCl_2$(*p*-cymene)(PPh_2Me)	52.3(2)
$PPhMe_2$	$OsCl_2$(*p*-cymene)($PPhMe_2$)	58.6(3)
PEt_3	$OsCl_2$(*p*-cymene)(PEt_3)	59.4(5)
PMe_3	$OsCl_2$(*p*-cymene)(PMe_3)	61.6(5)

[a] Enthalpy values are reported with 95% confidence limits.

Results and Discussion

A facile entryway into the thermochemistry of (*p*-cymene)OsCl$_2$(PR$_3$) (*p*-cymene = $CH_3C_6H_4CH(CH_3)_2$) complexes is made possible by the rapid and quantitative reaction of [(*p*-cymene)OsCl$_2$] (**1**) with monodentate phosphine ligands (eq 4).



(4)

PR$_3$ = Tertiary Phosphine

This type of phosphine binding reaction appears to be general and was found to be rapid and quantitative for all ligands calorimetrically investigated at 30.0 °C in methylene chloride. All reaction enthalpy data shown in Table 1 refer to the solution phase and include the enthalpy of solution of **1**.

Relative Importance of Steric vs Electronic Parameter. The enthalpy values presented in Table 1 are based on a molar amount of the dimer and span some 23 kcal/mol. This represents a variation of the single Os−PR$_3$ bond disruption enthalpy of some 11.5 kcal/mol as a function of varied tertiary phosphine ligand.

A number of research groups have been interested in discriminating between steric and electronic ligand factors.[25,26] Giering and co-workers have applied the quantitative analysis of ligand effects (QALE) approach to the question of stereoelectronic contributions to

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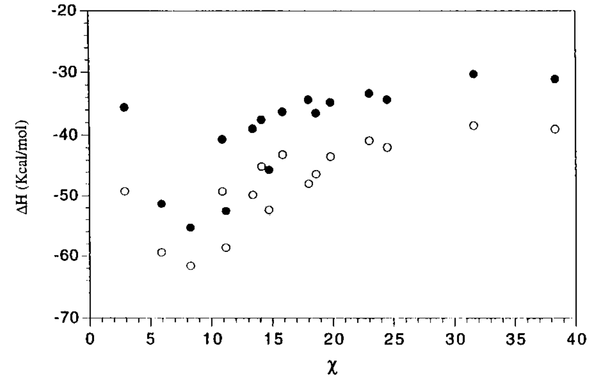


Figure 1. Enthalpies of reaction (kcal/mol) of [(*p*-cymene)-MCl$_2$]$_2$ (M = Ru (●) and Os (○) with phosphine ligands vs electronic parameter (χ).

kinetic and thermodynamic data.[27] A quantitative analysis of the thermochemical data for the osmium system yields the relationship presented in eq 5.

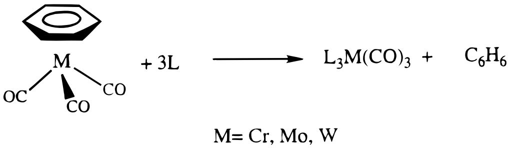
$$-\Delta H = -(0.75 \pm 0.08)\chi - (0.39 \pm 0.04)\theta + (2.87 \pm 0.89)\pi_{\mathrm{pyr}} + 114.1 \pm 5.6 \qquad n = 15; \quad r^2 = 0.96 \quad (5)$$

where ΔH is the enthalpy of reaction (kcal/mol), χ is the electronic parameter[28] associated with a given phosphine ligand, θ represents the phosphine steric factor, and π_{pyr}[29] deals with the π contribution to the electronic factor when the pyrrolyl phosphines are employed. This treatment was performed for 15 ligands and yields $R^2 = 0.960$ as a representation of the goodness of the fit. A similar treatment was performed for the related ruthenium system. The stereoelectronic relationship is represented in eq 6.

