Articles

Estimating the Effective Steric Impact of P^tBu_2Me, P^iPr_3, and PCy_3

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Received May 20, 1996[⊗]

Enthalpies of reaction of $Ru(CO)_2L_2$ (L = P^iPr_3, P^tBu_2Me, and PCy_3) with MeNC, PhC≡CPh (both addition reactions) and PhCC−H (C−H oxidative addition) in toluene are exothermic in the range 10−25 kcal/mol and are interpreted in terms of P^tBu_2Me being more bulky than P^iPr_3 or PCy_3. Enthalpy comparisons show that the larger cone angle of PCy_3 than of P^iPr_3 can be overcome by the greater donor power of PCy_3; the origin of the greater donor power of PCy_3 is discussed.

Introduction

Bulky phosphine ligands, such as P^iPr_3, PCy_3, and $^iBu_2P(CH_2)_2P^iBu_2$, play an important role in the recent development of coordination and catalytic chemistry. While these phosphines are often employed simply because they are "bulky", there are some reports that a small steric modification of a phosphine ligand can dramatically alter the reactivity (or "performance") of a complex.[1,2] In addition, reaction products of $RuHCl(CO)L_2$ (L = P^tBu_2Me, P^iPr_3, or PCy_3) with CH_3Li are dependent on the phosphine. The P^tBu_2Me complex shows a clean conversion to a diastereomeric mixture of $RuH(CO)[P^+BuMe(CMe_2CH_2)]L$ while the other two complexes give mixtures of many uncharacterized species.[3]

A considerable body of catalytic chemistry is growing up around the specific bulky ligands shown in the title, primarily in the group of Esteruelas.[4] We have observed that $Os(H)_2(H_2)CO(P^tBu_2Me)_2$ dissociates H_2 significantly more easily than its P^iPr_3 analog, although we could not reliably and *independently* predict which of these two phosphines is more σ-basic and also which is more bulky.[5] It has been reported[6] that $OsHCl(CO)L_2$ with L = P^tBu_2Me or P^iPr_3 hydrogenate an enone by completely different mechanisms. The former, binding H_2 less well, involves an Os_2 species, while the latter proceeds via the H_2 adduct $OsHCl(H_2)(CO)(P^iPr_3)_2$. Phosphine ($PR_3$) cone angles,[7] as they are viewed with increasing scrutiny, are now found to be somewhat variable, just as are the conformations adopted by the three substituents, R. This is especially true for three secondary alkyl substituents (^{i}Pr and cyclohexyl). Finally, for phosphines whose three substituents are not identical (e.g., P^tBu_2Me), the concept of a single cone angle parameter becomes too simple, and rotation about M−P and P−C single bonds can offer a steric profile considerably smaller (or considerably larger) than any average value. We thus sought to measure some observables which would better (empirically) characterize the combined steric and electronic influence of these three phosphines, whose utility has increased in recent years. We present here these results, based on enthalpies of reaction for sterically small and large reagents, as well as on NMR line broadening measures of kinetic parameters.

Experimental Section

General Methods. All manipulations were carried out using standard Schlenk and glovebox techniques under prepurified argon. Pentane, heptane, THF, and toluene were dried over sodium benzophenone ketyl, distilled, and stored in gastight solvent bulbs. Benzene-d_6, toluene-d_8 and THF-d_8 were dried over sodium metal and vacuum-distilled prior to use. Only materials of high purity (as indicated by IR and NMR spectroscopies) were used in the calorimetric experiments. Phosphines (P^iPr_3 and PCy_3) were purchased from Aldrich Chemical Co. and used without purification. Diphenylacetylene and phenylacetylene were purchased from Aldrich Chemical Co. and used after purifying by appropriate methods (sublimation or distillation). Methylisocyanide was synthesized according to a published method.[8] Sodium amalgam was prepared from metallic sodium and mercury. Ru-

