Thermodynamics of Phosphine Coordination to the [PNP]Rh^{I} Fragment: An Example of the Importance of Reorganization Energies in the Assessment of Metal−Ligand "Bond Strengths"

Jinkun Huang,[†] **Christopher M. Haar,**[†] **Steven P. Nolan,***[†,§] **William J. Marshall,**[‡] **and Kenneth G. Moloy***[‡,||]

Contribution from the Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148, and Central Research and Development,[⊥] *E. I. du Pont de Nemours & Co., Inc., Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880-0328*

Received December 11, 1997

Abstract: Reaction enthalpies of the complexes [RPNP]Rh(COE) ([RPNP] = $N(SiMe_2CH_2PPh_2)_2$, $N(SiMe_2CH_2P^iPr_2)_2$; COE = cyclooctene) with a series of phosphine ligands and CO have been measured by solution calorimetry. The measured enthalpies span a range of ca. 40 kcal/mol. These systems favor coordination of strong π-acceptor/weak σ-donor ligands as shown by the trend in ΔH_{rxn}: CO ≫ $Ppyrl'_3$ > $Ppyrl_3$ > $PPhpyrl_2$ > PPh_2pyrl > PPh_3. This trend is exactly the opposite of that observed in another square planar rhodium(I) system, *trans*-$RhCl(CO)(PZ_3)_2$. With the exception of CO, the ligands investigated are isosteric, and so the observed trends are electronic in nature. Single-crystal X-ray diffraction studies on several of theses complexes ([RPNP]RhL where R, L = Ph, PPh_3; Ph, $Ppyrl_3$; Ph, CO; ^{i}Pr, PPh_3; ^{i}Pr, $Ppyrl_3$; ^{i}Pr, CO; ^{i}Pr, COE) have been performed. Although the structural trends are readily understood in terms of the electronic (donor/acceptor) nature of each ligand array, it is not obvious that the structural data predict the trends or, in particular, the trend reversal in ΔH_{rxn} in the two Rh(I) systems. Rather, these results illustrate the importance of reorganization energies in thermodynamic analyses of metal−ligand bonding, especially in the presence of synergistic bonding involving σ-donor, π-donor, and π-acceptor ligands, interacting through shared metal orbitals (electron push−pull). In such cases the interpretation of a metal−ligand bond dissociation enthalpy (D) as an intrinsic, universal, and transferable property of that bond (e.g., a "bond strength") is an invalid proposition.

Introduction

The quantitative assessment of metal−ligand thermochemistry has been of interest for some time.[1] This interest is driven by the need for a better understanding of metal−ligand interactions and thus reactivity. Significant progress has been made toward the accumulation of a great deal of information and insight on this subject. The ultimate goal is to apply the knowledge and understanding thus gained in a predictive manner to stoichiometric and catalytic chemistry.

Phosphines, PZ_3,[2] are a class of ligands that are prevalent in stoichiometric and catalytic organometallic chemistry.[3] They generally play a role as ancillary ligands used to fine-tune the reactivity of the metal center and appended ligands. A fundamental understanding of the mechanisms by which phosphines modulate metal reactivity is important for the development of new catalysts and reagents. To this end, we have been active in delineating, measuring, and calibrating the steric and electronic contributions of phosphine ligands to organometallic thermochemistry by means of solution calorimetry. We have studied a number of systems which probed the steric ($CpRu(PZ_3)_2Cl$, $Cp^*Ru(PZ_3)_2Cl$) and electronic ($Fe(CO)_3(PZ_3)_2$, $RhCl(CO)(PZ_3)_2$, $Rh(acac)(CO)(PZ_3)$) contributions of phosphine ligands, as shown in eqs 1−4.[4−6]

[†] University of New Orleans.

[‡] E. I. du Pont de Nemours & Co., Inc.

[§] E-mail: spncm@uno.edu.

[||] E-mail: moloykg@esvax.email.dupont.com.

[⊥] Contribution No. 7647.

(1) (a) Nolan, S. P. Bonding Energetics of Organometallic Compounds. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; J. Wiley and Sons: New York, 1994; Vol. 1, p 307. (b) Hoff, C. D. *Prog. Inorg. Chem.* **1992**, *40*, 503. (c) Marks, T. J., Ed. Bonding Energetics in Organometallic Compounds. *ACS Symp. Ser.* **1990**, *428*. (d) Martinho Simões, J. A. Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

(2) We use the term "phosphine" here to refer in a very generic sense to P(III)-donor ligands of the type PZ_3, where Z may be carbon or a heteroatom, especially oxygen and nitrogen (e.g., phosphites and phosphoramides).

(3) See the following and references therein: (a) McAuliffe, C. A.; Mackie, A. G. P-Donor Ligands. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; J. Wiley and Sons: New York, 1994; Vol. 6, p 2989. (b) Wilson, M. R.; Woska, D. C.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 1742. (c) Caffery, M. L.; Brown, T. L. *Inorg. Chem.* **1991**, *30*, 3907. (d) Dunne, B. J.; Morris, R. B.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 653. (e) Corbridge, D. E. C. *Phosphorus. An Outline of its Chemistry, Biochemistry and Technology*, 5th ed.; Elsevier: New York, 1995; Chapter 10. (f) Levason, W. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: New York, 1990; Vol. 1, Chapter 15. (g) McCauliffe, C. A. *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 2, p 989. (h) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 66. (i) Pignolet, L. H., Ed. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983. (k) Alyea, E. C.; Meek, D. W. *Adv. Chem. Ser.* **1982**, *196*.

S0002-7863(97)04200-5 CCC: $15.00

$$\mathrm{Cp'Ru(COD)Cl} + \mathrm{PZ_3} \xrightarrow{\Delta H_{\mathrm{rxn}}} \mathrm{Cp'Ru(PZ_3)_2Cl} + \mathrm{COD} \tag{1}$$

$$\mathrm{Cp'} = \mathrm{C_5H_5},\ \mathrm{C_5(CH_3)_5}$$

$$\mathrm{Fe(BDA)(CO)_3} + 2\mathrm{PZ_3} \xrightarrow{\Delta H_{\mathrm{rxn}}} \mathrm{Fe(CO)_3(PZ_3)_2} + \mathrm{BDA} \tag{2}$$

$$\mathrm{BDA} = \mathrm{PhCHCHCOCH_3}$$

$$\tfrac{1}{2}[\mathrm{RhCl(CO)_2}]_2 + 2\mathrm{PZ_3} \xrightarrow{\Delta H_{\mathrm{rxn}}} trans\text{-}\mathrm{RhCl(CO)(PZ_3)_2} + \mathrm{CO} \tag{3}$$

$$\mathrm{Rh(CO)_2(acac)} + \mathrm{PZ_3} \xrightarrow{\Delta H_{\mathrm{rxn}}} \mathrm{Rh(CO)(PZ_3)(acac)} + \mathrm{CO} \tag{4}$$

In the systems examined to date, and where electronic contributions dominate, phosphine substitution becomes increasingly favored as the basicity of the phosphine increases. Thus, ΔH_{eq} for the equilibrium in eq 5, where $\mathrm{L}_n\mathrm{M} = \mathrm{RhCl(CO)}$ or $\mathrm{Fe(CO)_3}$, follows the order $\mathrm{P}(p\text{-}\mathrm{CH_3OC_6H_4})_3 > \mathrm{PPh_3} > \mathrm{P}(p\text{-}\mathrm{CF_3C_6H_4})_3 > \mathrm{Ppyrl_3} > \mathrm{Ppyrl'_3}$.[7]

$$\mathrm{L}_n\mathrm{M(PZ_3)_2} + 2\mathrm{PZ'_3} \rightleftharpoons \mathrm{L}_n\mathrm{M(PZ'_3)_2} + 2\mathrm{PZ_3} \tag{5}$$

This series of ligands has been shown[7] to be isosteric, and thus, the observed ordering is due solely to changes in ligand electronic (donor/acceptor) properties. The range in stabilities can be quite significant; our calorimetry data show that the enthalpy for the equilibrium shown in eq 6 favors products by 25.9 kcal/mol when $\mathrm{PZ'_3} = \mathrm{P}(p\text{-}\mathrm{CH_3OC_6H_4})_3$ and $\mathrm{PZ_3} = \mathrm{Ppyrl'_3}$.[6a]

$$trans\text{-}\mathrm{RhCl(CO)(PZ_3)_2} + 2\mathrm{PZ'_3} \rightleftharpoons trans\text{-}\mathrm{RhCl(CO)(PZ'_3)_2} + 2\mathrm{PZ_3} \tag{6}$$

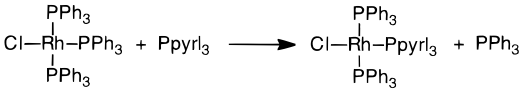
While the enthalpic ordering in the systems studied favors better donors, clearly this will not be the case with all metal centers. For example, CO, a very good π-acceptor, readily displaces $\mathrm{PPh_3}$ from $\mathrm{RhCl(PPh_3)_3}$ to give *trans*-$\mathrm{RhCl(CO)(PPh_3)_2}$.[8] Although steric factors certainly contribute to this observation, it is likely that the reaction is also favored by the electronic properties of CO *vis-à-vis* $\mathrm{PPh_3}$. A more conclusive example is provided by the example of the complexes $\mathrm{ML_4}^-$, where M = Rh(1−) or Ir(1−) and L = $\mathrm{PZ_3}$ or CO. These complexes are stabilized by weak donors/good π-acceptors, even when sterics are not at issue.[9] For example, equilibrium 7 lies too far to the right to be measured spectroscopically.[7e] These observations suggested to us that the electronic ordering described above should be reversed in cases where π-back-donation is an important component of the molecular bonding, such as in the case of electron-rich metal-centered systems.

$$[\mathrm{Rh(CO)_3(PPh_3)}]^- + \mathrm{Ppyrl_3} \xrightleftharpoons{K_{\mathrm{eq}} > 10^3} [\mathrm{Rh(CO)_3(Ppyrl_3)}]^- + \mathrm{PPh_3} \tag{7}$$

In an effort to test our hypothesis we sought to examine the thermodynamics of phosphine substitution at electron-rich metal centers or coordination sites. As described in this contribution, solution reaction calorimetry results show that the reaction enthalpy scale can indeed be reversed. By combining the thermochemical results with crystallographic studies, we further show that these results cannot be understood simply in terms of differences in intrinsic bond strengths. Rather, they provide a good example of the necessary consideration that must be given to reorganization energies when evaluating metal−ligand bond strengths and the role they play in the relative stabilities of metal complexes.

