Thermodynamics of Addition of CO, Isocyanide, and H_2 to $Rh(PR_3)_2Cl$

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Abstract: The enthalpies of the addition of CO, H_2, or Bu^tNC to $[Rh(P^iPr_3)_2Cl]_2$ (**1**) to give the mononuclear complexes $Rh(P^iPr_3)_2Cl(CO)$ (**2**), $Rh(P^iPr_3)_2ClH_2$ (**3**), and $Rh(P^iPr_3)_2Cl(CNBu^t)$ (**4**) are reported. 2-Ethylhexanal is decarbonylated by **1** to give *n*-heptane and **2**; solution-phase calorimetric measurement of this reaction enables calculation of the enthalpy of addition of CO to **1**. The coordinatively unsaturated dihydride **3** reacts with Bu^tNC to give **4**; measurement of the enthalpy of this reaction, and the direct reaction of **1** with Bu^tNC, permits calculation of the enthalpy of addition of H_2 to **1**. These results afford the relative enthalpies of addition to the hypothetical fragment $Rh(P^iPr_3)_2$-Cl. Although **1** was previously formulated as monomeric in solution, the complex is exclusively dimeric. Based on the observation that no measurable concentration of $Rh(P^iPr_3)_2Cl$ monomer exists in solution, a lower limit for the bridge strength of **1** is calculated which, in turn, affords lower limits for the exothermicity of additions to the hypothetical monomer: 48.2 kcal/mol for addition of CO (i.e. the Rh—CO BDE of **1**), 42.4 kcal/mol for addition of Bu^tNC, and 32.5 kcal/mol for addition of H_2. Although these values represent lower limits, the Rh—CO BDE and particularly the exothermicity of H_2 addition are quite high compared with previously reported values for second-row transition metals. These results are consistent with and help to explain the unusual ability of $Rh(PMe_3)_2Cl(CO)$ to efficiently catalyze photo- and thermochemical alkane functionalization reactions.

The dearth of reliable thermodynamic data for organometallic complexes has recently been appreciated and numerous bond dissociation enthalpies (BDE's) have been determined in the past decade.[1,2] Nevertheless, the range of such data is somewhat limited, with emphasis found on weaker bonds in coordinatively saturated complexes.

In particular, surprisingly few BDE measurements have been reported for what is perhaps the most important class of bonds in organotransition-metal chemistry, that between a metal (M) and CO. This results in part from the fact that CO is a gas, complicating calorimetric measurements. Further, the (presumably) high M—CO BDE's make kinetic-based determinations difficult especially when other, more weakly bound, ligands are present; accordingly the relatively few reported values are for homoleptic metal carbonyls[3] or complexes with strongly bound ancillary ligands, e.g. π-arene[4] or η^2-bis(dimethylphosphino)-ethane.[5]

Kinetic-based determinations, or even estimations, are particularly difficult when the complex in question is coordinatively unsaturated. For example, to our knowledge there are no absolute values published for ligand addition to d^8 three-

coordinate fragments (i.e. BDE's for dative M—L bonds in complexes with the very important d^8 square-planar configuration).[6,7] This situation stems in part from the fact that substitution reactions of such complexes generally proceed via facile associative mechanisms, precluding an estimation of BDE's based on rates of ligand dissociation. Similar considerations apply to the enthalpy of oxidative addition to d^8 three-coordinate fragments as the d^6 five-coordinate product configuration likewise permits facile associative substitution. While stable complexes of this configuration are relatively rare (further compounding the difficulty in obtaining thermodynamic values), d^6 five-coordinate intermediates, as well as the addition process itself, are critical in organometallic catalyses such as hydrogenation and hydroformylation.[8] In this contribution we examine the thermodynamics of (i) addition of CO and Bu^tNC to the three-coordinate fragment $Rh(PR_3)_2Cl$ (R = ^iPr, Me) to give d^8 square-planar complexes and (ii) addition of H_2 to give the corresponding d^6 five-coordinate adduct $Rh(PR_3)_2ClH_2$ (stable for R = ^iPr).