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S0276-7333(96)00380-9 CCC: $12.00

thenium trichloride hydrate was a generous loan from Johnson Matthey and used as received. $Ru(CO)_2(P^tBu_2Me)_2$,[3,9] $Ru(CO)_2(P^iPr_3)_2$,[3,9] and *cis*,*cis*,*trans*-$RuCl_2(CO)_2(PCy_3)_2$[10] were synthesized as reported. ^{1}H and ^{31}P NMR spectra were recorded on Varian XL300, Bruker AM500, Nicolet NT-360, Varian Gemini 300, or Oxford 400 spectrometers. ^{1}H NMR chemical shifts are reported in ppm downfield of tetramethylsilane using residual solvent resonances as internal standards. ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4. Infrared spectra were recorded using Perkin-Elmer FTIR Model 2000 and Nicolet 510P spectrometers in 0.1 mm NaCl cells. Elemental analyses were performed on Perkin-Elmer 2400 CHN/S elemental analyzer at the Department of Chemistry, Indiana University.

Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[11] or the enthalpy of solution of KCl in water.[12] The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter has been previously described,[13] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

$Ru(CO)_2(PCy_3)_2$. In a Schlenk flask, *cis*,*cis*,*trans*-$RuCl_2(CO)_2(PCy_3)_2$ (500 mg, 0.63 mmol) and sodium amalgam (4.3 g, 1% sodium content, 1.87 mmol of sodium) were placed together with THF (25 mL). The suspension was vigorously stirred for 24 h under argon. During this period, the color of the suspension changed from colorless to deep red. The THF supernatant was transferred to another Schlenk flask by means of cannula transfer and evaporated to dryness, then the dark red residue was extracted with toluene (5 mL × 3). After filtering away insoluble material, the solution was concentrated to *ca.* 3 mL and cooled to −40 °C, yielding red crystals; yield 321 mg (0.45 mmol, 71%). ^{1}H NMR (C_6D_6, 23 °C): δ 1.15−1.28 (m, 18H), 1.56−1.77 (m, 30H), 2.08−2.17 (m, 18H). ^{31}P{^{1}H} NMR (C_6D_6, 23 °C): δ 59.3 (s). IR: ν_{CO} (Nujol) = 1890 and 1823 cm^{-1}. Anal. Calcd for $RuC_{38}H_{66}O_2P_2$: C, 63.57; H, 9.27. Found: C, 63.29; H, 9.09.

$Ru(CO)_2(CNMe)(P^iPr_3)_2$. A pentane (5 mL) solution of $Ru(CO)_2(P^iPr_3)_2$ (80 mg, 0.17 mmol) was placed in a Schlenk flask fitted with a rubber septum. To this solution, methyl isocyanide (7.0 mg, 0.17 mmol) was added via syringe at room temperature. Immediately, the dark-red solution color changed to yellow. The solution was concentrated to *ca.* 1 mL and cooled to -40 °C to give bright yellow needles: yield 65 mg (0.13 mmol, 75%). ^{1}H NMR (C_6D_6, 23 °C): δ 1.30 (dvt, $J_{HH} \approx J_{HP}$ = 7.2 Hz, 18H, PCC*H*$_3$, 1.31 (dvt, $J_{HH} \approx J_{HP}$ = 7.2 Hz, 18H, PCC*H*$_3$), 2.22 (sept of vt, J_{HH} = 7.2 Hz, J_{HP} = 3.4 Hz, 6H, PC*H*Me), 2.49 (t, J_{HP} = 1.8 Hz, 3H, CH_3NC). ^{31}P{^{1}H} NMR (C_6D_6, 23 °C): δ 74.1 (s). IR: ν_{CO} (C_6D_6) = 1879 and 1836 cm^{-1}, ν_{CN} (C_6D_6) = 2072 cm^{-1}. Anal. Calcd for $RuC_{22}H_{45}NO_2P_2$: C, 50.95; H, 8.75; N, 2.70. Found: C, 51.02; H, 8.91; N, 2.89.