Results

Calorimetry. During our search for an appropriate electron-rich metal center, we examined Wilkinson's catalyst, $\mathrm{RhCl(PPh_3)_3}$. As noted above, it is known that this complex reacts rapidly and cleanly with CO to yield *trans*-$\mathrm{RhCl(CO)(PPh_3)_2}$.[8] Thus, replacement of the $\mathrm{PPh_3}$ trans to chlorine with a good π-acceptor ligand is favorable in this example, exactly the situation sought. Indeed, $\mathrm{PPh_3}$ is displaced by the ligand $\mathrm{Ppyrl_3}$ according to eq 8. The reaction proceeds rapidly on mixing at room temperature and in quantitative yield as determined by NMR. The product is easily characterized by its ^{31}P NMR spectrum, which shows two distinct sets of phosphorus resonances: a doublet of doublets due to the pair of mutually trans $\mathrm{PPh_3}$ ligands (δ $^{31}\mathrm{P} = 34.3$, $J_{\mathrm{Rh-P}} = 133$ Hz, $J_{\mathrm{P-P}} = 42$ Hz) and a doublet of triplets assignable to the unique $\mathrm{P(pyrl)_3}$ ligand (δ $^{31}\mathrm{P} = 101.1$, $J_{\mathrm{Rh-P}} = 278$ Hz, $J_{\mathrm{P-P}} = 42$ Hz).[10] A calorimetric study of this reaction shows that $\Delta H_{\mathrm{rxn}} = -3.2(3)$ kcal/mol. We previously showed that $\mathrm{Ppyrl_3}$ is isosteric with



$$\mathrm{Cl{-}Rh(PPh_3)_2{-}PPh_3} + \mathrm{Ppyrl_3} \longrightarrow \mathrm{Cl{-}Rh(PPh_3)_2{-}Ppyrl_3} + \mathrm{PPh_3} \tag{8}$$

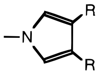
---

[4] For organoruthenium systems, see: (a) Serron, S. A.; Luo, L.; Li, C.; Cucullu, M. E.; Nolan, S. P. *Organometallics* **1995**, *14*, 5290. (b) Serron, S. A.; Nolan, S. P. *Organometallics* **1995**, *14*, 4611. (c) Luo, L.; Li, C.; Cucullu, M. E.; Nolan, S. P. *Organometallics* **1995**, *14*, 1333. (d) Luo, L.; Li, C.; Cucullu, M. E.; Nolan, S. P.; Fagan, P. J.; Jones, N. L.; Calabrese, J. C. *Organometallics* **1995**, *14*, 289. (e) Luo, L.; Nolan, S. P. *Organometallics* **1994**, *13*, 4781. (f) Li, C.; Cucullu, M. E.; McIntyre, R. A.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1994**, *13*, 3621. (g) Luo, L.; Zhu, N.; Zhu, N.-J.; Stevens, E. D.; Nolan, S. P.; Fagan, P. J. *Organometallics* **1994**, *13*, 669. (h) Luo, L.; Fagan, P. J.; Nolan, S. P. *Organometallics* **1993**, *12*, 4305. (i) Nolan, S. P.; Martin, K. L.; Stevens, E. D.; Fagan, P. J. *Organometallics* **1992**, *11*, 3947.

[5] For organoiron systems, see: (a) Li, C.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1995**, *14*, 3791. (b) Li, C.; Nolan, S. P. *Organometallics* **1995**, *14*, 1327. (c) Luo, L.; Nolan, S. P. *Inorg. Chem.* **1993**, *32*, 2410. (d) Luo, L.; Nolan, S. P. *Organometallics* **1992**, *11*, 3483.

[6] For organorhodium systems, see: (a) Serron, S.; Nolan, S. P.; Moloy, K. G. *Organometallics* **1996**, *15*, 4301. (b) Serron, S.; Huang, J.; Nolan, S. P. *Organometallics* **1998**, *17*, 534.

[7] We recently reported the results of several studies on *N*-pyrrolylphosphine ligands (pyrl and pyrl′ are defined below). The cumulative data demonstrate that these ligands are potent π-acceptors and are also isosteric with $\mathrm{P}(p\text{-}\mathrm{XC_6H_4})_3$; see the following references and also ref 6. (a) Huang, A.; Marcone, J. E.; Mason, K. L.; Marshall, W. J.; Moloy, K. G.; Serron, S.; Nolan, S. P. *Organometallics* **1997**, *16*, 3377. (b) Serron, S.; Nolan, S. P. *Inorg. Chim. Acta* **1996**, *252*, 107. (c) Li, C.; Serron, S.; Nolan, S. P.; Petersen, J. L. *Organometallics* **1996**, *15*, 4020. (d) Moloy, K. G.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 7696.



pyrl: R = H

pyrl′: R = $\mathrm{CO_2Et}$

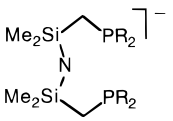
[8] (a) Hughes, R. P. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, A., Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 35. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; p 900 ff.

[9] (a) Chan, A. S. C. *Inorg. Chim. Acta* **1993**, *210*, 5. (b) Chan, A. S. C. Shieh, H.-S.; Hill, J. R. *J. Organomet. Chem.* **1985**, *279*, 171. (c) Chan, A. S. C. Carroll, W. E.; Willis, D. E. *J. Mol. Catal.* **1983**, *19*, 377. (d) Bogdanovic, B.; Leitner, W.; Six, C.; Wilczok, U.; Wittmann, K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 502.

[10] A single-crystal X-ray determination of the structure of *trans*-$\mathrm{RhCl(PPh_3)_2(Ppyrl_3)}$ confirms the atom connectivity. However, a lack of high angle data resulted in large thermal parameters and unreasonable bond lengths, precluding any meaningful conclusions regarding the bonding in this complex.

PPh_3 but is a much better π-acceptor and a weaker donor.[7] Thus, eq 8 demonstrates that, in the absence of steric effects, replacement of ligands trans to chlorine is favored by weak donors/strong acceptors, exactly the opposite of the systems previously studied.

However, extension of this chemistry to other isosteric PZ_3 ligands ($PPh_x pyrl_{3-x}$, $P(p\text{-}XC_6H_4)_3$) resulted in complex mixtures of products, presumably due to competing ligand substitution and scrambling of all sites on rhodium, i.e., positions cis as well as trans to chlorine.[8a] This outcome is not surprising considering the small reaction enthalpy obtained for eq 8 and that PPh_3 and $Ppyrl_3$ lie at opposite extremes of donor/acceptor character. As a result we were forced to search for a more suitable, well-behaved system. The result in eq 8 indicated that the direction investigated showed promise and thus the possibility of blocking the troublesome scrambling reactions by use of a multidentate spectator ligand was considered. An ideal candidate is provided by Fryzuk's tridentate bis(phosphino)-amido ligands RPNP, shown below.[11] These ligands form a number of square-planar complexes of the type [PNP]RhL, where L is a neutral donor such as PPh_3, CO, or olefin. In these complexes L is forced to coordinate trans to the amido and cis to the bis(phosphine) groups and thus occupies the position equivalent to that of $Ppyrl_3$ in eq 8. The amido group is a better donor (σ and π) than chloro,[12] and thus rhodium is also expected to be, overall, more electron rich in [PNP]RhL than in $RhCl(PPh_3)_2L$. The effect on the thermodynamics should be further magnified because L is forced into a position trans to the σ/π -donor (trans influence). These assumptions appear to be confirmed by a comparison of the IR spectra of *trans*-$RhCl(CO)(PPh_2Me)_2$ ($\nu_{CO} = 1974$ cm^{-1} [7c,13]) and [PhPNP]-Rh(CO) ($\nu_{CO} = 1950$ cm^{-1} [11a]).