In addition to the importance of thermodynamic values for these general reaction classes, addition of CO and H_2 to fragments of the form $Rh(PR_3)_2Cl$ is of particular interest. $Rh(PMe_3)_2Cl(CO)$ was reported to be the first efficient (greater than ca. 100 turnovers) organometallic alkane functionalization catalyst, effecting the photochemical dehydrogenation of alkanes

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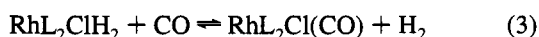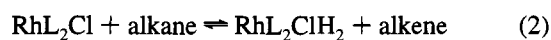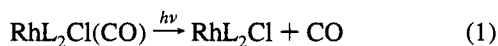(4) Burkey, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8329–8333.
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(8) See for example: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Tinke, R. G. *Principles of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 523–560, 620–632. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: New York, 1988; pp 190–201.
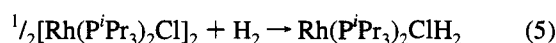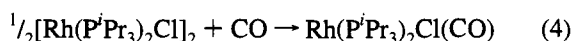
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to yield the corresponding alkenes.[9-11] The proposed mechanism for the catalytic cycle involves transfer of hydrogen from alkane to photogenerated $Rh(PMe_3)_2Cl$ (eqs 1 and 2; $L = PMe_3$), followed by the reaction of $H_2Rh(PMe_3)_2Cl$ with CO to displace H_2 thereby regenerating $Rh(PMe_3)_2Cl(CO)$ (eq 3).

$$RhL_2Cl(CO) \xrightarrow{h\nu} RhL_2Cl + CO \qquad (1)$$

$$RhL_2Cl + alkane \rightleftharpoons RhL_2ClH_2 + alkene \qquad (2)$$

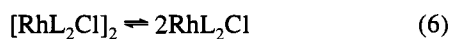$$RhL_2ClH_2 + CO \rightleftharpoons RhL_2Cl(CO) + H_2 \qquad (3)$$

While turnover rates as high as 300/h have been observed,[11] no intermediates are present in observable concentration, implying that both reactions 2 and 3 proceed very rapidly. This behavior implies that the exothermicity of H_2 addition to $Rh(PMe_3)_2Cl$ must be comparable to or greater than the enthalpy of dehydrogenation of the alkane substrates, 23−28 kcal/mol, and the Rh−CO BDE must be somewhat greater than that.

More recently we found that $Rh(PMe_3)_2Cl(CO)$ catalyzes the efficient *thermal* transfer-dehydrogenation of alkanes (>1000 mol of alkane/mol of Rh), but only under dihydrogen atmosphere.[12] The catalytic cycle consists simply of eq 2 and its microscopic reverse (where the alkene is a sacrificial hydrogen acceptor). The catalysis is proposed to be initiated by the reverse of eq 3; the active unsaturated species $Rh(PMe_3)_2Cl$ is thus generated *via* the unusual route of displacement of a ligand (CO) by H_2. The equilibrium of eq 3 lies too far to the right to permit observation of $Rh(PMe_3)_2ClH_2$; thus the Rh−CO BDE must be at least ca. 9 kcal/mol[13] greater than the enthalpy of H_2 addition. However, the catalysis proceeds fairly rapidly and with no measurable induction period implying that the difference cannot be *much* greater than ca. 9 kcal/mol or the reverse rate of reaction 3 would be insignificant.

$[Rh(P^iPr_3)_2Cl]_2$[14] (1) rapidly and irreversibly adds CO or H_2 to give $Rh(P^iPr_3)_2Cl(CO)$ (2) and $Rh(P^iPr_3)_2ClH_2$ (3), respectively.

$$\tfrac{1}{2}[Rh(P^iPr_3)_2Cl]_2 + CO \rightarrow Rh(P^iPr_3)_2Cl(CO) \qquad (4)$$

$$\tfrac{1}{2}[Rh(P^iPr_3)_2Cl]_2 + H_2 \rightarrow Rh(P^iPr_3)_2ClH_2 \qquad (5)$$

Herein we report calorimetric determinations of the enthalpies of reactions 4 and 5. These afford the relative enthalpies of CO and H_2 addition to the fragment $Rh(P^iPr_3)_2Cl$ (and thus the enthalpy of eq 3 where $L = P^iPr_3$) but not absolute values. Based on the observation that no measurable concentration of Rh-$(P^iPr_3)_2Cl$ monomer exists in solution, a lower limit for the bridge strength of 1 (ΔH_6; $L = P^iPr_3$) can be calculated.

$$[RhL_2Cl]_2 \rightleftharpoons 2RhL_2Cl \qquad (6)$$

In combination with the enthalpies of eqs 4 and 5, this reveals lower limits for the exothermicity of additions to the hypothetical

species $Rh(P^iPr_3)_2Cl$: 48.2 kcal/mol for addition of CO (i.e. the Rh−CO BDE) and 32.5 kcal/mol for addition of H_2. Even though these values represent lower limits (for fairly crowded complexes) they are still quite high compared with previously reported values for second-row transition metals; we believe this is consistent with and helps explain the remarkable catalytic reactivity of the $Rh(PR_3)_2Cl$ fragments.