$RuH(C{\equiv}CPh)(CO)_2(P^iPr_3)_2$. A pentane (5 mL) solution of $Ru(CO)_2(P^iPr_3)_2$ (100 mg, 0.21 mmol) was placed in a Schlenk flask fitted with a rubber septum. To this solution, 24 μL of phenylacetylene (22.3 mg, 0.22 mmol) was added via syringe at room temperature. Immediately, the dark red solution color changed to pale yellow. The solution was evaporated to dryness, and the yellow residue was extracted with hot heptane (2 mL × 3). The filtrate was concentrated to *ca.* 2 mL and cooled to −40 °C to give pale yellow needles; yield 107 mg (0.19 mmol, 88%). ^{1}H NMR (C_6D_6): δ −6.75 (t, J_{HP} = 20.6 Hz, 1H, Ru-H), 1.25 (dvt, $J_{HH} \approx J_{HP}$ = 6.9 Hz, 18H, PCC*H*$_3$), 1.27 (dvt, $J_{HH} \approx J_{HP}$ = 6.9 Hz, 18H, PCC*H*$_3$), 2.47 (sept of vt, J_{HH} = 7.0 Hz, J_{HP} = 3.6 Hz, 6H, PC*H*Me), 6.93 (m, 1H, *p*-H), 7.10 (m, 2H, *m*-H), 7.42 (m, 2H, *o*-H). ^{31}P{^{1}H} NMR (C_6D_6, 23 °C): δ 62.6 (s). IR: ν_{CO} (C_6D_6) = 2012 and 1958 cm^{-1}, ν_{CC} (C_6D_6) = 2105 cm^{-1}, ν_{RuH} (C_6D_6) = 1912 cm^{-1}. Anal. Calcd for $RuC_{28}H_{48}O_2P_2$: C, 58.01; H, 8.35. Found: C, 57.95; H, 8.22.

$Ru(\eta^2\text{-}PhC{\equiv}CPh)(CO)_2(P^iPr_3)_2$. To a solution of $Ru(CO)_2(P^iPr_3)_2$ (100 mg, 0.21 mmol) in pentane (5 mL) was added diphenylacetylene (38 mg, 0.21 mmol). Immediately, the deep-red solution became yellow. After filtration, the solution was concentrated to *ca.* 2 mL and cooled to −40 °C to give bright yellow solid; yield 113 mg (0.17 mmol, 82%). ^{1}H NMR (C_6D_6, 20 °C): δ 1.10 (br, 36H, PCC*H*$_3$), 1.90 (m, 6H, PC*H*Me), 7.02 (t, J_{HH} = 7.2 Hz, 2H, p-H), 7.26 (t, J_{HH} = 7.8 Hz, 4H, *m*-H), 8.08 (d, J_{HH} = 7.5 Hz, 4H, *o*-H). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 45.8 (s). IR: ν_{CO} (C_6D_6) = 1950 and 1887 cm^{-1}, ν_{CC} (C_6D_6) = 1746 cm^{-1}. Anal. Calcd for $RuC_{34}H_{52}O_2P_2$: C, 62.27; H, 7.99. Found: C, 62.15; H, 7.55.

$Ru(CO)_2(CNMe)(PCy_3)_2$. To a benzene solution (5 mL) of $Ru(CO)_2(PCy_3)_2$ (60 mg, 0.084 mmol), methyl isocyanide (3.5 mg, 0.085 mmol) was added using a microsyringe. Immediately the color of the solution changed from deep red to pale yellow. The solution was evaporated to dryness, and the residual pale yellow solid was extracted with hot acetone. After filtration, the solution was concentrated to *ca.* 5 mL and cooled to −40 °C to give pale yellow microcrystals; yield 42 mg (0.055 mmol, 66%). ^{1}H NMR (C_6D_6, 20 °C): δ 1.18−1.32 (m, 18H), 1.61−1.82 (m, 30H), 2.11−2.17 (m, 6H), 2.29−2.32 (m, 12H), 2.77 (t, J_{HP} = 1.8 Hz, 3H, CH_3NC). ^{31}P{^{1}H} NMR (C_6D_6, 23 °C): δ 66.2 (s). IR: ν_{CO} (C_6D_6) = 1877 and 1840 cm^{-1}, ν_{CN} (C_6D_6) = 2062 cm^{-1}. Anal. Calcd for $RuC_{40}H_{69}NO_2P_2$: C, 63.30; H, 9.16; N, 1.85. Found: C, 62.92; H, 8.79; N, 1.53.