PhPNP, R = Ph
^{i}PrPNP, R = ^{i}Pr

Substitution of cyclooctene in [RPNP]Rh(COE) was shown previously to provide an efficient route to complexes of the type [RPNP]RhL, where L = PPh_3, PMe_3, and CO.[11a] We thus chose this substitution reaction for calorimetric investigation. NMR monitoring of the reactions in eq 9 shows that they proceed quantitatively and at 60 °C are sufficiently rapid (ca. 2 h) for reaction calorimetry.

$$[RPNP]Rh(COE) + L \longrightarrow [RPNP]RhL + COE \qquad (9)$$

Complex	R	PZ_3
1	Ph	PPh_3
2	Ph	PPh_2pyrl
3	Ph	$PPhpyrl_2$
4	Ph	$Ppyrl_3$
5	Ph	$Ppyrl'_3$
6	Ph	CO
7	^{i}Pr	PPh_3
8	^{i}Pr	PPh_2pyrl
9	^{i}Pr	$PPhpyrl_2$
10	^{i}Pr	$Ppyrl_3$
11	^{i}Pr	$Ppyrl'_3$
12	^{i}Pr	CO

Table 1. Enthalpies of Substitution for Eq 9

complex	R	L	$-\Delta H_{rxn}$[a] (kcal/mol)	χ[b]
1	Ph	PPh_3	7.2(3)	13.25
2	Ph	PPh_2pyrl	11.1(2)	21
3	Ph	$PPhpyrl_2$	13.0(2)	29
4	Ph	$Ppyrl_3$	13.8(1)	37
5	Ph	$Ppyrl'_3$	14.9(2)	48
6	Ph	CO	48.9(3)	
7	^{i}Pr	PPh_3	10.9(3)	13.25
8	^{i}Pr	PPh_2pyrl	13.0(4)	21
9	^{i}Pr	$PPhpyrl_2$	15.4(3)	29
10	^{i}Pr	$Ppyrl_3$	18.9(2)	37
11	^{i}Pr	$Ppyrl'_3$	20.2(3)	48
12	^{i}Pr	CO	53.3(4)	

[a] Enthalpy values are provided with 95% confidence limits (paranthesis). [b] χ is Tolman's electronic parameter (ref 14).

Reaction calorimetry shows conclusively and convincingly that better acceptor ligands give the more stable complexes in the [RPNP]RhL system. As shown in Table 1, progression from PPh_3, a *relatively* good σ-donor/weak π-acceptor ($\chi = 13.25$[14]), through $PPh_x py_{3-x}$ and ultimately to $Ppyrl'_3$, a potent acceptor/weak donor ($\chi = 48$),[7a] produces a substantial increase in the reaction enthalpy for both sets of [RPNP] complexes. The enthalpies of reaction involving the [^{i}PrPNP] series are larger than the enthalpy values for the related [PhPNP] series. This trend is consistent with the expected increase in electron density on rhodium upon substitution of the bulky alkyl for phenyl, as demonstrated by the 18 cm^{-1} drop in ν_{CO} for [^{i}PrPNP]Rh(CO) ($\nu_{CO} = 1932$ cm^{-1}) versus [PhPNP]Rh(CO) ($\nu_{CO} = 1950$ cm^{-1}).

This situation is exaggerated for L = CO, where binding of CO is favored by some 42 kcal/mol over PPh_3 in the ^{i}PrPNP system. In the case of CO, however, reduced steric effects cannot be excluded from influencing the magnitude of ΔH_{rxn}. Sterics are unlikely to play a role in the enthalpy trend obtained with the series of phosphorus donors examined, as discussed in further detail below.

Structural Studies of [RPNP]RhL. Crystallographic studies of complexes **1**, **4**, **6**, **7**, **10**, **12**, and [^{i}PrPNP]Rh(COE) (**13**) were performed in an effort to better understand the calorimetry results. Structural parameters relevant to this discussion are provided in Tables 2 and 3. More detailed crystallographic information may be found in the Supporting Information.

The description of these complexes is straightforward. All are pseudo-square-planar complexes, quite similar in their gross features to the isoelectronic complexes [PhPNP]MCl, M = Ni, Pd.[11b] Distortions from ideal square-planar geometry are observed and best described by comparison of the *trans*-ligand−Rh−ligand angles. These angles most closely approach 180° in the case of the sterically unencumbered CO ligand, where for complexes **6** and **12**, both pairs of angles are >172°. In the remaining complexes these angles decrease from the ideal 180° by up to 23°, presumably in response to the presence of the bulkier ligands L. This angle compression is larger for ∠*trans*-PRhP than for ∠*trans*-NRhP in all cases. The chelate rings in all cases are puckered to varying degrees, as judged by the Si−N−Si angles and intra-ring P−Rh−N−Si torsion angles,

---

(11) (a) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* **1986**, *5*, 2469. (b) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* **1982**, *1*, 918.

(12) Poulton, J. T.; Sigalas, M. P.; Folting, K.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 1476.

(13) See also ref 8a, Table 13.

(14) χ is Tolman's electronic parameter;[14a] the commonly used value for PPh_3 ($\chi = 13.25$) is taken from ref 14b. (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29.

Table 2. Bond Lengths and Angles in the Inner Coordination Sphere of the Complexes [RPNP]RhL^{a,b}

	1	**4**	**6**^{c}	**7**	**10**	**12**	**13**
Rh−N, Å	2.151(2)	2.130(2)	2.099(2); 2.117(2)	2.158(2)	2.128(3)	2.097(2)	2.125(2)
Rh−P, Å	2.2773 (6) 2.2918(7)	2.3261(8) 2.2923(8)	2.2986(7) 2.3270(6); 2.3243(7); 2.2938(6)	2.3329(16) 2.3387(16)	2.3221(10) 2.3523(10)	2.3074(9) 2.3085(8)	2.3061(6) 2.3590(6)
Rh−L, Å	2.2121(6)	2.1404(7)	1.797(3); 1.811(3)	2.2226(5)	2.1333(9)	1.802(3)	2.140(2) 2.174(2)
∠PRhN, deg	79.96(6) 85.69(6)	82.71(6) 83.86(6)	84.77(6) 88.40(6); 88.77(6); 87.78(6)	82.74(5) 84.58(5)	80.30(9) 85.29(9)	87.17(6) 87.20(6)	84.68(6) 84.64(6)
∠PRhL, deg	95.70(2) 101.49(2)	95.00(3) 98.72(3)	92.77(8) 94.13(8); 93.69(8); 89.78(8)	98.71(2) 97.52(2)	98.22(3) 98.37(3)	93.1(1) 92.5(1)	
∠NRhL, deg	168.41(6)	170.92(9)	177.1(1); 177.1(1)	165.21(5)	167.00(8)	179.2(3)	
∠PRhP, deg	157.34(3)	166.26(4)	172.60(5); 176.47(7)	159.92(2)	161.61(3)	174.17(6)	168.76(4)
∠SiNSi, deg	128.5(1)	123.2(1)	127.2(1); 123.5(1)	122.7(1)	124.2(2)	124.5(1)	119.3(1)
∠PRhNSi, deg^d	27.4, 49.7	26.7, 40.5	14.0, 0.9; 26.7, 27.8	17.47, 42.70	26.7, 47.5	31.3, 25.2	20.4, 31.8

^{a} Complete structural details are provided as Supporting Information. ^{b} Parameters referring to P involve phosphorus of the PNP chelate only; those referring to L refer to the ligand trans to nitrogen (PPh$_3$, Ppyrl$_3$, or CO). ^{c} Two molecules per asymmetric unit. ^{d} Intra-ring torsion angle.

Table 3. Important Structural Parameters in the Rh−PZ$_3$ Fragment of the Complexes [RPNP]Rh−PZ$_3$

	1	**4**	**7**	**10**
av P−Z, Å	1.845	1.724	1.849	1.732
$\sum\angle$ZPZ, deg	305.1	296.9	300.7	294.1
av ∠RhPZ, deg	116.4	118.6	117.6	119.3
$^2/_3(\sum\angle$PRhH),^{b} deg	117	115	110	115
Rh−P, Å	2.2121(6)	2.1404(7)	2.2226(5)	2.1333(9)

^{a} Complete structural details are provided as Supporting Information. ^{b} See the text for a description of this parameter

and there are no clear trends with respect to the ligand L. A possible exception is for L = PZ$_3$, where in each case, one "normal" torsion angle (15−30°) is accompanied by one large torsion angle (>40°), indicating that one ring is twisted more severely than the other. Other than the unsurprisingly longer Rh−P(chelate) bonds in the [^{i}PrPNP] series (ca. 2.33 vs 2.30 Å for [PhPNP]), there are no gross differences between the phenyl- and isopropyl-substituted chelates.

Trends are apparent in the metal−ligand bond lengths. In all cases Rh−Ppyrl$_3$ is shorter than Rh−PPh$_3$ by ca. 0.08 Å. This is indicative of greater π-acceptor character in the case of Ppyrl$_3$, as we previously demonstrated.[7] This shortening may alternatively be attributed to differences in phosphorus hybridization resulting from the greater electronegativity of the *N*-pyrrolyl substituents relative to phenyl. However, note that the decreased Rh−P bond length is also accompanied by a shortening of Rh−N by 0.02−0.03 Å. A reasonable explanation for these observations is that the degree of π-donation from nitrogen to rhodium increases in the presence of a superior trans π-acceptor (electron push−pull). In further support of this explanation, note that Rh−N shortens by another 0.02−0.03 Å on replacement of Ppyrl$_3$ with CO, a more potent π-acceptor. Variations in the Rh−P(chelate) distances from complex to complex are slightly less than the internal variations within each complex (these distances are crystallographically distinct in all cases). Thus, no meaningful conclusions may be drawn regarding this parameter, other than it appears to be rather insensitive to the variable ligand L.