$$-\Delta H = -(0.55 \pm 0.08)\chi - (0.51 \pm 0.04)\theta + (1.53 \pm 0.96)\pi_{\mathrm{pyr}} + 122.8 \pm 6.4 \qquad n = 19; \quad r^2 = 0.94 \quad (6)$$

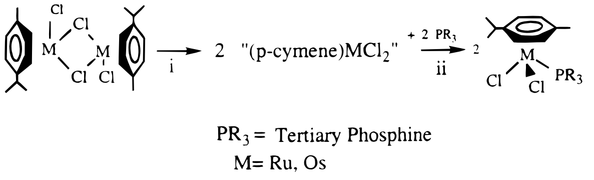
From the two equations, it is statistically defensible to state that the steric and electronic factors both appear to contribute in a relatively equal fashion to the enthalpy of reaction in the (*p*-cymene)RuCl$_2$(PR$_3$) system. Any such comparison between the ruthenium and osmium systems would probably reflect the major difference in electronic properties since Os and Ru are of similar sizes. The data illustrate this point since the osmium system displays a relatively more important electronic contribution. This can be understood in terms of the increased metal−ligand orbital overlap provided by 5d orbital involvement. A plot of enthalpy of reaction versus the phosphine electronic parameter is helpful in illustrating the parallel behavior of the two systems (Figure 1).

The two sets of data appear to follow a similar electronic trend, the osmium enthalpies of reaction being on average some 9 kcal/mol more exothermic than their ruthenium counterparts. A similar increase in reaction enthalpy on descending a group has been observed by Hoff and co-workers[30] in their investigations of group 6 thermochemistry. An average difference of some 10 kcal/mol was observed in the ligand substitution enthalpies between molybdenum- and tungsten-centered systems (eq 7).



(7)

The enthalpy difference between the two systems does not represent the straightforward increase in metal−ligand bond energy. The overall reactions involving these dimeric [(*p*-cymene)MCl$_2$]$_2$ complexes can be thought of as occurring in two steps (eq 8):



(8)

The first step (i) involves dimer scission, which will be more endothermic for the Os system since it will form stronger bonds to the bridging chlorides. A similar trend has been observed by Hoff in his investigations focusing on group 6.[30] The second step (ii) deals with ligand binding to the coordinatively unsaturated intermediate. Keeping this in mind, we now see that the average difference between the ruthenium and osmium systems of 9 kcal/mol is in reality the sum of these two individual reactions and must include the differences in dimer scission enthalpies. This enthalpy difference then becomes a lower limit for M−PR$_3$ bond enthalpy differences between the two systems.

The PPh$_{3-x}$Me$_x$ (x = 0−3) Series. The QALE treatment allows for a global understanding of the thermochemical data in terms of stereoelectronic effect partitioning. A number of thermochemical studies have been performed on the PPh$_{3-x}$Me$_x$ (x = 0−3) series of ligands, and regardless of the stereoelectronic partitioning, it is viewed as a classical example of stepwise variation of both steric and electronic properties.[31] The present system does validate this point. Since the osmium system appears more responsive to changes in electronics, a simple one-parameter relation is sufficient to correlate the enthalpy of reaction and the electronic parameter χ.

Von Philipsborn and co-workers have recently discussed the existence of relationships between ^{187}Os NMR data and the Tolman electronic parameter.[32] A simple relationship between ^{31}P NMR data for the complexed phosphine ligand χ also exists within the

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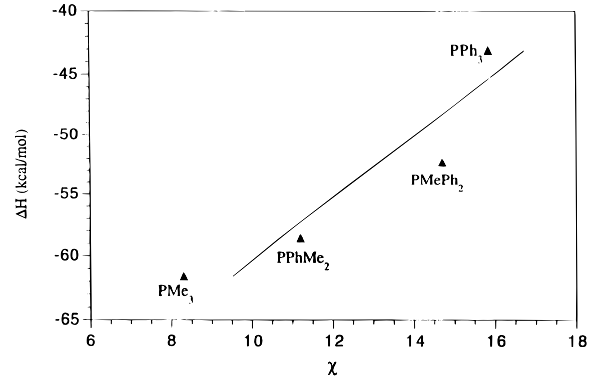

Figure 2. Electronic parameter (χ) vs enthalpy of reaction (kcal/mol) for the $PPh_{3-x}Me_x$ ($x = 0-3$) series. Slope = 0.39; $R = 0.93$.