$RuH(C{\equiv}CPh)(CO)_2(PCy_3)_2$. $Ru(CO)_2(PCy_3)_2$ (100 mg, 0.14 mmol) was dissolved in benzene (5 mL) in a Schlenk flask. To this solution, phenylacetylene (17 μL, 15.8 mg, 0.15 mmol) was added by means of syringe. The obtained colorless solution was evaporated to dryness, and the oily residue was extracted with heptane (2 mL × 3). The heptane solution was concentrated to *ca.* 2 mL, and cooled to −40 °C to give colorless powder; yield 75 mg (0.09 mmol, 66%). ^{1}H NMR (C_6D_6, 20 °C): δ −6.43 (t, J_{HP} = 20.7 Hz, 1H, Ru-H), 1.25 (m, 18H, 1.62 (m, 6H), 1.77 (m, 24 H), 2.19 (m, 12H), 2.45 (m, 6H), 6.94 (m, 1H, *p*-H), 7.16 (m, 2H, *m*-H), 7.59 (m, 2H, *o*-H). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 53.8 (s). IR: ν_{CO} (C_6D_6) = 2010 and 1958 cm^{-1}, ν_{CC} (C_6D_6) = 2101 cm^{-1}, ν_{RuH} (C_6D_6) = 1916 cm^{-1}. Anal. Calcd for $RuC_{46}H_{72}O_2P_2$: C, 67.37; H, 8.85. Found: C, 67.36; H, 8.48.

$Ru(\eta^2\text{-}PhC{\equiv}CPh)(CO)_2(PCy_3)_2$. To a solution of $Ru(CO)_2(PCy_3)_2$ (120 mg, 0.17 mmol) in toluene (5 mL) was added diphenylacetylene (30 mg, 0.17 mmol). Immediately, the deep red solution became yellow. After filtration, the solution was concentrated to *ca.* 2 mL and cooled to −40 °C to give yellow solid; yield 109 mg (0.12 mmol, 73%). This material is very slightly contaminated with free PhCCPh. ^{1}H NMR (C_6D_6, 20 °C): δ 0.99−1.13 (m, 18H), 1.49−1.70 (m, 30H), 1.84−1.91 (m, 6H), 2.07−2.13 (m, 12H), 7.05 (t, J_{HH} = 7.2 Hz, 2H, *p*-H), 7.33 (t, J_{HH} = 7.8 Hz, 4H, *m*-H), 8.17 (d, J_{HH} = 6.9 Hz, 4H, *o*-H). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 39.7 (s). IR: ν_{CO} (C_6D_6) = 1948 and 1883 cm^{-1}, ν_{CC} (C_6D_6) = 1744 cm^{-1}. Anal. Calcd for $RuC_{52}H_{76}O_2P_2$: C, 69.69; H, 8.55. Found: C, 70.23; H, 8.33.

NMR Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount (±0.2 mg) of the organometallic complex was placed in a Wilmad screw-capped NMR tube fitted with a septum, and toluene-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 conditions. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all organometallic reactions investigated. Only reactants and products were observed in the course of titration.