Progression from [PhPNP]RhL to the analogous [^{i}PrPNP]-RhL complex does not result in significant changes in the Rh−L distance, although Rh−PPh$_3$ increases slightly, Rh−Ppyrl$_3$ decreases, and Rh−CO is unchanged. The observations indicate that sterics are not significantly different between the two chelates. Within each pair of PPh$_3$ and Ppyrl$_3$ complexes, progression from [PhPNP] to [^{i}PrPNP] causes the P−Z bond length to increase. This is accompanied by a slight folding of the Z groups away from rhodium (the sum of ZPZ angles decreases, and the average RhPZ angle increases). The bending in the PZ$_3$ fragment is consistent with a greater degree of π-back-bonding in the [^{i}PrPNP]RhL complexes due to increased electron donation on replacement of Ph with ^{i}Pr.[1g] Further note that, for each pair of complexes [RPNP]RhPPh$_3$ and [RPNP]-RhPpyrl$_3$ (i.e., **1** vs **4**, and **7** vs **10**), the value $\sum\angle$ZPZ (Table 3) is always smaller for Ppyrl$_3$. This trend has been observed in related systems[7a,d] and is further evidence for a greater degree of π-back-bonding in the Ppyrl$_3$ complexes.

Consistent with previous work, both by us[7] and by others,[15] the steric sizes of the PPh$_3$ and Ppyrl$_3$ ligands are found to be indistinguishable. This conclusion is drawn by a comparison of $^2/_3(\sum\angle$PRhH), which measures the sum of angles centered at rhodium and formed by rhodium, phosphorus, and the hydrogen of each substituent Z forming the closest rhodium contact. The parameter thus defined is similar to the Tolman cone angle[14] but is measured directly and more easily from the X-ray data.[16] In all cases the closest Rh−H contact occurs with a hydrogen β to phosphorus. Values for this parameter are provided in Table 3 and show that PPh$_3$ and Ppyrl$_3$ possess equivalent cone angles. By inference we conclude that the series of PPh$_x$pyrl$_{3-x}$ ligands described in this work form an isosteric series.

Discussion

As shown in Table 1, ΔH_{rxn} for the reaction in eq 9 increases with increasing π-acceptor character of the incoming ligand L.

---

(15) Trzeciak, A. M.; Glowiak, T.; Grzybek, R.; Ziolkowski, J. J. *J. Chem. Soc., Dalton Trans.* **1997**, 1831.

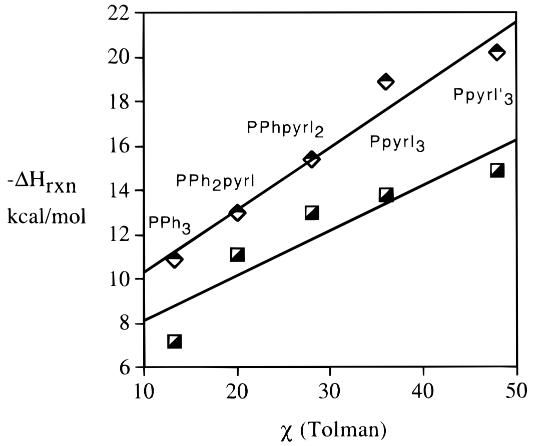


Figure 1. Reaction enthalpy vs Tolman's electronic parameter (χ) for eq 9. Squares = [PhPNP]RhL, diamonds = [^{i}PrPNP]RhL.

These data are plotted versus Tolman's electronic parameter χ in Figure 1, which shows a fairly steady increase in ΔH_{rxn} with increasing χ for both the [PhPNP] and [^{i}PrPNP] systems studied.[17]

We ascribe the trends depicted in Figure 1 to an electronic preference for π-acceptor ligands and not to steric effects. It would be expected that sterics would contribute significantly to the observed ΔH_{rxn} because the coordination site at which substitution occurs is rather congested, due to the presence of the pair of bulky *cis*-R$_2$P groups. This likely explains in part the large ΔH_{rxn} values obtained with CO. However, we, and others, have shown that the ligands $PPh_x pyrl_{3-x}$ are isosteric,[7,15] differing substantially only in their electronic properties. Ppyrl$_3$ thus possesses the same cone angle as PPh$_3$ but is a much more potent π-acceptor. This argument is supported by a comparison of the crystallographically determined structures of complexes **1**, **4**, **7**, and **10**, where the steric sizes of Ppyrl$_3$ and PPh$_3$ are indistinguishable (Table 3). Furthermore, the calorimetric data for Ppyrl′$_3$ also correlate with Tolman's χ. Evidence has been presented[7a] which indicates that Ppyrl′$_3$ is essentially isosteric with $PPh_x pyrl_{3-x}$. This is a result of both the remoteness of the $-CO_2Et$ groups from the metal center and the way in which they are directed away from the metal by the five-membered ring. Most importantly, it is unlikely that Ppyrl′$_3$ could be smaller than $PPh_x pyrl_{3-x}$, which would be required if steric changes (toward smaller cone angles) were responsible for the enthalpy trend found in the [RPNP] systems presented herein.

The correlation of ΔH_{rxn} with χ is most consistent with, and suggestive of, an electronic explanation for the trend. The evidence indicates that substitution is increasingly favored with increasing π-acceptor character of the incoming ligand. The π-acceptor character of PZ$_3$ ligands in turn increases with increasing χ (and the σ-donor character likewise generally decreases). The structural data support this idea; for each pair of complexes **1**−**4** and **7**−**10**, Rh−Ppyrl$_3$ is shorter than Rh−PPh$_3$ by ca. 0.08 Å (see Figures 2 and 3). Increased π-back-bonding in the case of Ppyrl$_3$ is also reflected by structural differences in the PZ$_3$ fragment (P−Z distance, $\sum\angle$ZPZ) as discussed above. Similar trends have been previously observed[7] and, along with spectroscopic data (IR), are attributed to increased metal-to-ligand back-bonding. The ^{31}P NMR data are also informative in that it is seen that J_{Rh-PZ_3} steadily increases with increasing ligand χ. In fact, Figure 4 shows that J_{Rh-P} correlates well with ΔH_{rxn}. Metal−phosphorus coupling constants depend on a number of factors, some related, including the degree of σ-bonding (and possibly π-bonding), the electronegativity of the substituents at phosphorus, the metal−P distance, the s character of the bond, and the polarizability of phosphorus.[18] While the correlation in Figure 4 cannot be assigned to any single contributing factor, we interpret this correlation as evidence for an electronic role in the enthalpy ordering.

The enthalpy trend presented here is best explained in terms of an electronic preference for placement of a good π-acceptor trans to nitrogen. Nitrogen is a good σ/π-donor and is expected to render rhodium relatively electron rich for a 16 e$^-$ metal center.[12] As the electron density on rhodium is increased it is not unexpected that coordination of weak donors and/or good π-acceptors, particularly those trans to nitrogen, will be favored. This is corroborated by noting the shortening of the Rh−N bond length as one progresses from PPh$_3$ to Ppyrl$_3$ to CO, indicative of the synergistic bonding between nitrogen and the ligand trans to nitrogen.

Having thus rationalized the enthalpy trends for phosphine substitution on the [RPNP]Rh(I) fragment, we now turn attention to the dichotomy presented by the examples of [RPNP]Rh(PZ$_3$) and *trans*-RhCl(CO)(PZ$_3$)$_2$. Both complexes are square-planar Rh(I) and possess similar ligand arrays. However, the thermodynamic trends for phosphine coordination in these systems are exactly the *opposite* (eqs 10 and 11). This contrast is clearly depicted in Figure 5, where Tolman's χ is plotted versus the measured substitution enthalpies for eqs 3 and 9.[19] The substitution enthalpy data allow us to write the equilibrium preferences for phosphine coordination in these systems as shown in Scheme 1.

The major difference in the two examples presented in Scheme 1 is the site at which the substitution occurs. In the case of [RPNP]Rh(PZ$_3$), substitution occurs trans to a good σ/π-donor (N), as discussed above. For RhCl(CO)(PZ$_3$)$_2$ the substitution occurs cis to a good σ-donor and modest π-donor (Cl). In addition, RhCl(CO)(PZ$_3$)$_2$ already contains a potent π-acceptor ligand, CO. Clearly, the resulting electronic changes and requirements in each system are significantly different. For the example of RhCl(CO)(PZ$_3$)$_2$ our explanation of the enthalpic ordering follows that described previously.[6a,7e] Rhodium in these complexes is formally 16 e$^-$ and thus electron deficient.

---

(16) There are two major differences between our method and that used to measure the Tolman cone angle θ. First, θ is the angle defined by phosphorus, the metal, and the line defined by the metal and the tangent to van der Waals radius of the hydrogen atom closest to the metal.[14] Our measure is from the center of the hydrogen atom and thus does not incorporate the van der Waals radius. Second, θ is the maximum cone angle obtained upon rotating the Z groups about the P−Z bond, whereas our measure is derived from the structure as observed and without such manipulation. The estimation of phosphine sterics directly from X-ray data, but incorporating the hydrogen van der Waals radius correction, has been previously reported.[16a−c] We suggest only that our method is useful for comparing relative steric sizes and that Ppyrl$_3$ possesses the same, well-established Tolman cone angle as PPh$_3$ ($\theta = 145°$). (a) DeSanto, J. T.; Mosbo, J. A.; Storhoff, B. N.; Bock, P. L.; Bloss, R. E. *Inorg. Chem.* **1980**, *19*, 3086. (b) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Restino, R. *J. Inorg. Chem.* **1977**, *16*, 2329. (c) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *25*, L41.

