# **ORGANOMETALLICS**

# Correlations among <sup>31</sup>P NMR Coordination Chemical Shifts, Ru–P Bond Distances, and Enthalpies of Reaction in Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl Complexes (Cp' = $\eta^5$ -C<sub>5</sub>H<sub>5</sub>, $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>; PR<sub>3</sub> = PMe<sub>3</sub>, PPhMe<sub>2</sub>, PPh<sub>2</sub>Me, PPh<sub>3</sub>, PEt<sub>3</sub>, P<sup>n</sup>Bu<sub>3</sub>)

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**Supporting Information** 

**ABSTRACT:** The <sup>31</sup>P NMR spectra of CpRu(PR<sub>3</sub>)<sub>2</sub>Cl and Cp\*Ru-(PR<sub>3</sub>)<sub>2</sub>Cl complexes with PR<sub>3</sub> = PMe<sub>3</sub>, PPhMe<sub>2</sub>, PPh<sub>2</sub>Me, PPh<sub>3</sub>, PEt<sub>3</sub>, P<sup>n</sup>Bu<sub>3</sub> have been measured; these data correlate with and can be used to predict Ru–P bond distances and enthalpies. Their <sup>31</sup>P NMR coordination chemical shifts ( $\Delta$ (ppm) =  $\delta_{complex} - \delta_{free}$ ) show significant linear correlations with literature values of both the enthalpies of the ligand exchange reactions to form the Ru–P bonds and the average Ru–P bond distances from crystal structures. The strong correlation between  $\Delta$ (ppm) and Ru–P distance can be extended to include the first-generation Grubbs metathesis catalyst (PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru=C(H)Ph and four of its derivatives, (PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru=C(H)(*p*-C<sub>6</sub>H<sub>4</sub>X) (X = OCH<sub>3</sub>, CH<sub>3</sub>, Cl, Br), the four related Fischer carbenes (PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru=C(H)ER (ER = OEt, SPh, N(carbazole), N(pyrrolidinone)), the second-generation Grubbs catalyst



 $(PCy_3)(IMes)Cl_2Ru=C(H)Ph$ , and its derivative  $(PCy_3)(IMes)Cl_2Ru=C(H)OEt$ . Other significant correlations in the  $Cp'Ru(PR_3)_2Cl$  complexes are found between the enthalpies of reaction and Ru-P bond distances and between the cone angle and the Ru-P enthalpy, Ru-P bond distance, and  $\Delta(ppm)$  values. The <sup>31</sup>P NMR shifts for six phosphines correlate nearly linearly with their crystallographic cone angles, allowing prediction of cone angles from <sup>31</sup>P NMR data.

# INTRODUCTION

Ruthenium phosphine complexes show great utility and promise as catalysts.<sup>1,2</sup> Experimental Ru-P bond enthalpies and distances give insight into metal-phosphine bonding.<sup>3</sup> Nolan and co-workers measured Ru-P bond enthalpies in Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl complexes, where Cp' is either the cyclopentadienyl (Cp,  $C_5H_5$ )<sup>4</sup> or pentamethylcyclopentadienyl (Cp\*, C<sub>5</sub>Me<sub>5</sub>) ligand.<sup>5</sup> Ru–P bond distances are known for  $CpRu(PR_3)_2Cl$  with  $PR_3 = PMe_3$  (1),  $PPhMe_2$  (2),  $PPh_2Me_3$ (3), PPh<sub>3</sub> (4), PEt<sub>3</sub> (5) but not for  $CpRu(P^{n}Bu_{3})_{2}Cl$  (6). The structures of  $Cp^*Ru(PR_3)_2Cl$  with  $PR_3 = PMe_3$  (7), PPhMe<sub>2</sub> (8), PPh<sub>2</sub>Me (9), PPh<sub>3</sub> (10), PEt<sub>3</sub> (11), P<sup>n</sup>Bu<sub>3</sub> (12) are also known.<sup>4,5</sup> While <sup>31</sup>P NMR spectroscopy should offer insight into Ru-P bonding, the <sup>31</sup>P NMR spectra for most of these complexes were not given in the literature; therefore, we measured them to look for correlations among NMR data, Ru-P bond enthalpies and distances, and phosphine parameters.