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Calorimetric Measurement of Reactions between $Ru(CO)_2(P^iPr_3)_2$ and Methyl Isocyanide (MeNC). 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 $Ru(CO)_2(P^iPr_3)_2$ was accurately weighed into the lower vessel; it was closed and sealed with 1.5 mL of mercury. A 4 mL volume of a stock solution of MeNC in toluene was added, and the remainder of the cell was assembled, removed from the glovebox and inserted in the calorimeter. In order to hinder possible further substitution reactions, addition of five equivalents of phosphine ligand was used as suppressant in the stock solution. Furthermore, MeNC used in the preparation of the stock solution was present in an amount requiring stoichiometric reaction with the ruthenium complex. The reference vessel was loaded in an identical fashion with the exception that no ruthenium 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 then removed from the calorimeter, taken into the glovebox, opened, and the infrared cell filled under inert atmosphere. An infrared spectrum of each product was recorded using this procedure. Conversion to $Ru(CO)_2L(P^iPr_3)_2$ was found to be quantitative under these reaction conditions. The enthalpy of reaction -17.9 ± 0.1 kcal/mol represents the average of five individual calorimetric determinations. A similar procedure was employed for all ruthenium complexes reacting with MeNC or PhCCPh. Measurements for reactions with PhCCH were similar, but it was not necessary to add free phosphine ligand. Conversion to $RuH(C{\equiv}CPh)(CO)_2(P^iPr_3)_2$ was found to be quantitative under these reaction conditions. The enthalpy of reaction -11.1 ± 0.1 kcal/mol represents the average of five individual calorimetric determinations.

Calorimetric Measurement of Enthalpies of Solution of the Complexes in Toluene. In order to consider all species in solution, the solvation enthalpies of $Ru(CO)_2L_2$ species had to be directly measured. This was performed by using a procedure similar to 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, for $Ru(CO)_2(P^iPr_3)_2$, is measured as 3.6 ± 0.1 kcal/mol.

Results and Discussion

Comparison of P^tBu_2Me and P^iPr_3. It is first useful to note that the quantitative infrared intensity ratios[14] for $Ru(CO)_2L_2$ in solution yield angles between the CO vectors of 130° (P^tBu_2Me) and 129° (P^iPr_3). The $\nu_{sym} - \nu_{asym}$ values (71 and 70 cm^{-1}) indicate identical CO/CO interaction force constants and thus provide independent evidence for identical ∠C−Ru−C values in the two compounds. With these points established, the fact that ν_{sym} and ν_{asym} are each 3 cm^{-1} lower for L = P^iPr_3 than for P^tBu_2Me indicates that P^iPr_3 (cone angle 160°) is a slightly better donor than P^tBu_2Me (cone angle 161°), and thus that $Ru(CO)_2(P^iPr_3)_2$ is a somewhat better π-base toward any entering ligand.

The ligand binding enthalpies (Table 1) permit several conclusions about the two phosphines. In each case, $\Delta H°$ is more negative when L = P^iPr_3, and is more negative for MeNC than for PhCCPh. This originates in some combination of steric and electronic effects. Comparing the two phosphine complexes, $\Delta\Delta H°$ is smaller for MeNC as the added ligand (2.1 kcal/mol) than for PhCCPh (4.6 kcal/mol). We interpret this as

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Table 1. Enthalpies of Reaction[a] for Reagent L′ with $Ru(CO)_2L_2$ in Toluene at 30 °C

	L		
L′	P^tBu_2Me	P^iPr_3	PCy_3
MeNC	−19.4(1)	−21.5(2)	−21.0(2)
PhC≡CPh	−10.1(1)	−14.7(1)	−16.1(2)
PhCC−H	−23.9(2)	−24.0(1)	−25.5(3)

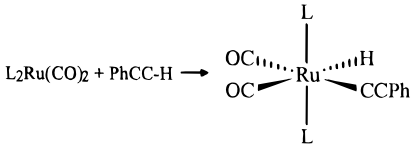
[a] Enthalpies are reported with 95% confidence limits in the last digit given.