(17) The curvature in the data plotted in Figure 1 suggests that more than one electronic parameter may be required to fully explain the observed trends, particularly in the [PhPNP] series. However, we consider the correlation with χ to be sufficiently good for the purposes of this discussion. For a recent and thorough discussion of phosphine ligand parametrization, see the following and references therein: Fernandez, A.; Reyes, C.; Wilson, M. R.; Woska, D. C.; Prock, A.; Giering, W. P. *Organometallics* **1997**, *16*, 342.

(18) Alyea, E. C.; Song, S. *Inorg. Chem.* **1995**, *34*, 3864.

(19) The enthalpy data reported herein are given on the basis of 1 mol of the product *trans*-RhCl(CO)(PZ$_3$)$_2$ and therefore correspond to eq 3 as written. They are one-half the values given in our initial report on this system,[6a] which was based on 1 mol of the dimeric starting material, [RhCl(CO)$_2$]$_2$.

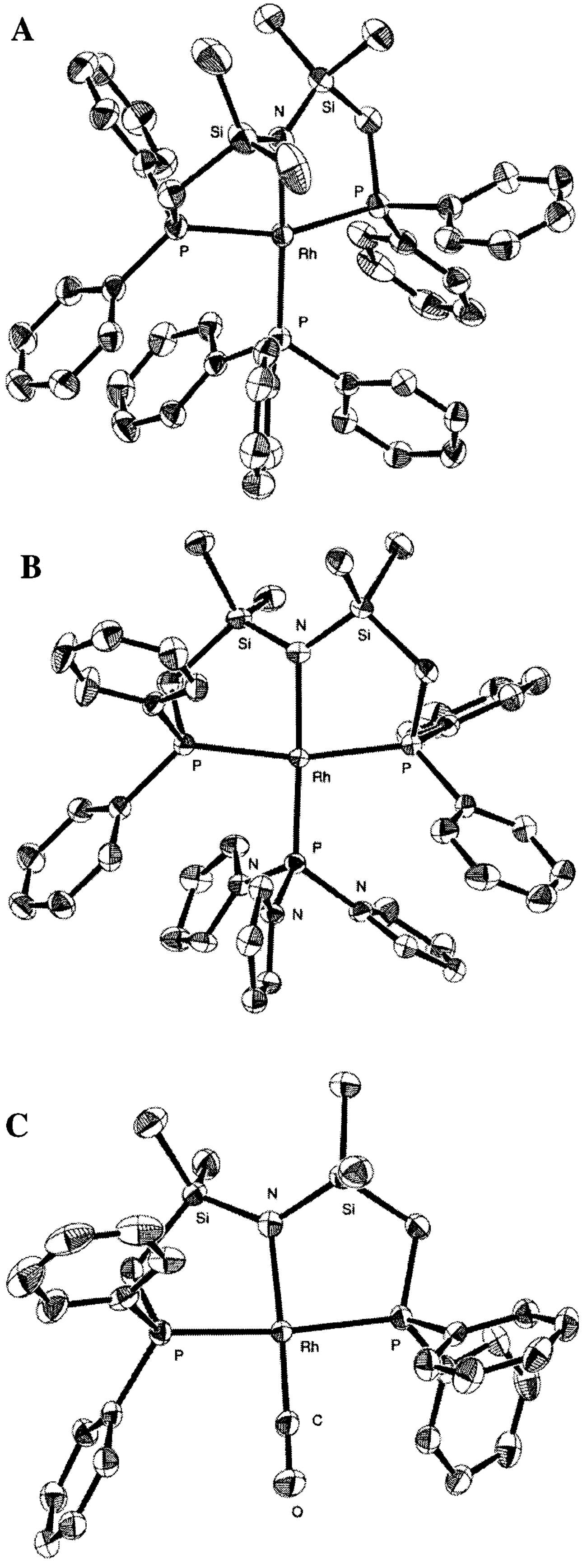


Figure 2. ORTEP drawings of the complexes (a) [PhPNP]RhPPh$_3$ (**1**), (b) [PhPNP]RhPpyrl$_3$ (**4**), and (c) [PhPNP]Rh(CO) (**6**); thermal ellipsoids are drawn at the 50% probability level.

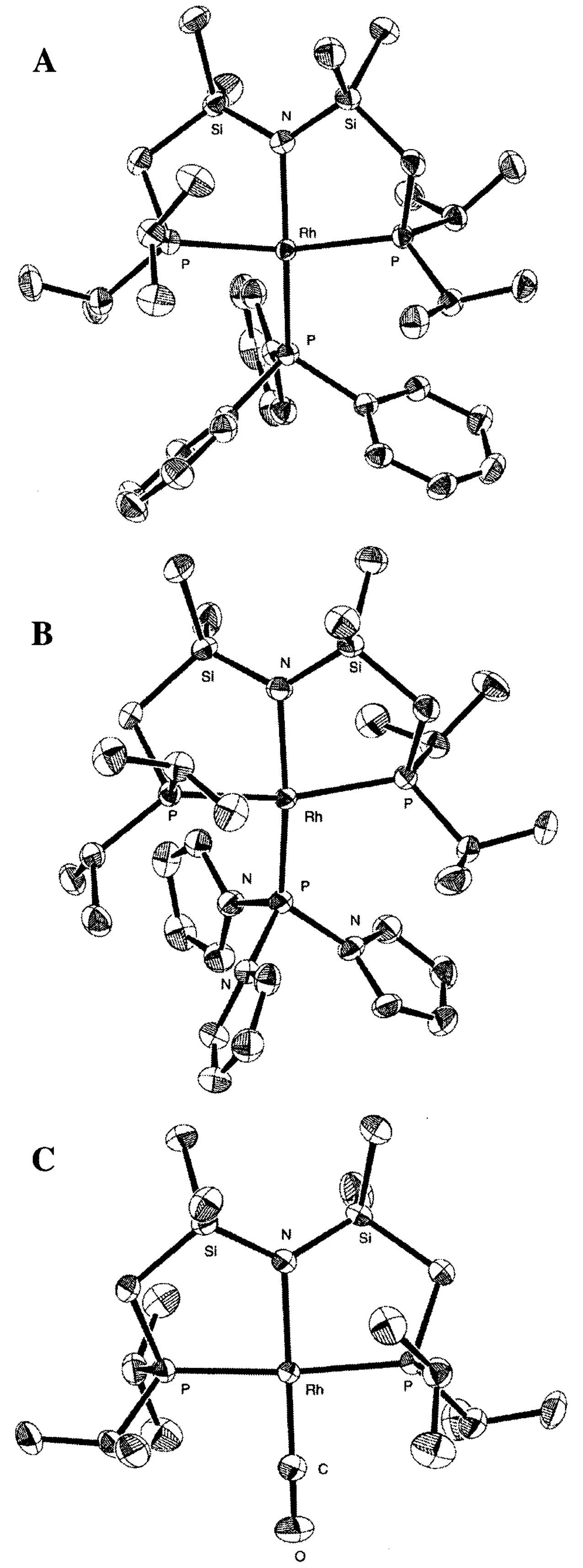


Figure 3. ORTEP drawings of the complexes (a) [^{i}PrPNP]RhPPh$_3$ (**7**), (b) [^{i}PrPNP]RhPpyrl$_3$ (**10**), and (c) [^{i}PrPNP]Rh(CO) (**12**); thermal ellipsoids are drawn at the 50% probability level.

This is at least partially compensated for by σ/π-donation from chlorine as determined by the shortening of Rh−Cl as PZ$_3$ becomes less donating (χ increases). Coordination of a weak donor/strong π-acceptor ligand (CO) trans to chlorine is

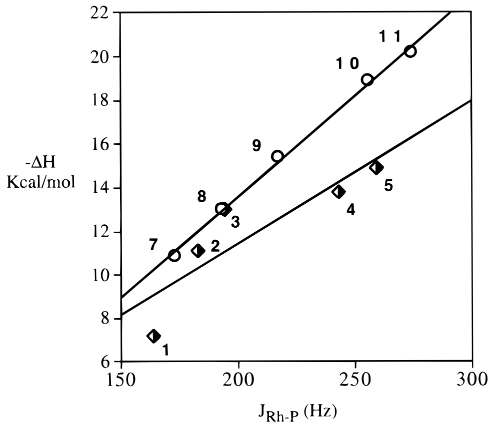


Figure 4. Reaction enthalpy vs J_{Rh-P} for eq 9. Circles = [^{i}PrPNP]RhL, diamonds = [PhPNP]RhL; individual points are labeled according to eq 9.