Nolan et al. determined the enthalpies of substitution reactions with monodentate phosphines to give 1-12 in THF solution at 30 °C, using the general reaction shown in eq  $1:^{4,5}$ 

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

The enthalpies of reaction and Ru–P bond distances showed that  $PMe_3$  formed the strongest bond to ruthenium and  $PPh_3$  the weakest bond, for both the Cp and Cp\* series.<sup>4,5</sup> Since Cp is a poorer electron donor than Cp\*, the ruthenium centers in the Cp series are able to accept more electron density from the phosphine ligands in comparison to those in the corresponding Cp\* complexes. This enhanced metal basicity in the Cp complexes can be seen in stronger Ru–P bonds; for the same phosphine, the Cp complex has a more exothermic enthalpy and a shorter bond length in comparison to those with Cp\*.<sup>4a</sup>

As we did not know what might be found, we decided to also look for correlations between <sup>31</sup>P NMR data and phosphine parameters: two steric and three electronic. Tolman's cone angle ( $\theta$ ) measures the steric bulk (size) of phosphine ligands, calculated from angular measurements of CPK space-filling models.<sup>6</sup> Müller and Mingos determined crystallographic cone angles for six common phosphines (PMe<sub>3</sub>, PPhMe<sub>2</sub>, PPh<sub>2</sub>Me, PPh<sub>3</sub>, PEt<sub>3</sub>, and PCy<sub>3</sub>) from thousands of X-ray crystal structures;<sup>7</sup> many other ways to understand  $\theta$  have been proposed.<sup>3b</sup> Tolman's electronic parameter ( $\nu$ ) is based on the A<sub>1</sub>-symmetrical CO infrared stretching frequencies of Ni-

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PR <sub>3</sub>	Tolman $\theta^6$ (deg)	cryst $\theta^7$ (deg)	$\nu^{6} (\mathrm{cm}^{-1})$	$pK_a^{12}$	$\chi^{12}$	<sup>31</sup> P <sup><i>a</i></sup> (ppm)
PMe <sub>3</sub>	118	111.1	2064.1	8.65	8.55	-60.6
PPhMe <sub>2</sub>	122	119.9	2065.3	6.5	10.6	-45.0
PPh <sub>2</sub> Me	136	134.5	2067.0	4.57	12.1	-26.4
PPh <sub>3</sub>	145	148.2	2068.9	2.73	13.25	-5.0
PEt <sub>3</sub>	132	137.3	2061.7	8.69	6.3	-18.1
PCy <sub>3</sub>	170	160.1	2056.4	9.70	1.40	10.5
$P^nBu_3$	132	$(132)^{b}$	2060.3	8.43	5.25	-30.1
$a_{\text{Th}}$ , $b_{C}$						

Table 1. General Parameters for Phosphine Ligands

<sup>a</sup>This work. <sup>b</sup>Cone angle not found from X-ray crystallographic data; Tolman's cone angle used instead.

(CO)<sub>3</sub>(PR<sub>3</sub>) complexes<sup>6</sup> and contains both  $\sigma$ -donor and  $\pi$ acceptor bonding components. Computational chemistry has successfully modeled  $\nu$ ,<sup>8,9</sup> which has also been corrected using local instead of normal vibrational frequencies.<sup>10</sup> The effects of  $pK_a$  and  $\sigma$  bond donicity ( $\chi$ ) on  $\nu$  have been studied.<sup>3b,6,9,11,12</sup> While Nolan et al. included arsine, phosphite, and chelating phosphine ligands in their studies,<sup>4,5,13,14</sup> we chose to focus on cyclopentadienyl Ru complexes with six monodentate phosphines for which the Ru–P bond enthalpies and almost all bond distances were known. Measuring <sup>31</sup>P NMR spectra for these complexes should not only provide new data and insights but is also comparatively easier, quicker, and less expensive than single-crystal X-ray crystallography or air-sensitive solution calorimetry.