PhCCPh showing greater discrimination or selectivity between the two phosphine derivatives. If we take the 2.1 kcal/mol for the sterically compact MeNC as indicating primarily electronic effects (i.e., the P^iPr_3 complex is a better π-base), the greater discrimination involving PhCCPh is attributed to steric effects for this bulky alkyne. The $\Delta H°$ value for PhCCPh adding to $Ru(CO)_2(P^tBu_2Me)_2$ is so small (only comparable to a strong hydrogen bond) that the implied steric strain leads to another outlet for relief of steric repulsion: loss of one phosphine (eq 1).

$$(PhCCPh)Ru(CO)_2L_2 \rightleftharpoons (PhCCPh)Ru(CO)_2L + L \quad (1)$$

This reaction is evident from the observation of a broad $^{31}P\{^1H\}$ NMR signal ($W_{1/2} \simeq$ ca. 400 Hz) for $Ru(PhCCPh)(CO)_2L_2$ coalesced with free L in benzene at 23 °C.[3] Since this chemical shift is essentially that of the complex at −40 °C, the mole fraction of the monophosphine complex must be less than ∼3% at 23 °C. For comparison, the $W_{1/2}$ of the $^{31}P\{^1H\}$ NMR signal of $Ru(PhCCPh)(CO)_2(P^iPr_3)_2$ is only ca. 40 Hz (at 23 °C), indicating that *the effective size of P^tBu_2Me is larger than that of P^iPr_3*.[15] This is the first direct size comparison of these two ligands. However, it certainly gives additional support to the interpretation of reaction enthalpies for PhCCPh binding to $Ru(CO)_2L_2$ as being significantly influenced by steric effects.

This hypothesis of certain substrates being especially sensitive to steric effects is subject to test. Another alkyne, but one which binds only with a small steric profile because it effects oxidative addition of its H−C(sp) bond, is PhCC−H (eq 2). The slender profile of the



(2)

resulting hydride and acetylide ligands, together with the *trans* disposition of the bulky phosphines in both reactant and product in eq 2, suggests that the ΔH of eq 2 should be more similar for L = P^iPr_3 and P^tBu_2Me than is ΔH for addition of PhCCPh. Indeed (Table 1), the values are −24.0 and −23.9 kcal/mol, respectively. This confirms the idea that certain reactions can be significantly less subject to steric influence than others. Given the H−C(sp) BDE of 132 kcal/mol,[16] the sum of the Ru−H and Ru−C_2Ph BDE's is 156 kcal/mol. Esti-

(15) Indeed $Ru(PhCCPh)(CO)_2L_2$ is not isolable for L = P^tBu_2Me due to the phosphine dissociation described above, but yellow crystals were obtained in pure form for L = P^iPr_3.

(16) McMillan, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

mating the Ru−H BDE as 60 kcal/mol gives a value of 96 for the Ru−C_2Ph BDE. It is also significant that the greater π-basicity (reducing power) deduced for $Ru(CO)_2(P^iPr_3)_2$ from ν(CO) values is too small to alter ΔH for oxidative addition of PhC_2−H by more than 1 kcal/mol.

Comparison to PCy_3. The cone angle of PCy_3 (170°) is significantly larger than that of P^iPr_3 (160°). Our initial attempt at magnesium reduction of *cis*,*cis*,*trans*-$RuCl_2(CO)_2(PCy_3)_2$ (**1**) as reported for analogous complexes with P^tBu_2Me or P^iPr_3 failed, presumably due to a very low solubility of **1** in THF. Sodium amalgam reduces **1**, which is suspended in THF, to give $Ru(CO)_2(PCy_3)_2$ in high yield. $Ru(CO)_2(PCy_3)_2$ is spectroscopically quite similar to the other two $Ru(CO)_2L_2$ species studied here. In particular, there is no (^{31}P NMR line broadening) evidence for dissociative equilibrium of PCy_3 or of agostic or oxidative addition of a cyclohexyl group, or of association or reaction with benzene solvent.