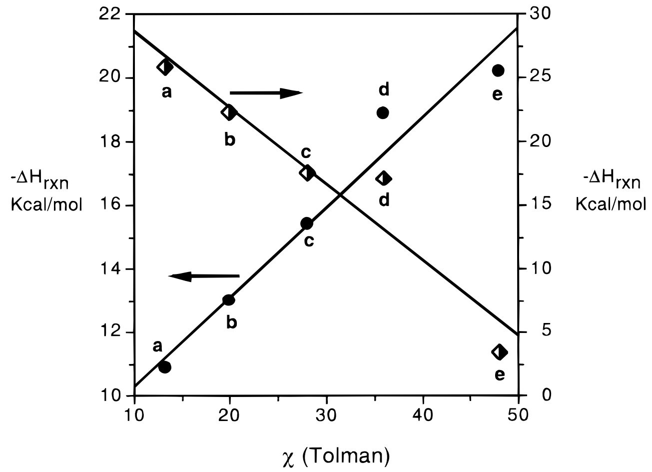
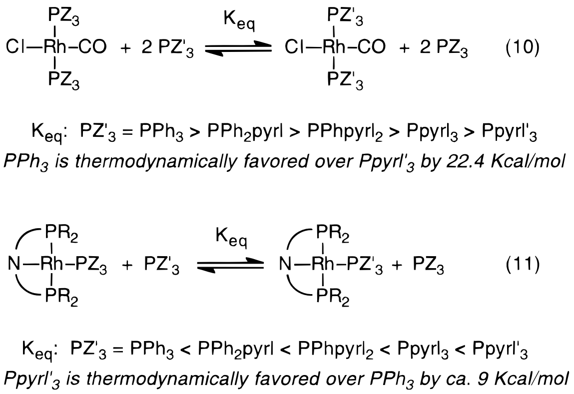
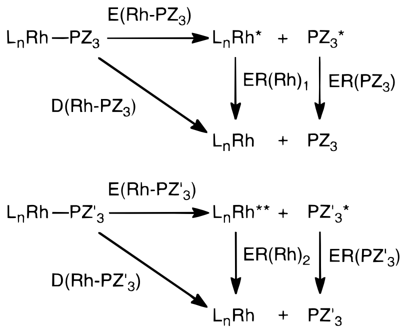


Figure 5. Reaction enthalpy vs Tolman's electronic parameter (χ) for eq 9 ([RPNP] = [^{i}PrPNP]) and eq 3. Circles = [^{i}PrPNP]RhL (eq 9); diamonds = *trans*-RhCl(CO)L_2 (eq 3). Letters correspond to the ligands L = PPh_3 (a), PPh_2pyrl (b), PPhpyrl$_2$ (c), Ppyrl$_3$ (d), and Ppyrl'$_3$ (e).

Scheme 1



Scheme 2



$$L_nRh{-}PZ_3 + PZ'_3 \rightleftharpoons L_nRh{-}PZ'_3 + PZ_3 \qquad (12)$$

$$\Delta H_{rxn} = D(Rh\text{-}PZ'_3) - D(Rh\text{-}PZ_3)$$

$$= [E(Rh\text{-}PZ'_3) + ER(Rh)_2 + ER(PZ'_3)] - [E(Rh\text{-}PZ_3) + ER(Rh)_1 + ER(PZ_3)]$$

$$= [E(Rh\text{-}PZ'_3) - E(Rh\text{-}PZ_3)] + [ER(Rh)_2 + ER(PZ'_3) - ER(Rh)_1 - ER(PZ_3)]$$

stabilizing due to efficient, synergistic π-donation/π-backbonding, which is the same argument used to explain the enthalpy trends in the [RPNP]Rh systems. Addition of further weak σ-donors/strong π-acceptors PZ_3 cis to CO and Cl is unfavorable due to competition between PZ_3 and CO as π-acids. This conclusion is based on the observation that the Rh−CO bond length increases in *trans*-RhCl(CO)$(PZ_3)_2$ as χ(PZ_3) increases (e.g., PZ_3 becomes increasingly more "CO-like"). This argument also explains why RhCl$(CO)_3$ is only observed under high CO pressure, being more stable with respect to elimination of CO and formation of stronger σ-donor bonds (μ-Cl) via dimerization to $[RhCl(CO)_2]_2$.[20]

Comparing the two sets of complexes it is concluded that the balance of σ-donor, π-donor, and π-acceptor ligands ultimately determines the position of a ligand exchange equilibrium such as eq 5. This is a direct consequence of the synergistic bonding between these donor/acceptor ligands and shared metal orbitals.[21]

The dichotomy presented by these two examples highlights a fundamental requirement when analyzing thermochemical information, whether derived from equilibrium measurements, calorimetry or other physicochemical measurements, or kinetics (rates of forward and reverse reactions). Very often this information is used to derive conclusions, qualitative and/or quantitative, regarding the relative and absolute strengths of the bonds being broken and formed. However, before meaningful conclusions regarding bond strengths can be drawn from such thermochemical data, consideration must be given to reorganization energies. The contributions of reorganization energies to the overall thermodynamic picture for the present system is shown in Scheme 2. Following the convention described by Martinho Simões and Beauchamp,[1d] it is seen that the bond dissociation enthalpy, $D(Rh{-}PZ_3)$, is composed of contributions from both an "intrinsic" bond enthalpy term $E(Rh{-}PZ_3)$ (i.e., the "bond strength") and the reorganization energies E_R(Rh) and $E_R(PZ_3)$. The position of an equilibrium such as that shown in eq 12, and thus the difference in bond dissociation enthalpies (D), is determined by the combination of six factors: two bond enthalpy terms (E) and four reorganization energy terms (E_R) (entropic contributions aside). As the reorganization energy terms become large the interpretation of D as an intrinsic property of a particular bond becomes increasingly meaningless.

From the structural data accumulated on the complexes [RPNP]Rh(PZ_3) and *trans*-RhCl(CO)$(PZ_3)_2$, it is easy to see why the reorganization energies are substantial. In both cases progression from phosphines with low χ values to those with high χ values is accompanied by extensive changes in bond lengths and angles in the rhodium and PZ_3 fragments. Moreover, the similar structural trends for the complexes [RPNP]-

---

(20) Morris, D. E.; Tinker, H. B. *J. Organomet. Chem.* **1973**, *49*, C53.

(21) For a related argument relating to exchange of anionic σ/π-donor ligands, see: Poulton, J. T.; Hauger, B. E.; Kuhlman, R. L.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 3325.

$Rh(PZ_3)$ and *trans*-$RhCl(CO)(PZ_3)_2$ offer no clue to the reversed enthalpic ordering between the two families. In each case, as χ increases, the $Rh-PZ_3$ and $Rh-X$ bond lengths decrease, the PZ_3 group adopts more of an inverted umbrella shape, and the $P-Z$ bond lengths increase. Bond lengths to other ligands generally increase, e.g., $Rh-CO$ in *trans*-$RhCl(CO)(PZ_3)_2$. Breaking the $Rh-PZ_3$ bond will thus be expected to result in significant changes in the bonding between rhodium and the remaining ligands in the fragment L_nRh ($E_R(Rh)$) and also in the liberated ligand PZ_3 ($E_R(PZ_3)$. The structural parameters, and especially the $Rh-PZ_3$ bond distance, are of no use in predicting the reversed enthalpic ordering between these two families, indicating that the use of structural data to infer conclusions regarding thermodynamics can be risky and misleading.

An extensive amount of effort is required, and a number of assumptions and simplifications are often made, to account for the E_R terms. In many cases they are assumed to be insignificant and/or are ignored. These contributions are significant when the bonds being broken and formed are involved in synergistic bonding. Our results, showing that trends in thermodynamic data can be completely reversed in very related systems emphasizes the importance of reorganization energies and the consideration they must be given. These results also underscore the caution that must be employed when attempting to interpret experimental thermochemical results and bond dissociation enthalpies as intrinsic, transferable properties of individual bonds. In cases involving synergistic bonding between σ-donors, π-donors, and π-acceptors (electron push−pull), even the concept of an individual bond strength becomes increasingly ambiguous.[22]

Experimental Section

General Considerations. All manipulations were performed under inert atmospheres of argon or nitrogen using standard high-vacuum or Schlenk line techniques or in a glovebox containing less than 1 ppm oxygen and water. Solvents, including deuterated solvents for NMR analyses, were dried by standard methods[23] and distilled under nitrogen or vacuum transferred before use. NMR spectra were recorded using Varian Gemini 300-MHz or Varian Unity 400-MHz spectrometers. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Only materials of high purity as indicated by NMR spectroscopy were used in the calorimetric experiments. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction[24] or the enthalpy of solution of KCl in water.[25] This calorimeter has been previously described,[26] and typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits. The complexes [^{i}PrPNP]Rh(COE), [PhPNP]Rh(COE), [PhPNP]$RhPPh_3$, and [PhPNP]Rh(CO) were synthesized according to literature procedures,[11a] as were the ligands PPh_2pyrl, $PPhpyrl_2$, $Ppyrl_3$,[7d] and $Ppyrl'_3$.[7a] Triphenylphosphine (Aldrich) was recrystallized from ethanol prior to use, and carbon monoxide (Matheson, UHP grade) was used as received.

NMR Titrations. Prior to every set of calorimetric experiments involving a new ligand, an accurately weighed amount (±0.1 mg) of the [RPNP]Rh(COE) complex was placed in an NMR tube along with toluene-d_8 and >1.2 equiv of ligand. The sample was heated at 60 °C in an oil bath for 1 h, after which both ^1H and ^{31}P NMR spectra indicated that the reactions were clean and quantitative under experimental calorimetric conditions. These conditions are necessary for accurate and meaningful calorimetric results and were satisfied for all reactions investigated.