# RESULTS AND DISCUSSION

While the single-crystal X-ray structures of all six Cp\* complexes and five of the six Cp complexes (all but 6) have been given in the literature, previous structural studies of the Cp complexes looked at only  $1-4^{4b}$  or at 1, 4, 5, AsEt<sub>3</sub>, and  $P(OMe)_{3}^{4a}$  Studies of the Cp\* complexes looked at 7-12 along with AsEt<sub>3</sub> and the chelating bis(dimethylphosphino)methane (dmpm).<sup>5b</sup> To allow for direct comparisons between our results and the literature, we calculated the correlations between Tolman's cone angle and enthalpy of reaction for just the six-member series of complexes with Cp (1-6, R = 0.889,slope = 0.496) and with Cp\* (7-12, R = 0.886, slope = 0.473). As has previously been reported,<sup>4,5</sup> smaller cone angles in these complexes are correlated with more stable Ru-P bonds, presumably because less steric bulk allows the phosphines to more closely approach the ruthenium center. Steric and electronic parameters associated with the phosphine ligands are given in Table 1.

Crystallographic structural studies in the literature confirm that shorter Ru–P distances are found with smaller cone angles in these complexes.<sup>4,5</sup> Müller and Mingos' experimental cone angles correlate somewhat better with the average Ru–P bond distances for both the Cp (1-5, R = 0.952, slope = 0.0015) and Cp\* (7-12, R = 0.799, slope = 0.0012) series than do Tolman's cone angles with the same distances (Cp, R = 0.950; Cp\*, R = 0.788). Presumably the use of crystallographic structural data makes Müller and Mingos' cone angles somewhat more accurate.

Tolman noted in 1977 that "cone angles…also increase with the downfield shift of  $\delta({}^{31}\text{P})$ ",<sup>6b</sup> and the six free phosphine ligands' crystallographic cone angles found by Müller and Mingos show a near-perfect linear correlation with their <sup>31</sup>P NMR resonances (Figure 1, R = 0.997). While PCy<sub>3</sub> was included to determine the overall correlation, its complexes are not a focus of this investigation. Although the crystallographic cone angle for PBu<sub>3</sub> has not been determined, when its <sup>31</sup>P



**Figure 1.** Plot of the crystallographic cone angle vs <sup>31</sup>P NMR chemical shift of six monodentate phosphine ligands (R = 0.997, slope = 1.44). If the P<sup>*n*</sup>Bu<sub>3</sub> Tolman cone angle (circle) is included, the fit is almost the same (R = 0.997, slope = 1.44).

NMR signal and Tolman cone angle are included, the correlation is nearly unchanged. A phosphine's <sup>31</sup>P NMR spectrum can thus predict its cone angle, which is of considerable utility.

Of the phosphines in this study, PMe<sub>3</sub> has the smallest cone angle, most shielded <sup>31</sup>P NMR signal, and highest electron density on the phosphorus atom, while PPh<sub>3</sub> has the largest cone angle, least shielded <sup>31</sup>P signal, and lowest phosphorus electron density. A nonlinear correlation between <sup>1</sup>H NMR (of MeOH coordinated to cobalt phosphine complexes) and PR<sub>3</sub> cone angle has been reported.<sup>15</sup> Although phosphines show both steric and electronic variations, there is no significant correlation between the electronic parameter and the <sup>31</sup>P NMR resonances. The C–P–C angles vary with the cone angle and also affect the orbitals involved in bonding between the R groups and phosphorus center, as well as their  $\sigma$ -donor and  $\pi$ -acceptor character, all of which play a role in the amount of electron density at the phosphorus atom as measured by the <sup>31</sup>P NMR chemical shift.<sup>6</sup>