The ν_{CO} intensity ratio (I_{asym}/I_{sym}) is significantly smaller for $Ru(CO)_2L_2$ when L = PCy_3 (3.7) than when L = P^tBu_2Me or P^iPr_3 (4.6−4.4). This yields an ∠C−Ru−C of 126° in $Ru(CO)_2(PCy_3)_2$. Thus, more than merely metal electron density changes as we change the phosphine to PCy_3; the structural change will also influence the reaction enthalpy. The larger σ-donor power of PCy_3 makes Ru more electron-rich; this, in turn, causes ∠C−Ru−C to decrease, since a small angle enhances back bonding to the *two* carbonyls.[9]

The molecule reacts rapidly with MeNC and PhC_2Ph by simple adduct formation, and with PhCCH by oxidative addition. The reaction enthalpy for addition of MeNC to $Ru(CO)_2(PCy_3)_2$ is essentially identical to that of the P^iPr_3 analog, and shows no strong evidence that the greater donor power of PCy_3 over P^iPr_3 (judged by Tolman's electronic parameters)[17] influences this reaction enthalpy, and certainly confirms the idea that MeNC is a sterically-undemanding addend which is not significantly influenced by the different cone angles of these two phosphines. Comparing the C−H oxidative addition enthalpies for the sterically-undemanding reagent PhCC−H, the more σ-donating phosphine PCy_3 causes a more negative reaction enthalpy. This confirms that PCy_3 is a stronger electron donor than P^iPr_3. The surprising result is that the reaction enthalpy for addition of the sterically-demanding PhC≡CPh is more negative for the significantly more bulky PCy_3 than for P^iPr_3. Quite unpredictably, but consistent with the reaction enthalpy, $Ru(PhC_2Ph)(CO)_2(PCy_3)_2$ shows little or no line broadening in its $^{31}P\{^1H\}$ NMR spectrum, indicating that loss of PCy_3 occurs to a lesser extent than it does for P^tBu_2Me or P^iPr_3. Indeed, $Ru(PhCCPh)(CO)_2(PCy_3)_2$ can be isolated as a crystalline solid.[3,15] Thus, electronic factors dominate steric ones for binding of PhCCPh.

Why is a larger phosphine (PCy_3) more (σ) donating (i.e., Tolman electronic parameter) than a smaller one (P^iPr_3)? This can perhaps be understood as a consequence of the *sterically dictated* larger C-P−C angle of PCy_3 enforcing more p character to the phosphorus lone pair, which causes its energy to rise. A higher HOMO of PR_3 then makes it a stronger σ-donor.[18]

One additional feature will influence only certain of the reaction enthalpies. P^tBu_2Me has a unique geometric feature compared to the other two phosphines discussed here: it has two big (^{t}Bu) and one small (Me) substituents on the phosphorus atom. In the solid-state structure of $Ru(CO)_2(P^tBu_2Me)_2$, the orientation of the phosphines is staggered; i.e., the Me groups of each phosphine ligand point to opposite directions. However, it is expected that both Me's are oriented toward the PhC_2Ph ligand in $Ru(PhC_2Ph)(CO)_2(P^tBu_2Me)_2$ to decrease steric interaction between PhC_2Ph and the phosphines. Thus, unique among the phosphines studied here, P^tBu_2Me can respond to increased steric demand during adduct formation.

Studies[19,20] of several reactions of $Ru(CO)_5$ reveal that they begin with dissociation of one CO, to form transient $Ru(CO)_4$ with $\Delta H^‡ = 27.6$ kcal/mol (and $\Delta S^‡ = 15.2$ cal/(K mol)). This establishes the approximate Ru−CO bond dissociation energy to form unsaturated Ru(0) unassisted by steric effects, and it compares remarkably well with the enthalpy of binding of MeNC to $Ru(CO)_2L_2$ in Table 1.

Acknowledgment. This work was supported by the National Science Foundation Grants CHE-93-05492 and 94-12830 and by material support from Johnson Matthey/Aesar.

OM960380Q

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