Results and Discussion

Bridge Strength of $[Rh(P^iPr_3)_2Cl]_2$ (1). While the related complex $[Rh(PCy_3)_2Cl]_n$ (Cy = cyclohexyl) exists in a monomer−dimer equilibrium[15] (eq 6) in benzene and toluene solutions, the P^iPr_3 analog 1 shows no measurable concentration of monomer in either solvent (see the Appendix for characterization and spectroscopic properties of 1 and $[Rh(PCy_3)_2Cl]_n$). A lower limit for the bridge strength of 1 can be determined based on this observation. For example, a ^{31}P NMR spectrum of a 50 mM solution of 1 in benzene has no observable monomer with a detection limit (conservatively) estimated as 0.2 mM. Thus K_6 under these conditions is less than 8×10^{-7} M. A similar calculation may be made based on the fact that the UV−visible spectra of 1 obey Beer's law over the range 0.25−12 mM. In a 0.25 mM solution the estimated detection limit of monomer is 0.02 mM; thus K_6 must be less than 1.6×10^{-6} M. Assuming that ΔS for formation of the hypothetical unsolvated monomer would be at least as great as ΔS for formation of the solvated $Rh(PCy_3)_2Cl$ monomer in toluene (32 eu; see Appendix), then the lower limit of ΔH_6 for cleavage of $[Rh(P^iPr_3)_2Cl]_2$ is calculated to be +17.8 kcal/mol. This value is close to that calculated by Drago for the bridge strength of the closely related complex $[RhL_2Cl]_2$ (L = P(4-tolyl)_3),[7] 19.7 kcal/mol, extrapolated from calorimetric measurements of the reaction of that dimer with several Lewis bases. Our calculated lower limit of the bridge strength of 1 (17.8 kcal/mol) is therefore probably not far below the actual value.

Thermodynamics of CO Addition. Addition of CO to 1 (eq 4) is rapid and quantitative. However, in order to avoid problems associated with calorimetric measurements with a gas-phase reactant, we have developed and exploited the following reaction to determine the enthalpy of eq 4.

$$\tfrac{1}{2}[Rh(P^iPr_3)_2Cl]_{2(soln)} + RCHO_{(soln)} \rightarrow$$
$$\mathbf{1}$$

$$Rh(P^iPr_3)_2Cl(CO)_{(soln)} + RH_{(soln)} \quad (7)$$
$$\mathbf{2}$$

$$\Delta H_7 = -36.0 \pm 0.5 \text{ kcal/mol}$$

While reaction 7 is general for R = alkyl,[16] we found it to proceed cleanly and most rapidly when R was a secondary alkyl; R = 3-heptyl was chosen for the purpose of this study.

Conversion of 1 (ca. 10 mM) to $Rh(P^iPr_3)_2Cl(CO)$ (2; eq 7) proceeded quantitatively in the presence of 0.16 M 2-ethylhexanal as determined by GC, IR, and ^1H- and ^{31}P-NMR measurements. The enthalpy of mixing solid 1 (30−40 mg) with 4.0 mL of a stock benzene solution of 0.16 M 2-ethylhexanal was determined to be −31.2 ± 0.2 kcal/mol, the average of five individual calorimetric determinations.[17-19] Independent determination of the enthalpy of solution (benzene) gave a value of +4.8 ± 0.3 kcal/mol. The enthalpy of eq 7 is thus −36.0 ±

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(13) The minimum value for the equilibrium constant of eq 3 is ca. 5 × 10⁶, calculated based on a failure to observe any reaction of 2 even under 1000 psi H₂; ΔS is assumed to be approximately zero.
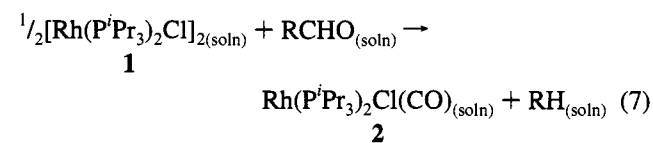
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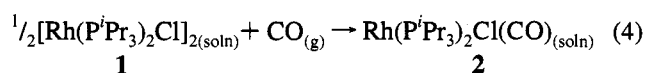
0.5 kcal/mol. Consistent with the lack of solvent dependence of the ^{31}P NMR spectrum of **1** (Appendix), calorimetric measurement of eq 7 in a different solvent, mesitylene, is measured to be -35.2 ± 0.4 kcal/mol, equal to the value in benzene within the limits of experimental error.