Previously, NMR resonances of transition-metal phosphine complexes have been found to depend on both steric and electronic parameters. A study of *cis*- $(PR_3)_2PtMe_2$  complexes found Pt–P bond enthalpies correlated with sterics; thus, larger cone angles led to less stable complexes. However, crystallographic Pt–P bond lengths and <sup>31</sup>P NMR data did not follow the enthalpy and steric trends but instead correlated somewhat with the electronic character of the PR<sub>3</sub> ligands.<sup>16</sup> The <sup>195</sup>Pt NMR resonances of *cis*-PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> complexes correlate with the electronic parameter contributions of the phosphine R groups, while the <sup>195</sup>Pt NMR signals in *trans*-PtXCl(PCy<sub>3</sub>)<sub>2</sub>

complexes are deshielded more as X becomes more sterically bulky.<sup>17</sup> In  $[Fe(Cp)(SnPh_3)(CO)(PR_3)]$  complexes the <sup>57</sup>Fe chemical shift and phosphine cone angle show a good correlation.<sup>11</sup>

For the ruthenium complexes studied, no significant correlations were found among the phosphine electronic parameter  $\nu$  or donicity  $\chi$  with the  $\Delta H$  value of the reaction, any of the structural parameters, or NMR data. Comparisons between p $K_a$  and  $\Delta H$  for the Cp series did show a correlation (R = 0.856, slope = -1.86), but no other significant correlations were found between p $K_a$  and the other Cp values or any of the Cp\* data.

The cone angles, electronic parameters, and other properties of free phosphines do not depend on the metal complexes into which the phosphines are incorporated. Examining experimental properties specific to the Cp and Cp\* complex series, the enthalpy of reaction to form the Ru–P bonds and the average Ru–P bond distances show significant correlations for both series considered individually (for the Cp complexes 1-5, R = 0.968, slope = 0.0038; for the Cp\*complexes 7-12, R = 0.877, slope = 0.0035).

While previous studies looked at the Cp and Cp\* complexes as individual series,<sup>4,5</sup> the  $-\Delta H$  values for the reaction forming the Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl complexes correlate well with the average Ru–P bond distances of all 11 known structures from both series as one group (Figure 2). Thus, despite the different steric



**Figure 2.** Plot of the  $-\Delta H$  value of reaction vs average Ru–P bond distance for the Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl complexes (R = 0.937, slope = -0.0036).

and electronic natures of the Cp and Cp\* ligands, the  $Cp'Ru(PR_3)_2Cl$  complexes share the same overall relation between their enthalpies of reaction and Ru–P bond distances, and both of these are most influenced by the steric (and not electronic) properties of the phosphines involved.

The <sup>31</sup>P NMR spectra of the free phosphines and their corresponding Cp and Cp\* complexes **1–12** were measured. Since <sup>31</sup>P NMR spectroscopy depends on the electronic environment of the phosphorus atom, it should also give information on the Ru–P bonds. On bonding, the phosphorus in a phosphine donates some of its electron density to the metal, which causes a downfield (deshielded) shift in its <sup>31</sup>P NMR signal in comparison to the free, uncomplexed phosphine. The change in NMR signal when a ligand binds to a metal is known as a coordination chemical shift ( $\Delta$ (ppm)) and can be calculated using eq 2.

$$\Delta(\text{ppm}) = \delta_{\text{complexed ligand}} - \delta_{\text{free ligand}}$$
(2)

The enthalpies of reaction, Ru–P bond lengths and angles, and <sup>31</sup>P NMR data for the Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl complexes are given in Table 2. As expected, the <sup>31</sup>P NMR signal of each complex is shifted downfield relative to the corresponding free phosphine signal. Phosphines bound to a ruthenium center coordinated to Cp (the poorer electron donor) are deshielded more than the Cp\* complex with the same phosphine. All of the Cp complexes also have greater coordination chemical shifts, consistent with the greater metal basicity of ruthenium–Cp complexes.

The crystallographic cone angle shows a significant correlation with the coordination chemical shift for both the  $CpRu(PR_3)_2Cl$  and  $Cp*Ru(PR_3)_2Cl$  series of complexes, though the slopes of the two best-fit lines differ somewhat



**Figure 3.** Plot of the crystallographic cone angle ( $\theta$ ) vs coordination chemical shift ( $\Delta$ (ppm)) for the Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl complexes (Cp, *R* = 0.971, slope = -0.638; Cp\*, *R* = 0.945, slope = -0.823).