Solution Calorimetry. In a representative experimental trial, 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 sample of [^{i}PrPNP]Rh(COE) (21.1 mg, 34.8 μmol) was weighed into the lower vessel, which was closed and sealed with 1.5 mL of mercury. A solution of PPh_3 (11.1 mg, 42.3 μmol) in toluene (4 mL) was added, and the remainder of the cell was assembled, removed from the glovebox, and inserted into the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organorhodium complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 60.0 °C (ca. 2 h), it was inverted, thereby allowing the reactants to mix. The reaction was considered complete after the calorimeter had once again reached thermal equilibrium (ca. 2 h). Control reactions with Hg and phosphine show no reaction. The enthalpy of ligand substitution (-10.9 ± 0.3 kcal/mol) listed in Table 1 represents the average of at least three individual calorimetric determinations with all species in solution. The enthalpy of solution of [^{i}PrPNP]Rh(COE) ($+9.6 \pm 0.2$ kcal/mol) in neat toluene was determined using identical methodology. Other examples were performed in an identical fashion with the exception of [PhPNP]Rh(COE) + PPh_3, which was conducted at 80.0 °C.

[PhPNP]Rh(PPh_2pyrl) (2). In the glovebox, a 25-mL flask fitted with a frit and a magnetic stir bar was charged with [PhPNP]Rh(COE) (100.0 mg, 0.135 mmol) and PPh_2pyrl (33.9 mg, 0.135 mmol). Toluene (3−5 mL) was added; the vessel was sealed, removed from the glovebox, and heated with stirring in a 60 °C oil bath for 1−2 h. The reaction vessel was then interfaced to a high-vacuum line, and the toluene was removed in vacuo. The oily residue was triturated several times with pentane (3−5 mL) to ensure complete removal of cyclooctene. The resulting orange powder was then taken up in pentane (ca. 5 mL) and filtered and the solvent reduced to ca. 1 mL. Slow cooling of this solution afforded **2** as orange crystals, which were collected on a frit and dried under flowing argon. Yield: 83 mg (70%). ^1H NMR (toluene-d_8): δ 0.03(s, 12 H, $Si(CH_3)_2$), δ 1.66 (m, 4 H, PCH_2Si), δ 6.15 (m, 2 H, pyrrolyl), δ 7.52(m, 2 H, pyrrolyl), δ 6.45 (m, 4H, phenyl), δ 6.48 (m, 2 H, phenyl), δ 7.01 (m, 4 H, phenyl), δ 6.80(m, 12 H, PNP-phenyl), δ 7.42(m, 8 H, PNP-phenyl). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 32.5 (dd, J_{PP} = 43 Hz, J_{Rh} = 140 Hz), δ 89.6 (dt, J_{Rh} = 183 Hz). Anal. Calcd for $C_{46}H_{50}N_2P_3RhSi_2$: C, 62.58; H, 5.71; N, 3.17. Found: C, 62.71; H, 6.03; N, 2.94.

[PhPNP]Rh($PPhpyrl_2$) (3). This complex was prepared in a manner similar to that for **2**, using [PhPNP]Rh(COE) (80.0 mg, 0.108 mmol) and $PPhpyrl_2$ (25.9 mg, 0.108 mmol). Yield: 54 mg (57%) as yellow crystals. ^1H NMR (toluene-d_8): δ 0.02 (s, 12 H, $Si(CH_3)_2$), δ 1.72 (m, 4 H, PCH_2Si), δ 6.05 (m, 4 H, pyrrolyl), δ 7.34 (m, 4 H, pyrrolyl), δ 6.21 (m, 2 H, phenyl), δ 6.42 (m, 1 H, phenyl), δ 7.04 (m, 2 H, phenyl), δ 6.86 (m, 12 H, PNP-phenyl), δ 7.48 (m, 8 H, PNP-phenyl). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 32.9 (dd, J_{PP} = 44 Hz, J_{Rh} = 137 Hz), δ 105.8 (dt, J_{Rh} = 194 Hz). Anal. Calcd for $C_{44}H_{49}N_3P_3RhSi_2$: C, 60.61; H, 5.66; N, 4.82. Found: C, 60.23; H, 5.68; N, 4.62.

[PhPNP]Rh($Ppyrl_3$) (4). This complex was prepared in a manner similar to that for **2**, using [PhPNP]Rh(COE) (80.0 mg, 0.108 mmol) and $Ppyrl_3$ (24.7 mg, 0.108 mmol). Yield: 78 mg (84%) as yellow crystals. ^1H NMR (toluene-d_8): δ 0.08 (s, 12 H, $Si(CH_3)_2$), δ 1.78 (m, 4 H, PCH_2Si), δ 5.85 (m, 6 H, pyrrolyl), δ 6.72 (m, 6 H, pyrrolyl), δ 6.94 (m, 12 H, phenyl), δ 7.61 (m, 8 H, phenyl). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 33.0 (dd, J_{PP} = 47 Hz, J_{Rh} = 134 Hz), δ 103.5 (dt, J_{Rh} = 243 Hz). Anal. Calcd for $C_{42}H_{48}N_4P_3RhSi_2$: C, 58.60; H, 5.62; N, 6.51. Found: C, 58.49; H, 5.62; N, 6.41.

[PhPNP]Rh($Ppyrl'_3$) (5). This complex was prepared in a manner similar to that for **2** using [PhPNP]Rh(COE) (40.0 mg, 0.0539 mmol) and $Ppyrl'_3$ (35.7 mg, 0.0540 mmol). After trituration, the product was washed with pentane to obtain pure **5** as a yellow power, yield: 57 mg (82%). ^1H NMR (toluene-d_8): δ 0.02 (s, 12 H, $Si(CH_3)_2$), δ 0.95 (t, 12 H, $CO_2CH_2CH_3$), δ 1.10 (t, 6 H, $CO_2CH_2CH_3$), δ 1.82 (m, 4 H, PCH_2Si), δ 3.94 (q, 8 H, $CO_2CH_2CH_3$), δ 4.15 (q, 4 H, $CO_2CH_2CH_3$), δ 7.03(m, 12 H, phenyl), δ 7.58 (m, 8 H, phenyl), δ 7.34 (s, 6 H, pyrrolyl). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 31.8 (dd, J_{PP} = 46 Hz, J_{Rh} =

---

[22] Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders: Philadelphia, PA, 1977; pp 119−123.

[23] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.

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

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

[26] (a) Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. *Inorg. Chem.* **1986**, *25*, 4446. (b) Nolan, S. P.; Hoff, C. D. *J. Organomet. Chem.* **1985**, *282*, 357.

Table 4. Crystallographic Data for the Complexes [RPNP]RhL

	1	4	6	7	10	12	13
formula	$C_{48}H_{51}NP_3RhSi_2$	$C_{42}H_{48}N_4P_3RhSi_2$	$C_{31}H_{36}NOP_2RhSi_2$	$C_{36}H_{59}NP_3RhSi_2$	$C_{30}H_{56}N_4P_3RhSi_2$	$C_{19}H_{44}NOP_2RhSi_2$	$C_{26}H_{58}NP_2RhSi_2$
fw	893.95	860.88	659.67	757.88	724.81	523.60	605.79
color	red-orange	yellow	yellow-orange	red-orange	yellow	yellow	orange
space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$Pca2_1$ (no. 29)	$P\bar{1}$ (no. 2)
a, Å	11.716(1)	13.218(1)	18.140(1)	11.084(1)	11.876(1)	14.653(1)	11.026(1)
b, Å	21.023(1)	12.697(1)	18.570(1)	16.615(1)	15.462(1)	14.850(1)	15.045(1)
c, Å	18.958(1)	25.079(1)	10.014(1)	21.243(1)	11.493(1)	12.365(1)	10.874(1)
α, deg			99.04(1)		101.11(1)		109.76(1)
β, deg	104.86(1)	99.26(1)	93.27(1)	91.75(1)	117.52(1)		110.16(1)
γ, deg			107.10(1)		89.87(1)		89.45(1)
formula units per cell	4	4	4	4	2	4	2
R^a	0.031	0.027	0.032	0.028	0.040	0.020	0.032
$R_w{}^a$	0.036	0.029	0.038	0.033	0.051	0.026	0.042
GOF	1.98	1.41	2.12	1.87	2.96	1.58	2.55

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_w = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$.

125 Hz), δ 97.2 (dt, J_{Rh} = 259 Hz). Anal. Calcd for $C_{60}H_{72}N_4P_3RhSi_2$: C, 55.72; H, 5.61; N, 4.33. Found: C, 55.53; H, 5.47; N, 4.52.

