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Notes

Ligand (L) Influence on CO Binding Enthalpies to $Ru(CO)_2L_2$

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Summary: Reaction enthalpies for the addition of CO to $Ru(CO)_2L_2$ *(L =* P^tBu_2Me, P^iPr_3, *and* PCy_3*) in toluene are −26.2(3), −31.4(2), and −28.9(4) kcal/mol, respectively. These are larger than the enthalpies of reaction with MeNC, PhC≡CPh, and PhCC−H.* P^tBu_2Me *consistently gives the least amount of enthalpy released, but only when CO (and MeNC) is the reagent does* P^iPr_3 *yield a more exothermic enthalpy of reaction than* PCy_3*. The generally subtle influences on* ΔH *by* P^iPr_3 *and* PCy_3 *are rationalized in terms of the contradictory steric and electronic effects as isopropyl is replaced by cyclohexyl.*

An extraordinary amount of organometallic research activity[1] on unsaturated Rh, Ir, Ru, and Os has employed bulky monodentate phosphines. The influence of these phosphines is to prevent dimerization and to sterically shield the Lewis acid site. Another consequence is the creation of considerable steric selectivity toward substrate binding: the (two) bulky phosphines are generally both *cis* to the open coordination site. This field has advanced using P^iPr_3, PCy_3, P^tBu_2Me, P^iPr_2Ph, and P^tBu_2Ph in a somewhat unsystematic and empirical manner. The choice of phosphine employed, and those factors which differentiate these phosphines from one another, are not rationally and objectively established: as an example, Chaudret has isolated RuH_6L_2 complexes, and for L = PCy_3 a mononuclear complex can be isolated,[2] while for L = P^iPr_3 the reaction yields a mixture of $Ru_2H_6L_4$ and RuH_6L_2 (detected only by NMR, and that transforms into the dimer, slowly in solution and rapidly in vacuo).[3] We have observed that $HC{\equiv}CSiMe_3$ inserts into the Os−H bond of $OsHCl({=}C{=}CHSiMe_3)L_2$, giving $OsCl\{(E)\text{-}CH{=}CHSiMe_3\}({=}C{=}CHSiMe_3)L_2$ when L = P^iPr_3 but not when L = P^tBu_2Me.[4] As we move to quantitative comparative measurements on complexes of these phosphines, this ignorance becomes increasingly irritating. Describing the enthalpy for binding Lewis bases to $M(CO)_3(PCy_3)_2$ (M = Mo and W), Hoff has stated "...experimental data on steric strain present no clear picture...for...second- and third-row metals".[5] He particularly cites an imperfect understanding "...for sterically crowded systems where the conflicting demands of entropy−enthalpy of reaction shows up".[5] Indeed, it was our objective in a recent solution calorimetric study[6] to try to rank some of the above phosphines based on the reaction enthalpies for eq 1 (ligand binding) or eq 2 (oxidative addition). Such a ranking is clearly a composite consequence of the changes in steric as well as electronic influences of the substituents on the phosphines. Separating these contributions is not our objective. However, original thermodynamic studies by Tolman[7] have certainly proven quite useful.

$$Ru(CO)_2L_2 + D \rightarrow Ru(CO)_2L_2(D) \qquad (1)$$

$$D = MeNC,\ PhCCPh$$

$$Ru(CO)_2L_2 + HCCPh \rightarrow RuH(CCPh)(CO)_2L_2 \qquad (2)$$

The challenge of distinguishing among our chosen phosphines is great. For example, both P^iPr_3 and PCy_3 bear three secondary alkyl substituents, so their electronic and steric effects might be very similar. Moreover, P^iPr_3 and P^tBu_2Me are isomers of formula PC_9H_{21}, so it is not intuitively obvious which is the larger phosphine. Finally, while phenyl is probably larger than methyl, its flat profile (anisotropy) might make it able to create a small steric demand at certain orientations, thus frustrating the comparison of P^tBu_2R for R = Me and Ph.

We present here the solution calorimetric measurements of reaction enthalpies for another reaction of the type in eq 1, where now D = CO. We hope that such "operational" evidence will help to define the net (i.e., electronic and steric) difference among subtly different but very bulky phosphines and thus prove useful in the future.