A reaction enthalpy of -3.3 ± 0.5 kcal/mol can be calculated using the available thermodynamic data for the components of eq 8.[20]

$$RH_{(soln)} + CO_{(g)} \rightarrow RCHO_{(soln)} \qquad (8)$$

$$\Delta H_8 = -3.3 \pm 0.5 \text{ kcal/mol}$$

The sum of the enthalpies of eqs 7 and 8, -39.3 ± 0.7 kcal/mol, equals the enthalpy of eq 4.

$$^1/_2[Rh(P^iPr_3)_2Cl]_{2(soln)} + CO_{(g)} \rightarrow Rh(P^iPr_3)_2Cl(CO)_{(soln)} \qquad (4)$$
$$\textbf{1} \qquad\qquad\qquad\qquad\qquad \textbf{2}$$

$$\Delta H_4 = -39.3 \pm 0.7 \text{ kcal/mol}$$

Addition of one-half the lower limit of the bridge strength of **1** (17.8 kcal/mol) gives a lower limit of 48.2 kcal/mol for the absolute Rh—CO BDE of **2**.

Analogous experiments were conducted with the PMe_3 analog of **1**, $[Rh(PMe_3)_2Cl]_2$. Equation 9 was found to proceed most efficiently with 2,3-dimethylvaleraldehyde (less bulky aldehydes, including 2-ethylhexanal, gave substantial amounts of ester, the product of Tishchenko coupling of aldehyde).

$$^1/_2[Rh(PMe_3)_2Cl]_{2(soln)} + RCHO_{(soln)} \rightarrow$$
$$Rh(PMe_3)_2Cl(CO)_{(soln)} + RH_{(soln)} \qquad (9)$$
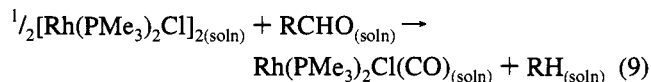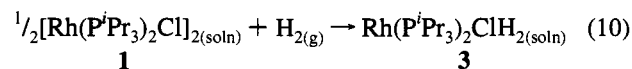
$$\Delta H_9 = -31.3 \text{ kcal/mol}$$

Due to the small steric requirements of coordinated CO we do not believe that steric effects should greatly weaken the Rh—CO bond of **2**. While the Rh—CO bond of the PMe_3 complex would be sterically less hindered than that of **2**, electronic factors should favor the bond in **2**. Thus these factors are of opposite direction; if, as seems plausible, neither is of great magnitude then the Rh—CO BDE's would be nearly equal. To the extent that this approximation is valid, the difference between the enthalpies of eqs 7 and 9 (ignoring any small difference in decarbonylation enthalpies of the two secondary aldehydes) reflects a stronger halide bridge in the less crowded PMe_3 dimer, corresponding to a difference of $2(\Delta H_9 - \Delta H_7) = 9.4$ kcal/mol. However, if steric effects in **2** are in fact significant, than the Rh—CO BDE of the PMe_3 complex may be significantly greater; a correspondingly greater bridge strength in the PMe_3 dimer would then lead to the relatively similar enthalpies of eqs 7 and 9.

Thermodynamics of H_2 and *t*-BuNC Addition. Addition of H_2 to **1**, like addition of CO, is rapid and quantitatively gives the corresponding (monomeric[21]) adduct.

$$^1/_2[Rh(P^iPr_3)_2Cl]_{2(soln)} + H_{2(g)} \rightarrow Rh(P^iPr_3)_2ClH_{2(soln)} \qquad (10)$$
$$\textbf{1} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{3}$$

As with CO, in order to avoid problems associated with calorimetric measurements using a gas-phase reactant, we measured a liquid-phase reaction, in this case using the adduct **3** as a reactant.

$$Rh(P^iPr_3)_2ClH_{2(soln)} + Bu^tNC_{(soln)} \rightarrow$$
$$\textbf{3}$$
$$Rh(P^iPr_3)_2Cl(CNBu^t)_{(soln)} + H_{2(g)} \qquad (11)$$
$$\textbf{4}$$

$$\Delta H_{11} = -9.9 \pm 0.4 \text{ kcal/mol}$$

The enthalpy of the reaction of Bu^tNC with **1** was then measured.

$$^1/_2[Rh(P^iPr_3)_2Cl]_{2(soln)} + Bu^tNC_{(soln)} \rightarrow$$
$$\textbf{1}$$
$$Rh(P^iPr_3)_2Cl(CNBu^t)_{(soln)} \qquad (12)$$
$$\textbf{4}$$

$$\Delta H_{12} = -33.5 \pm 0.5 \text{ kcal/mol}$$

The Rh—$CNBu^t$ BDE of **4** is thus 5.8 ± 0.9 kcal/mol less than the corresponding Rh—CO BDE of **2**; the minimum Rh—$CNBu^t$ BDE (calculated as above) is thus 42.4 kcal/mol.