[^{i}PrPNP]RhPPh$_3$ (7). In the glovebox, a storage tube fitted with a Teflon valve and a magnetic stir bar was charged with [^{i}PrPNP]Rh(COE) (**13**) (100.1 mg, 0.1652 mmol) and PPh_3 (43.3 mg, 0.165 mmol). Toluene (3−5 mL) was added; the vessel was sealed, removed from the glovebox, and heated with stirring in a 60 °C oil bath for 1−2 h. The reaction vessel was then interfaced to a high-vacuum line, and the toluene was removed in vacuo. The residue was triturated several times with pentane (3−5 mL) to ensure complete removal of cyclooctene. The resulting yellow-orange powder was then taken up in pentane (ca. 5 mL) and filtered via cannula into another vessel, and the solvent was reduced to ca. 1 mL. Slow cooling of this solution afforded **3a** as large, transparent, ruby red blocks, which were isolated by cannula decantation of the mother liquor and drying under flowing argon. Yield: 63.8 mg (51%). An additional crop of smaller crystals (20.1 mg, 16%) was recovered from the mother liquor. Thorough drying under high vacuum caused the crystals to become opaque and return to the yellow-orange color observed in the crude product. ^{1}H NMR (C_6D_6): δ 0.52 (s, 12 H, Si(C*H*$_3$)$_2$), δ 0.90 (m, 4 H, PC*H*$_2$Si; m 12 H, CH(C*H*$_3$)$_2$), δ 1.08 (m 12 H, CH(C*H*$_3$)$_2$), δ 1.17 (m, 4 H, C*H*(CH$_3$)$_2$), δ 7.04 (m, 9 H, phenyl), δ 8.05 (m, 6 H, phenyl). ^{31}P{^{1}H} NMR (C_6D_6): δ 40.1 (dd, J_{PP} = 40 Hz, J_{Rh} = 130 Hz), δ 44.8 (dt, J_{Rh} = 173 Hz). Anal. Calcd: C, 57.05; H, 7.85; N, 1.85 Found: C, 56.77; H, 8.03; N, 1.54.

[^{i}PrPNP]Rh(PPh$_2$pyrl) (8). This complex was prepared in a manner similar to **7** using [^{i}PrPNP]Rh(COE) (79.5 mg, 0.131 mmol) and PPh$_2$-pyrl (33.0 mg, 0.131 mmol). Yield: 66 mg (67%) as yellow crystals. ^{1}H NMR (C_6D_6): δ 0.54 (s, 12 H, Si(C*H*$_3$)$_2$), δ 0.93 (m, 4 H, PC*H*$_2$Si; m 12 H, CH(C*H*$_3$)$_2$), δ 1.11 (m 12 H, CH(C*H*$_3$)$_2$), δ 1.29 (m, 4 H, C*H*(CH$_3$)$_2$), δ 6.42 (s, 2 H, pyrrolyl), δ 6.95 (br s, 6 H, phenyl), δ 7.72 (s, 2 H, pyrrolyl), δ 7.78 (m, 4 H, phenyl). ^{31}P{^{1}H} NMR (C_6D_6): δ 42.0 (dd, J_{PP} = 42 Hz, J_{Rh} = 127 Hz), δ 84.7 (dt, J_{Rh} = 193 Hz). Anal. Calcd: C, 57.05; H, 7.85; N, 1.85 Found: C, 56.77; H, 8.03; N, 1.54.

[^{i}PrPNP]Rh(PPhpyrl$_2$) (9). This complex was prepared in a manner similar to that for **7** using [^{i}PrPNP]Rh(COE) (67.2 mg, 0.111 mmol) and PPhpyrl$_2$ (26.7 mg, 0.111 mmol). Yield: 80 mg (98%) as a foamy yellow solid. Thorough drying afforded a product pure by NMR. ^{1}H NMR (C_6D_6): δ 0.49 (s, 12 H, Si(C*H*$_3$)$_2$), δ 0.94 (m, 4 H, PC*H*$_2$Si; m 12 H, CH(C*H*$_3$)$_2$), δ 1.08 (m 12 H, CH(C*H*$_3$)$_2$), δ 1.36 (m, 4 H, C*H*(CH$_3$)$_2$), δ 6.32 (s, 4 H, pyrrolyl), δ 6.86 (m, 3 H, phenyl), δ 7.17 (m, 2 H, phenyl), δ 7.58 (br s, 4 H, pyrrolyl). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.3 (dd, J_{PP} = 43 Hz, J_{Rh} = 125 Hz), δ 101.1 (dt, J_{Rh} = 217 Hz).

[^{i}PrPNP]Rh(Ppyrl$_3$) (10). This complex was prepared in a manner similar to that for **7** using [^{i}PrPNP]Rh(COE) (100.2 mg, 0.165 mmol) and Ppyrl$_3$ (37.9 mg, 0.165 mmol). Yield: 74 mg (62%) as light yellow crystals**.** ^{1}H NMR (C_6D_6): δ 0.43 (s, 12 H, Si(C*H*$_3$)$_2$), δ 0.91 (m, 4 H, PC*H*$_2$Si; m 12 H, CH(C*H*$_3$)$_2$), δ 1.09 (m 12 H, CH(C*H*$_3$)$_2$), δ 1.39 (m, 4 H, C*H*(CH$_3$)$_2$), δ 6.18 (s, 6 H, pyrrolyl), δ 7.18 (br s, 6 H, pyrrolyl). ^{31}P{^{1}H} NMR (C_6D_6): δ 45.1 (dd, J_{PP} = 46 Hz, J_{Rh} = 123 Hz), δ 96.7 (dt, J_{Rh} = 256 Hz).

[^{i}PrPNP]Rh(Ppyrl′$_3$) (11). This complex was prepared in a manner similar to that for **7** using [^{i}PrPNP]Rh(COE) (85.9 mg, 0.142 mmol) and Ppyrl′$_3$ (102.1 mg, 0.154 mmol). Yield: 58 mg (35%) as pale yellow microcrystals. ^{1}H NMR (C_6D_6): δ 0.36 (s, 12 H, Si(C*H*$_3$)$_2$), δ 0.8−1.1 (m, 4 H, PC*H*$_2$Si; m 12 H, CH(C*H*$_3$)$_2$; m, 12 H, CH(C*H*$_3$)$_2$; t, 18 H, CO$_2$CH$_2$C*H*$_3$), δ 1.44 (m, 4 H, C*H*(CH$_3$)$_2$), δ 4.07 (q, 12 H, CO$_2$C*H*$_2$CH$_3$), δ 7.91 (s, 6 H, pyrrolyl). ^{31}P{^{1}H} NMR (C_6D_6): δ 46.6 (dd, J_{PP} = 45 Hz, J_{Rh} = 115 Hz), δ 90.6 (dt, J_{Rh} = 274 Hz). Anal. Calcd: C, 49.82; H, 6.97; N, 4.84. Found: C, 50.05; H, 7.08; N, 4.63.

[^{i}PrPNP]Rh(CO) (12). This complex was prepared and isolated in a manner similar to that for **7**. After removing the storage tube from the glovebox, the solution of [^{i}PrPNP]Rh(COE) (104.4 mg, 0.172 mmol) was exposed to ca. 1 atm of CO for 30 min with efficient stirring. The bright yellow-orange of [^{i}PrPNP]Rh(COE) faded to pale yellow almost immediately upon exposure to the reactant gas. Yield: 70 mg (78%) as yellow crystals. IR (toluene): ν_{CO} 1932 cm^{-1} (vs). ^{1}H NMR (toluene-d_8): δ 0.28 (s, 12 H, Si(C*H*$_3$)$_2$), δ 0.66 (m, 4 H, PC*H*$_2$Si), δ 1.00 (m, 12 H, CH(C*H*$_3$)$_2$), δ 1.18 (m, 12 H, CH(C*H*$_3$)$_2$), δ 1.81 (m, 4 H, C*H*(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (toluene-d_8): δ 53.3 (d, J_{Rh} = 122 Hz). Anal. Calcd for $C_{19}H_{44}NOP_2RhSi_2$: C, 43.59; H, 8.47; N, 2.68. Found: C, 43.91; H, 8.93; N, 2.68.

X-ray Structural Analyses. The structures were determined from intensity data collected on a Rigaku RU300 R-AXIS image plate area detector equipped with Mo Kα radiation and a low-temperature apparatus. Data sets were corrected for Lorentz and polarization effects but not for absorption. All data sets were collected at −100 °C. The structures were solved by direct methods and refined by full-matrix least-squares techniques. The refinement and analysis of the structure was carried out using a package of local programs.[27] The atomic scattering factors were taken from the tabulations of Cromer and Waber; anomalous dispersion corrections were by Cromer.[28] In the least-squares refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$, with the weights, *w*, assigned as $[\sigma^2(I) + 0.0009I^2]^{-1/2}$. The crystallographic highlights for each complex are given in Table 4. Selected distances and angles are given in Tables 2 and 3, as described in the text. Because in each complex the refinement produced some unreasonable C−H bond lengths or hydrogen thermal parameters, the hydrogen atoms were placed in idealized positions close to their previously refined positions. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. Complete structural details including data collection and refinement, atomic coordinates, anisotropic thermal parameters, and hydrogen atom positions, are available as Supporting Information.

Acknowledgment. The National Science Foundation (CHE-9631611) and Du Pont (Educational Aid Grant) are gratefully acknowledged for support of this research. We also thank Alistair J. McGhie for expert technical assistance.

---

(27) Calabrese, J. C. Central Research and Development, E. I. Du Pont de Nemours and Co., Inc., P.O. Box 80228, Wilmington, DE 19880-0228, 1991.

(28) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1.

Supporting Information Available: Full crystallographic details including listings of atomic coordinates, *B* values, selected distances and angles, anisotropic thermal parameters, and ORTEP drawings for complexes **1**, **4**, **6**, **7**, **10**, **12**, and **13** (62 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA974200V