Experimental Section

General. All manipulations were carried out using standard Schlenk and glovebox techniques under prepurified argon. Pentane and toluene were dried over sodium ben-

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[1] See, for example: (a) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108,* 7000. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118,* 100. (c) Esteruelas, M.; Oro, L. A.; Valero, C. *Organometallics* **1992**, *11,* 3362. (d) Clark, H. C.; Hampden-Smith, M. J. *Coord. Chem. Rev.* **1987**, *79,* 229. (e) Flügel, R.; Windmüller, B.; Gevert, O.; Werner, H. *Chem. Ber.* **1996**, *129,* 1007.

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

	L		
L′	P^tBu_2Me	P^iPr_3	PCy_3
CO	−26.2(3)	−31.4(2)	−28.9(4)
PhCC−H[b]	−23.9(2)	−24.0(1)	−25.5(3)
MeNC[b]	−19.4(1)	−21.5(2)	−21.0(2)
PhC≡CPh[b]	−10.1(1)	−14.7(1)	−16.1(2)

[a] Enthalpies are reported with 95% confidence limits in the last digit given. [b] Reference 6.

zophenone ketyl, distilled, and stored in gastight solvent bulbs. CH_2Cl_2 was dried over calcium hydride, distilled, and stored in gastight solvent bulbs. Benzene-d_6 was dried over sodium metal and vacuum-distilled prior to use. $Ru(CO)_2(P^tBu_2Me)_2$,[8a] $Ru(CO)_2(P^iPr_3)_2$,[8b] and $Ru(CO)_2(PCy_3)_2$[6] were synthesized as reported. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Gemini 300 spectrometer. Infrared spectra were recorded using Nicolet 510P or Perkin Elmer 2000 spectrometers in 0.1 mm NaCl cells.

$Ru(CO)_3(P^tBu_2Me)_2$. A solution of $Ru(CO)_2(P^tBu_2Me)_2$ (120 mg, 0.25 mmol) in toluene (7 mL) was frozen in liquid N_2, the headspace of the Schlenk flask was evacuated, and excess CO (1 atm) was introduced. On warming to room temperature and stirring, the solution color immediately changed from deep red to yellow. After 2 h of stirring, the volatiles were removed under vacuum and pentane was added to provide a pale yellow solid. Yield: 90 mg (71%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 1954 (w), 1878 (s), 1852 (s). The NMR data are consistent with those reported previously.[9]

$Ru(CO)_3(PCy_3)_2$. This compound was prepared as described for $Ru(CO)_3(P^tBu_2Me)_2$, starting from $Ru(CO)_2(PCy_3)_2$ (100 mg, 0.14 mmol). Yield: 85 mg (82%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 1952 (w), 1870 (s), 1855 (s). ^1H NMR (C_6D_6, 300 MHz): δ 2.29−1.14 (m, 66 H, PCy_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.4 MHz): δ 63.5 (s).[10]

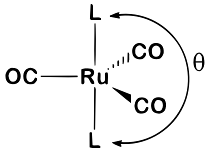
$Ru(CO)_3(P^iPr_3)_2$. This compound was prepared as described for $Ru(CO)_3(P^tBu_2Me)_2$, starting from $Ru(CO)_2(P^iPr_3)_2$ (100 mg, 0.21 mmol). Yield: 21 mg (20%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 1956 (w), 1875 (s), 1860 (s). The NMR data are consistent with those reported previously.[11]

Calorimetric Measurement of Reactions between $RuL_2(CO)_2$ and Carbon Monoxide, L = P^tBu_2Me, P^iPr_3, and PCy_3. The mixing vessels of the Setaram C-80 calorimeter were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20−30 mg sample of $RuL_2(CO)_2$ was accurately weighed into the lower vessel; it was then closed and sealed with 1.5 mL of mercury. A toluene solution (2.5 mL) saturated with CO was added. 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 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. When thermal equilibrium was reached again after the end of the reaction (1−2 h), the vessels were then removed from the calorimeter and taken into the glovebox and opened and the infrared cell filled under inert atmosphere. Conversion to the desired product was found to be quantitative under these reaction conditions. The enthalpies of reaction listed in Table 1 represent solution state values and are the average of five individual calorimetric determinations.

Results and Discussion

The structures of all $Ru(CO)_3L_2$ complexes formed here might be expected to be that of **I**. In fact, the infrared spectra of all of the complexes show one strong band, generally consistent with D_{3h} symmetry. However, all show varying degrees of splitting of this, the apparent E vibration (~1856 cm^{-1}) of **I** (θ = 180°).



I

Moreover, a very weak absorption is also present at 1954 cm^{-1}, consistent with some allowedness of the A vibration of **I**. It thus appears that all $Ru(CO)_3L_2$ complexes studied here may have structure **I**, but with θ slightly less than 180°.