Equation 12 plus the reverse of eq 11 gives eq 10.

$$^1/_2[Rh(P^iPr_3)_2Cl]_{2(soln)} + H_{2(g)} \rightarrow Rh(P^iPr_3)_2ClH_{2(soln)} \qquad (10)$$
$$\textbf{1} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{3}$$
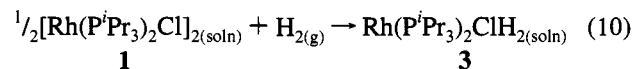
$$\Delta H_{10} = \Delta H_{12} - \Delta H_{11} = -23.6 \pm 0.6 \text{ kcal/mol}$$

Thus the enthalpy of H_2 addition to $Rh(P^iPr_3)_2Cl$ is 15.7 ± 0.9 kcal/mol less than addition of CO. Calculated as above, the minimum enthalpy of H_2 elimination is 32.5 kcal/mol, which corresponds to a lower limit of the average Rh—H BDE of 68.4 kcal/mol.[22]

Relevance to Alkane Dehydrogenation. Complex **1** reacts at room temperature with cyclooctane to give **3** and cyclooctene.[23] (The initial distribution of metal-containing products is the same as that formed when solutions of **1** and **3** are mixed, including several species such as $H_2[Rh(P^iPr_3)_2Cl]_2$; eventually **3** becomes the dominant product.[23]) Other alkanes however, e.g. *n*-hexane and cyclohexane, do not undergo dehydrogenation although they are rapidly dehydrogenated by the thermo- or photochemically generated $Rh(PMe_3)_2Cl$ fragment. Assuming that **1** reacts with alkane via the $Rh(P^iPr_3)_2Cl$ monomer, the much greater bulk of P^iPr_3 than PMe_3 would undoubtedly result in a much inhibited kinetic reactivity. The present work helps further clarify the difference between **1** and $Rh(PMe_3)_2Cl$. Firstly the finding that the stable form of **1** is dimeric (Appendix) reveals an additional kinetic barrier to reaction with alkanes. Additionally, determination of the enthalpy of eq 10 reveals that cyclooctane dehydrogenation by **1** is approximately thermoneutral while dehydrogenation of *n*-hexane and cyclohexane would be endothermic. (The dehydrogenation enthalpy of cyclooctane is anomalously low, $\Delta H°$
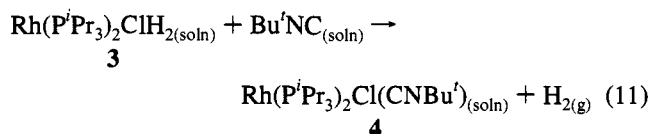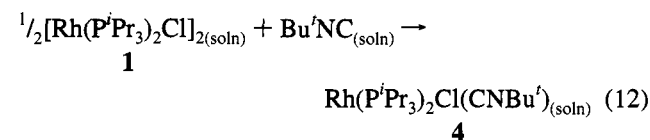
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= +23.3 kcal/mol, compared with the more typical +28.2 kcal/mol of cyclohexane.[24]) Taking into account the enthalpy of bridging reveals that the reactions of typical alkanes with monomeric Rh(P^{i}Pr₃)₂Cl would be at least moderately exothermic (>4 kcal/mol).

For the same reasons as those discussed above concerning CO addition, the difference between the enthalpy of H₂ addition to monomeric Rh(P^{i}Pr₃)₂Cl vs Rh(PMe₃)₂Cl is probably small: electronic and steric factors are probably of fairly small magnitude and opposite direction. Thus the calculated minimum enthalpy of H₂ elimination from Rh(P^{i}Pr₃)₂ClH₂, 32.5 kcal/mol, is probably approximately applicable to Rh(PMe₃)₂Cl. This or any greater value is entirely consistent with the proposed ability of Rh(PMe₃)₂Cl to rapidly dehydrogenate cyclooctane as well as typical alkanes. Further, the difference between the enthalpies of CO addition and H₂ addition to **1**, 15.7 ± 0.9 kcal/mol (for each rhodium center), is probably particularly close to the corresponding value for Rh(PMe₃)₂Cl. (Even if addition of both H₂ and CO to one of the two fragments is significantly more favorable, the *difference* between H₂ and CO addition is probably similar for the two fragments.) This value is large enough to explain the lack of observable reaction between Rh(PMe₃)₂Cl(CO) and H₂,[13] but small enough to permit the proposed formation of a small concentration of catalytically active species via the reverse of eq 3 under the reaction conditions (i.e., high H₂ pressure and no added CO).