(Figure 3). Thus, the enthalpy of reaction, Ru-P distance, and <sup>31</sup>P NMR coordination chemical shift for these complexes all correlate significantly with the cone angle, indicating that steric factors play a major role in bonding in these  $Cp'Ru(PR_3)_2Cl$  systems.

As has also been seen in *trans*-RhCl(CO)  $(PR_3)_2$  complexes,<sup>18</sup> the <sup>31</sup>P NMR signals of the free phosphines correlate strongly with the coordination chemical shifts found for both series of ruthenium phosphine complexes (for Cp, R = 0.982, slope = -0.431; for Cp\*, R = 0.952, slope = -0.555). The two sets of  $\Delta$ (ppm) values also correlate strongly with each other; the coordination chemical shift for the Cp series vs the Cp\* series has R = 0.989 (slope = 1.31).

The <sup>31</sup>P NMR coordination chemical shifts for these complexes exhibit correlations with both their enthalpies and structural parameters. The enthalpy of reaction for the ligand exchange reaction forming the Ru–P bonds shows a significant linear correlation with the coordination chemical shifts for all 12 complexes in the Cp and Cp\* series (Figure 4); therefore, <sup>31</sup>P NMR spectra can be used to estimate Ru–P bond enthalpies in these systems. Both  $\Delta H$  and  $\Delta$ (ppm) measure changes associated with the formation of the Ru–P bonds.

The average Ru–P bond distance for the 11 Cp and Cp\* complexes whose structures are known shows a stronger linear correlation with  $\Delta$ (ppm) (R = 0.905, slope = -432) than with  $\Delta H$  (R = 0.882). While CpRu(PR<sub>3</sub>)<sub>2</sub>Cl complexes can act as

Table 2. Enthalpies of Reaction, Average Bond Distances and Angles, and <sup>31</sup>P NMR Spectral Data for Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl Complexes

compd	formula	$-\Delta H (\text{kcal/mol})^{4,5}$	Ru–P (Å) <sup>4,5</sup>	P-Ru-P (deg) <sup>4,5</sup>	<sup>31</sup> P (ppm) <sup><i>a</i></sup>	$^{31}P (\Delta(ppm))^a$
1	CpRu(PMe <sub>3</sub> ) <sub>2</sub> Cl	38.4	2.275	94.85	8.1	68.7
2	CpRu(PMe <sub>2</sub> Ph) <sub>2</sub> Cl	35.9	2.285	95.31	17.0	62.0
3	CpRu(PMePh <sub>2</sub> ) <sub>2</sub> Cl	32.8	2.299	95.58	31.3	57.7
4	CpRu(PPh <sub>3</sub> ) <sub>2</sub> Cl	22.9	2.336	103.99	39.3	44.3
5	CpRu(PEt <sub>3</sub> ) <sub>2</sub> Cl	34.5	2.304	94.71	31.9	50.0
6	CpRu(P <sup>n</sup> Bu <sub>3</sub> ) <sub>2</sub> Cl <sup>b</sup>	35.4			24.9	55.0
7	Cp*Ru(PMe <sub>3</sub> ) <sub>2</sub> Cl	32.2	2.2969	91.08	2.5	63.1
8	Cp*Ru(PMe <sub>2</sub> Ph) <sub>2</sub> Cl	31.8	2.297	94.50	13.5	58.5
9	Cp*Ru(PMePh <sub>2</sub> ) <sub>2</sub> Cl	29.4	2.3100	93.02	26.6	53.0
10	Cp*Ru(PPh <sub>3</sub> ) <sub>2</sub> Cl	18.1	2.3422	96.80	27.5	32.4
11	Cp*Ru(PEt <sub>3</sub> ) <sub>2</sub> Cl	27.2	2.3208	92.80	22.5	40.6
12	Cp*Ru(P"Bu <sub>3</sub> ) <sub>2</sub> Cl	26.0	2.342	100.1	16.3	46.5

<sup>*a*</sup>This work. <sup>*b*</sup>The structure of CpRu(P<sup>*n*</sup>Bu<sub>3</sub>)<sub>2</sub>Cl has not been determined.