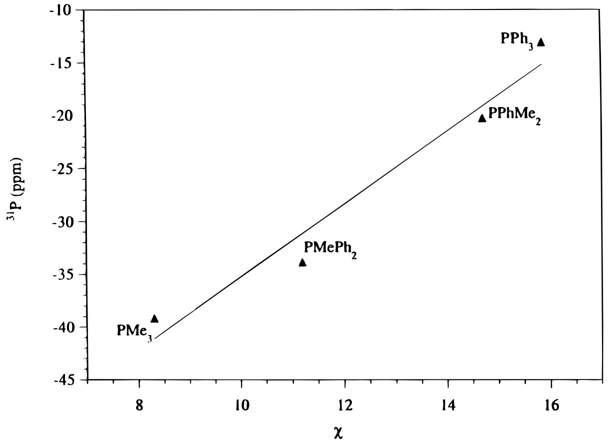

Figure 3. ^{31}P chemical shift (ppm) vs electronic parameter (χ) for the $PPh_{3-x}Me_x$ ($x = 0-3$) series. Slope = 1.43; $R = 0.97$.

$PPh_{3-x}Me_x$ ($x = 0-3$) series, pointing to the more pronounced electronic effects at play within this series (Figure 3).

Since both ΔH and ^{31}P correlate well with χ, it then follows that ΔH and ^{31}P should show good linear dependence ($R = 0.98$; slope = 3.43), reiterating in a more straightforward fashion the dependence of the ^{31}P chemical shift of these complexes as a principal function of an electronic factor.

The P(p-XC$_6$H$_4$)$_3$ (X = CF$_3$, Cl, F, H, CH$_3$, CH$_3$O) Series. The separation of steric from electronic effects is made possible by the investigation of an isosteric series focusing on para-substituted triphenyl phosphine ligands. We have recently reported on the utilization of such a series in a number of organometallic thermochemical studies.[33] Reaction 9 is given as a representative example.

$$Cp'Ru(COD)Cl(soln) + 2PR_3(soln) \rightarrow Cp'Ru(PR_3)_2Cl(soln) + COD(soln) \quad (9)$$

$$R = p\text{-}XC_6H_4; \quad X = Cl, F, Me, OMe, CF_3, \text{and } H$$

Since electronics dominate, in the present osmium system, the simple relationship between enthalpies of reaction and ^{31}P chemical shift (which we have just shown displays a principal electronic influence) should display a good linear fit. Indeed a correlation coefficient of $R = 1.00$ is obtained (slope = 0.33).

The PPh$_{3-x}$(NC$_4$H$_4$)$_x$ (x = 1−3) Series. We have recently explored the thermochemicial behavior of the $PPh_{3-x}(NC_4H_4)_x$ ($x = 1-3$) series.[34] It was determined that this ligand series possessed the capability to involve its π orbitals while interacting with metal centers. This series also proves to possess a unique set of properties. The enthalpies of reaction within this series correlate well with the electronic parameter χ ($R = 0.98$; slope = 0.35).

Conclusion

The labile nature of the chloride bridge in [(p-cymene)OsCl$_2$]$_2$ (**1**) was used to gain entry into the thermochemistry of ligand binding for monodentate phosphine ligands. The enthalpy trend can be explained in terms of electronic and steric contribution to the enthalpy of reaction, with both constituents playing important roles. A quantitative relationship is established between electronic and thermodynamic parameters and displays linear correlation. Reactions of monodentate ligands with **1** also show this reaction to be of synthetic use for isolation of complexes of formulation (p-cymene)Os(PR$_3$)Cl$_2$.

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