Comparison with other Dissociation Enthalpies. The bonds formed in the reactions discussed herein may be weakened by steric interactions with the bulky P^{i}Pr₃ ligands. Nevertheless, even the lower limits of the dissociation enthalpies which can be obtained from the present work are greater than the few other comparable values reported for second-row transition-metal carbonyls and hydrides. For example, the lower limit of 48.2 kcal/mol for the Rh—CO bond of **2** is greater than the M—CO BDE's of 40.5 and 43.0 kcal/mol reported respectively for Mo(CO)₆[4a] and even the very electron-rich species Ru(CO)(Me₂-PCH₂CH₂PMe₂)₂.[5]

The lower limit calculated for the exothermicity of H₂ addition to Rh(P^{i}Pr₃)₂Cl, 32.5 kcal/mol, corresponding to an average Rh—H BDE of 68.4 kcal/mol, is also unusually high. For example, addition of H₂ to Rh[P(4-tolyl)₃]₂BCl is exothermic by 11.0 ± 0.5 kcal/mol (B = P(4-tolyl)₃) and 11.6 ± 1.0 kcal/mol (B = tetrahydrothiophene);[7] addition to Ir(PPh₃)₂(CO)Cl is exothermic by 15.0 kcal/mol.[25] Note that the latter example is a third-row transition-metal complex, which is generally expected to form significantly stronger bonds; accordingly, addition to the analogous Rh(PMe₃)₂(CO)Cl is thermodynamically unfavorable even under 3 atm of H₂ at low temperatures (−90 °C), indicating an enthalpy of dissociation under ca. 5 kcal/mol.[26] Even the very electron-rich Ru(II) complex [Ru(PPh₃)₃H₃]⁻ has a reported *activation* enthalpy for H₂ loss of 21.8 ± 1.4 kcal/mol;[27] that value represents an approximate upper limit for ΔH° of dissociation and since H₂ addition to d^8 four-coordinate complexes generally has a significant kinetic barrier,[28] ΔH° is probably significantly less. While the above examples all represent H₂ elimination from six-coordinate d^6 complexes, elimination from several other 18-electron configurations seems to be even less endothermic. For example, the

activation barrier for elimination from d^4 seven-coordinate Ru(PPh₃)₃H₄ is 17.9 kcal/mol,[27] and for the third-row complexes IrH₅(P^{i}Pr₃)₂[29] and WH₂(CO)₃(P^{i}Pr₃)₂ (classical isomer),[30] the barriers are ca. 25 and 15 kcal/mol, respectively. ΔH° of elimination from the d^2 eight-coordinate complex W(PMe₃)₄H₂I₂ is 19.7 ± 6 kcal/mol.[31]

For a small number of examples the exothermicity of H₂ addition has been estimated to be comparable to or greater than that reported here for Rh(P^{i}Pr₃)₂Cl. H₂ addition to Cp*Ir(PMe₃)[32] and Cp₂W[33] has been estimated as being exothermic by 44 and 42 kcal/mol respectively. Certain other very stable dihydrides may have H₂ elimination enthalpies comparable to or greater than Rh(P^{i}Pr₃)₂Cl; these include complexes of the type ML₄H₂ (M = Fe, Ru, Os), CpRhLH₂, and PtL₂H₂. Notably, all of these are also examples in which the fragment is capable of hydrocarbon C—H addition,[34-40] in accord with an expected rough correlation between M—H and M—C BDE's for a given fragment M. Accordingly, we note that the high exothermicity of H₂ addition to RhL₂Cl is relevant to its catalytic alkane functionalization abilities in the context of C—H addition, as well as the context of eq 2. We also note that, with the exception of the platinum complexes, the dihydrides and corresponding alkyl hydrides in the examples given above are all 18-electron species. This would limit the ability of the alkyl hydrides to undergo β-H elimination and thereby effect alkane dehydrogenation. And while Whitesides has shown that the Pt(η²-Cy₂PCH₂CH₂PCy₂) fragment can add alkane C—H bonds to give formally unsaturated alkyl hydrides,[40] the resistance of d^8 square-planar platinum alkyls toward β-H elimination is well established.[41] These observations may help clarify the factors responsible for the unusual catalytic activity of Rh(PR₃)₂Cl as well as isoelectronic fragments thought to be catalytically active in iridium-based alkane dehydrogenation systems.[42]

Experimental Section

General Procedures. All manipulations were conducted under argon atmosphere either in a Vacuum Atmospheres Dry-Lab glovebox or using standard Schlenk techniques. **1** was synthesized according to Werner[14] and [Rh(PCy₃)₂Cl]ₙ as described by Van Gaal.[15] C₆D₆ and toluene-d₈ were dried over sodium and vacuum-distilled prior to use. Methylcyclohexane-d₁₄ was dried with molecular sieves and vacuum distilled. All other solvents were either distilled from dark purple

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solutions of benzophenone ketyl or dried over molecular sieves. Triisopropylphosphine, purchased from Strem Chemicals, and 2-bromopropane-d_7, from Cambridge Isotope Laboratories, were used as received. All other chemicals were purchased from Aldrich. Aldehydes were dried with molecular sieves before vacuum distillation.