**Figure 4.** Plot of the enthalpy of reaction (kcal/mol) vs coordination chemical shift ( $\Delta$ (ppm)) for the Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl complexes (R = 0.882, slope = 1.55).

catalysts,<sup>2</sup> we wanted to see if the correlation between the Ru– P bond distance and  $\Delta$ (ppm) extended to more well-known Ru catalysts. NMR spectroscopy has proven useful in the study of Grubbs catalysts; the relative energies of carbene derivatives of the first-generation catalyst correlate well with both their <sup>31</sup>P NMR signals and "the *difference* between the shifts of the carbene and the corresponding internal alkene protons".<sup>19</sup>

When the average Ru-P bond distances are plotted against the <sup>31</sup>P NMR coordination chemical shifts for the Cp and Cp\* complexes, Grubbs catalysts, their derivatives, and related Fischer carbenes, the correlation between distance and  $\Delta(ppm)$ found for the Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl complexes extends to include all of these compounds, and the R value improves to 0.956 (Figure 5). The compounds added to the correlation include the firstgeneration Grubbs catalyst  $(PCy_3)_2Cl_2Ru=C(H)(p-C_6H_4X)$ (X = H (13)) and its derivatives  $(X = OCH_3 (14), CH_3 (15))$ Cl (16), Br (17)),  $^{19-21}$  the related Fischer carbenes  $(PCy_3)_2Cl_2Ru=C(H)ER$ , (ER = OEt (18), SPh (19),N(carbazole) (20), N(pyrrolidinone) (21)),<sup>21</sup> and the second-generation Grubbs catalyst (PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru=C(H)R (R = H (22)) and its derivative (R = OEt (23)).<sup>21</sup> Literature data for 13-23 are given in Table 3, and the correlation for all 22 complexes is shown in Figure 5.

This is a surprising result, considering the wide variation in ligands attached to the ruthenium centers in these 22 complexes. Given the relative ease of obtaining a  $^{31}$ P NMR



**Figure 5.** Plot of the average Ru–P bond distance (Å) vs coordination chemical shift ( $\Delta$ (ppm)) for 11 Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl complexes, 2 Grubbs catalysts, 5 of their derivatives, and 4 related Fischer carbenes (R = 0.956, slope = -275).

Table 3. Average Ru–P Bond Distances and <sup>31</sup>P NMR Coordination Chemical Shifts for Grubbs' First- and Second-Generation Catalysts and Related Complexes

compd	formula	Ru-P (Å)	$^{31}P \Delta(ppm)^a$		
$(PCy_3)_2Cl_2Ru=C(H)(p-C_6H_4X)$ : Grubbs First-Generation Catalyst (13) an Four Derivatives $^{19-21}$					
13	X = H	2.4048	26.1		
14	$X = OCH_3$	2.4183	25.3		
15	$X = CH_3$	2.4145	25.6		
16	X = Cl	2.416	26.3		
17	X = Br	2.4165	26.4		
(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> Ru=C(H)ER: Fischer Carbenes <sup>21</sup>					
18	ER = OEt	2.3794	26.9		
19	ER = SPh	2.4104	22.8		
20	ER = N(carbazole)	2.4038	30.8		
21	ER = N(pyrrolidinone)	2.4008	28.0		
(PCy <sub>3</sub> )(IMes	s)Cl <sub>2</sub> Ru=C(H)R: Grubbs Se a Derivativ	econd-Generation ve <sup>21,22</sup>	Catalyst (22) and		
22	R = Ph	2.419	24.4		
23	R = OEt	2.4166	24.5		
<sup>a</sup> Calculated	using eq 2, data from ref	s 19–22, and +	10.5 ppm as the		

free PCy<sub>3</sub> chemical shift.