The CO reaction enthalpies (Table 1) are more negative than any we have reported earlier, and in particular, they are much more negative (by 5−10 kcal/mol) than those of the other sterically compact π-acid MeNC. This ranking of CO and MeNC is consistent with the previously reported evidence that $Ru(CO)_2L_2$ depends much more on its π-base (i.e., back-bonding) character for the strength of the Ru−L′ bond than on L′ → Ru σ donation. Indeed, d^8 $Ru(CO)_2L_2$ reveals itself to be very different from d^6 $W(CO)_3(PCy_3)_2$ in that the latter binds the (primarily) σ-bases THF, MeCN, N_2, and pyridine,[12] *none* of which binds detectably (NMR assay) to $Ru(CO)_2L_2$.[8]

Quantum calculations show that the energy to convert $Mo(CO)_6$ to $Mo(CO)_5$ + CO is 39.7[13] kcal/mol while that of $Ru(CO)_5$ to $Ru(CO)_4$ + CO costs distinctly less (33 kcal/mol).[13] Thus, the experimental value (27.6 kcal/mol)[14] for $Ru(CO)_5$ would lead to the expectation that any agostic interaction would reduce the reaction enthalpy for $Ru(CO)_2L_2$ + CO by about 10 kcal/mol (the enthalpy of the agostic interaction in $W(CO)_3(PCy_3)_2$[15]). The observed values (Table 1) of nearly 30 kcal/mol are high enough to confirm the absence of a significant agostic interaction (or interaction with solvent) in any of the three $Ru(CO)_2L_2$ species studied here. No agostic interaction is observed in $Ru(CO)_2(P^tBu_2Me)_2$ in an X-ray diffraction study.[8] Moreover, if we attribute the larger first BDE of $Mo(CO)_6$ than that of $Ru(CO)_5$ to the greater "instability" (electrophilicity) of $Mo(CO)_5$ *vs* $Ru(CO)_4$, then we can understand that any agostic interac-

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tion with $Mo(CO)_5$ might be $39.7 - 33 \approx 7$ kcal/mol weaker toward Ru.

The ligands L in Table 1 are arranged so that $-\Delta H$ generally increases to the right. It was on the basis of $L = P^tBu_2Me$ having the smallest $-\Delta H$ value that we concluded earlier that this was operationally bulkier than the isomeric P^iPr_3 analog. This trend persists for $L' = CO$.

Our prior comparison of P^iPr_3 and PCy_3 showed that, especially for the more sterically demanding reagents PhC≡CPh and PhCC−H, $-\Delta H$ was *larger* for the bulkier (by 10° in cone angle) PCy_3. In fact, the larger cone angle, 170°, for PCy_3 originates mainly from the larger $\angle C-P-C$ for this phosphine (106.3° *vs* 104.9 for P^iPr_3). However, this has the compensating electronic effect of raising the energy (hence the σ-basicity) of the lone pair, due to decreasing s character in that orbital. In this way, the bulkier phosphine has a compensating electronic advantage, which the enthalpy data shows to be dominant. However, this argument clearly fails for the CO binding enthalpy to $Ru(CO)_2L_2$, which is nearly 3 kcal/mol smaller for $L = PCy_3$. Note that for the binding of MeNC, $-\Delta H$ is also smaller for the bulkier PCy_3.

We propose that the opposing steric and electronic effects in comparing P^iPr_3 and PCy_3 are reagent dependent. For reactions which approach full oxidative addition (PhCC−H), the electronic superiority of PCy_3 dominates. For reactions which leave the metal zerovalent (even those with a high degree of back-bonding), electronic effects dominate for the bulkier L′ (PhC≡CPh) while steric effects dominate for the smaller L′ (CNMe, CO).

The enthalpies of binding CO to the several d^8 $Ru(CO)_2L_2$ reported here, −26 to −31 kcal/mol, are similar to that for d^6 $W(CO)_3(PCy_3)_2$ (−30.4 kcal/mol).[5] Since *all* of these unsaturated species have the “prepared” geometry of the product, this similarity is perhaps understandable. In stark contrast is the lower (−10.8 kcal/mol) enthalpy of binding CO to d^8, but planar, $Ir(CO)Cl(PPh_3)_2$;[16] in this case, some energetic price must be paid for deforming CO and Cl from their *trans* relationship in the reagent to a *cis* relationship in the product.

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