NMR spectra were recorded on either a Varian XL 200- or 400 MHz spectrometer. ^{31}P NMR chemical shift values were expressed in reference to 85% H_3PO_4. UV–visible and IR spectra were obtained on a Hewlett-Packard HP8452A diode array spectrophotometer and on a Mattson Cygnus 100 FTIR spectrometer, respectively. GC analysis was performed on a Varian 3400 gas chromatograph with a flame ionization detector and a 50-m methyl silicone gum capillary column.

Calorimetric Measurement of Reaction between [Rh(P^{i}Pr$_3$)$_2$Cl]$_2$ (1) and 2-Ethylhexanal. 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 30–40 mg sample of **1** was accurately weighed into the lower vessel which was then closed and sealed with 1.5 mL of mercury. Four milliliters of a stock solution of 2-ethylhexanal (0.5 mL of the aldehyde in 20 mL of freshly dried and distilled benzene) was added and the remainder of the cell was assembled, removed from the glovebox, and inserted in the calorimeter. The reference vessel was loaded in an identical fashion with the exception that no organorhodium complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (about 2 h), the calorimeter was inverted, thereby allowing the reactants to mix. After the reaction had reached completion and the calorimeter had once again reached thermal equilibrium (ca. 2 h) the vessels were removed from the calorimeter. Conversion to **2** was found to be quantitative under these reaction conditions. The enthalpy of reaction, −31.2 (0.2) kcal/mol, represents the average of five individual calorimetric determinations. This represents a typical calorimetric procedure. Other measurements conducted in the course of this study were performed using stoichiometric amounts of reagents when required.

Calorimetric Measurement of the Enthalpy of Solution of 1 in Benzene. In order to consider all species in solution, the enthalpies of solution of **1** had to be directly measured. This was performed by using a procedure similar to the one described above with the exception that no aldehyde was added to the reaction cell. This enthalpy of solution represents the average of five individual determinations and is 4.8 (0.3) kcal/mol.

Rh(P^{i}Pr$_3$)$_2$(CO)Cl (2). **1** (150 mg, 0.16 mmol) was dissolved in 15 mL of toluene and CO was bubbled through the solution for 30 s. The initial purple solution turned yellow immediately. The solvent was then removed *in vacuo*, and the product was recrystallized from toluene/hexanes (140 mg, 90% yield). ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 1.28 (q, ($^3J_{P-H}$ + $^5J_{P-H}$)/2 = J_{H-H} = 7 Hz, 36 H), 2.50 (m, 6 H). ^{31}P NMR (C$_6$D$_6$, 162 MHz): δ 49.8 (d, J_{Rh-P} = 117.5 Hz). IR(C$_6$D$_6$): 1943.2 (s) cm^{-1}.

Rh(P^{i}Pr$_3$)$_2$ClH$_2$ (3). **1** (350 mg, 0.38 mmol) was dissolved in 30 mL of toluene and H$_2$ was bubbled through the solution for 30 s. The initial purple solution turned yellow immediately. The solvent was then removed *in vacuo*, and the product was recrystallized from toluene/hexanes (320 mg, 90% yield). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 1.18 (q, ($^3J_{P-H}$ + $^5J_{P-H}$)/2 = $^3J_{H-H}$ = 6.8 Hz, 36 H), 2.18 (m, 6 H), −22.75 (dt, J_{Rh-H} = 26.3 Hz, J_{P-H} = 13.8 Hz, 2 H). ^{31}P NMR (C$_6$D$_6$, 162 MHz): δ 62.9 (dt, J_{Rh-P} = 115.3 Hz, J_{H-P} = 13.8 Hz).

Rh(P^{i}Pr$_3$)$_2$Cl(t-BuNC) (4). **1** (100 mg, 0.11 mmol) was dissolved in 10 mL of toluene and 27 μL (0.24 mmol) of t-BuNC dissolved in 5 mL of toluene was slowly added to the solution with stirring. The initial purple solution gradually turned to yellow. The solvent was the removed *in vacuo*, and the product was recrystallized from toluene/hexanes (95 mg, 80% yield). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 1.40 (q, ($^3J_{P-H}$ + $^5J_{P-H}$)/2 = J_{H-H} = 6.6 Hz, 36 H), 2.66 (m, 6 H), 0.96 (s, 9 H, t-Bu). ^{31}P NMR (C$_6$D$_6$, 162 MHz): δ 46.8 (d, J_{Rh-P} = 129.4 Hz). IR(C$_6$D$_6$): 2046.4 (s) cm^{-1}.