spectrum in comparison to determining a single-crystal X-ray structure, the linear relation found allows estimates of Ru-P

bond lengths to be made from NMR data. Using the correlation found and the  $\Delta$ (ppm) value for CpRu(P<sup>*n*</sup>Bu<sub>3</sub>)<sub>2</sub>Cl (6), its Ru-P bond distance is predicted to be about 2.30 Å (comparable to the 2.29 Å predicted using the enthalpy vs Ru-P correlation). Similar predictions can be made for Grubbs catalyst derivatives with known <sup>31</sup>P NMR shifts, such as the first-generation  $(PCy_3)_2Cl_2Ru = C(H)(p-C_6H_4NMe_2) (\Delta(ppm) = 24.4 ppm)^{20}$ Ru-P distance predicted to be 2.41 Å) and the secondgeneration  $(PCy_3)(H_2IMes)Cl_2Ru=C(H)OEt$   $(\Delta(ppm) =$ 22.1 ppm,<sup>21</sup> Ru-P distance predicted to be 2.42 Å). The structure and  $\Delta$ (ppm) of Cp\*RuCl(PCy<sub>3</sub>) are known (but not included in Figure 5), allowing a prediction to made and checked. The sterically bulky PCy3 forms a monosubstituted complex with  $\Delta(\text{ppm}) = 29.9 \text{ ppm}^{23}$  and a predicted Ru–P length of 2.39<sub>3</sub> Å. The actual Ru–P distance is 2.3834 Å,<sup>22</sup> for an error of  $0.01_0$  Å (0.4%).

There is scatter in the data for the correlation between Ru-P distance and coordination chemical shift; if the overall correlation and  $\Delta(ppm)$  values of the two biggest outliers (10 and 11) are used to predict their Ru-P distances, the results are too long by 0.04, Å (1.8%) and 0.03, Å (1.5%), respectively. Correlations with lower R values would have even greater errors. While molecular modeling of Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl complexes found steric factors to be important,<sup>24</sup> Nolan calculated the ratio of contributions from sterics to electronics to be 2.32:1 for Ru–P  $\Delta H$  values in Cp\*RuCl(PR<sub>3</sub>)<sub>2</sub>.<sup>13b</sup> Thus, contributions from the electronic parameter are not insignificant and may cause some of the scatter in the data. Another possible limit on the observed correlations is the  $\pi$ -accepting capacity of PR<sub>3</sub> ligands. M–PR<sub>3</sub> bonding includes significant  $\pi$ back-bonding, which is a factor in the lack of correlation between M-P bond lengths and energies in M(CO)<sub>5</sub>PX<sub>3</sub> complexes (M = Cr, Mo, W; X = H, Me, F, Cl).<sup>25,26</sup> Solvent effects on <sup>31</sup>P NMR signals are another, relatively small source of error.<sup>2</sup>

The correlations reported here are limited to ruthenium complexes with one or two alkyl or aryl phosphine ligands. Due to different  $\pi$ -acceptor properties, phosphites and halophosphines would probably not fit the correlations found. For chelating bidentate phosphines, <sup>31</sup>P NMR coordination chemical shift is dependent on the chelate ring size;<sup>3,6b,28</sup> therefore, ruthenium chelate complexes are also not expected to fit these correlations.<sup>5b</sup> It would be interesting to see if the correlations between enthalpies of reaction and the coordination chemical shifts or Ru-P bond distances for the  $Cp'Ru(PR_3)_2Cl$  complexes could be extended to ruthenium carbenes and Grubbs catalysts. Gas-phase enthalpy values have been measured for ruthenium carbene metathesis catalysts,<sup>29</sup> as have their relative energies,<sup>19</sup> but these values are not directly comparable to the solution-phase enthalpies for the Cp and Cp\* complexes.

In addition to cone angle, enthalpy, and bond distance, the coordination chemical shift has previously been correlated with other parameters. The <sup>31</sup>P NMR coordination chemical shifts in  $(PR_3)M(CO)_5$  (M = Cr, Mo, W; R = alkyl, aryl) complexes are metal dependent and have been found to follow the trend Cr > Mo > W. For complexes with the same phosphine, the value of  $\Delta$ (ppm) is greater by about 18 ppm for Cr vs Mo and for Mo vs W.<sup>30</sup> The <sup>31</sup>P coordination chemical shift has also been used to find formation constants for Ph<sub>3</sub>PO with Si, Ge, and Sn compounds.<sup>31</sup> We are examining <sup>31</sup>P NMR parameters in other ruthenium phosphine complexes, as well as in phosphine complexes with other metals.

# CONCLUSION

<sup>31</sup>P NMR spectroscopy is a powerful tool for examining and understanding ruthenium phosphine complexes, and the <sup>31</sup>P coordination chemical shift ( $\Delta$ (ppm) =  $\delta_{complex} - \delta_{free}$ ) can be used to predict their Ru–P bond enthalpies and distances. For CpRu(PR<sub>3</sub>)<sub>2</sub>Cl and Cp\*Ru(PR<sub>3</sub>)<sub>2</sub>Cl complexes (PR<sub>3</sub> = PMe<sub>3</sub>, PPhMe<sub>2</sub>, PPh<sub>2</sub>Me, PPh<sub>3</sub>, PEt<sub>3</sub>, P<sup>n</sup>Bu<sub>3</sub>), the <sup>31</sup>P NMR  $\Delta$ (ppm) value shows a significant linear correlation with both the  $\Delta H$  of reaction for forming the Ru–P bonds and the average Ru–P bond distances. This  $\Delta$ (ppm) vs distance correlation can be extended to include first- and second-generation Grubbs metathesis catalysts, their derivatives, and ruthenium Fischer carbene complexes, allowing predictions of their Ru–P bond distances to be made from <sup>31</sup>P NMR data.

Crystallographic cone angles correlate nearly linearly with <sup>31</sup>P NMR shifts of the free phosphines; thus, NMR data can predict PR<sub>3</sub> cone angles. The properties of Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl complexes are influenced by steric factors, as the cone angle correlates significantly with the reaction enthalpy, average Ru–P bond distance, and  $\Delta$ (ppm). While it was known that  $\Delta H$  and Ru–P distance showed significant correlations for each of the Cp and Cp\* series, there is also a significant correlation between them for all 11 Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl complexes with known structures.

Being able to predict Ru–P bond lengths and enthalpies, and phosphine cone angles from <sup>31</sup>P NMR spectra is of significant interest, given the comparative difficulty, time, and cost associated with obtaining crystallographic and calorimetric data.

# EXPERIMENTAL SECTION

**General Considerations.** All Cp'Ru(PR<sub>3</sub>)<sub>2</sub>Cl reactions were performed under an inert atmosphere of either nitrogen (in an MBraun Labmaster 130 glovebox with less than 1 ppm of oxygen and water) or argon (using standard Schlenk line techniques).<sup>32</sup> Reagents were used as purchased from Aldrich and Strem, except for THF, which was distilled from sodium and benzophenone. Complexes **1–6** were synthesized using literature methods.<sup>11</sup>a,<sup>33,34</sup> Since this research was conducted chiefly by undergraduate chemists, we wished to avoid any thallium-containing intermediates in the CpRu(COD)Cl synthesis.<sup>35</sup> Thus, complexes **7–12** were made following Clark's synthesis of CpRu(PEt<sub>3</sub>)<sub>2</sub>Cl (ligand exchange reactions with excess PR<sub>3</sub> and CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl in THF at 50 °C for several days).<sup>36</sup>

All NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer in 5 mm tubes in  $\text{CDCl}_3$  solvent. <sup>31</sup>P spectra (121.497 MHz) were recorded relative to an external standard of 85% H<sub>3</sub>PO<sub>4</sub> in a coaxial insert. Each complex was synthesized and its NMR spectra were measured several times by different researchers.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00444.

Equation of best fit line and *R* value for all plots, additional plots of data for correlations, and <sup>31</sup>P NMR spectra of 1-12 (PDF)

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# Notes

The authors declare no competing financial interest.

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