Syntheses of P^{i}Pr$_3$-d_{21} (P*) and Perdeuterio-[Rh(P^{i}Pr$_3$)$_2$Cl]$_2$ (1). P* was synthesized by modification of a reported method.[50] Na powder (3.6 g 0.156 mol) was suspended in 25 mL of dry n-butyl ether and stirred at 52 °C in an oil bath. A mixture of 2-bromopropane-d_7 (5.8 mL, 0.062 mol) and triphenyl phosphite (5.4 mL, 0.021 mol) was then added dropwise over 30 min. The mixture was stirred for ca. 1.5 h after addition was completed and the color changed to blue. The

mixture was then hydrolyzed with 30 mL of water, and the organic layer was separated and dried over MgSO$_4$ overnight. Fractional distillation gave 0.4 g of P* (10% yield). ^{31}P NMR (C$_6$D$_6$, 162 MHz): δ 18.2 (s).

1-d_{84} was synthesized in a method similar to that of the perprotio isotopomer. ^{31}P NMR (C$_6$D$_6$, 162 MHz): δ 56.0 (d, J_{Rh-P*} = 197 Hz).

Preparations of Perprotio- and Perdeuterio-[Rh(PMe$_3$)$_2$Cl]$_2$ (5). **5-h_{36}** was synthesized by a modification of Werner's procedure,[51] using [Rh(COE)$_2$Cl]$_2$[52] (COE = cyclooctene) instead of [Rh(C$_2$H$_4$)$_2$Cl]$_2$. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 1.17 (pseudo t, J_{P-H} = 4.2 Hz). ^{31}P NMR (C$_6$D$_6$, 162 MHz): δ 4.36 (d, J_{Rh-P} = 190.7 Hz). The perdeuterio isotopomer, **5-d_{36}**, was synthesized similarly. ^{31}P NMR (C$_6$D$_6$, 162 MHz): δ 2.38 (d, J_{Rh-P} = 190.4 Hz).

Phosphine Ligand Scrambling of Perprotio and Perdeuterio Rhodium Complexes. **5-h_{36}** (11.5 mg, 0.02 mmol) and 12.5 mg (0.02 mmol) of **5-d_{36}** were dissolved in 0.5 mL of C$_6$D$_6$ to yield a solution of 80 mM total dimer. The solution was allowed to stand at room temperature for ca. 30 min and then a ^{31}P NMR spectrum was taken. Ligand scrambling was observed and a statistical distribution of isotopomers was found: **5-h_{36}:5-d_{18}:5-d_{36}** = 1:2:1. ^{31}P NMR (C$_6$D$_6$, 162 MHz): δ 4.36 (d, J_{Rh-P} = 190.7 Hz, **5-h_{36}**), 2.38 (d, J_{Rh-P} = 190.4 Hz, **5-d_{36}**), 4.42 (dd, J_{Rh-P} = 190.6 Hz, J_{P*-P} = 59.9 Hz, P of **5-d_{18}**), 2.33 (dd, J_{Rh-P*} = 190.3 Hz, J_{P-P*} = 60.0 Hz, P* of **5-d_{18}**).

The ligand scrambling experiment of **1** was carried out similarly to that of **5**. **1-h_{84}** (4.6 mg, 0.005 mmol) and 5.4 mg (0.005 mmol) of **1-d_{84}** were mixed in 0.5 mL of C$_6$D$_6$ to make a solution of 10 mM in each. **1-h_{84}:1-d_{42}:1-d_{84}** = 1:2:1 was found from the ^{31}P NMR spectrum. ^{31}P NMR (C$_6$D$_6$, 162 MHz): δ 57.13 (d, J_{Rh-P} = 197 Hz, **1-h_{84}**), 56.03 (d, J_{Rh-P} = 197 Hz, **1-d_{84}**), 57.63 (dd, J_{Rh-P} = 197 Hz, J_{P*-P} = 54.6 Hz, P of **1-d_{42}**), 55.51 (dd, J_{Rh-P*} = 197 Hz, J_{P-P*} = 54.9 Hz, P* of **1-d_{42}**).

Reaction of 1 with 2-Ethylhexanal. 2-Ethylhexanal (8.0 μL, 0.05 mmol) was mixed with 0.5 mL of 20 mM **1** in C$_6$D$_6$ in an NMR tube. The color of the initial purple solution changed gradually to yellow. ^{31}P NMR spectra of the solution were taken periodically. It was found that **1** was completely consumed after ca. 5 min and **2** was the only product observed after 10 min. ^{1}H NMR spectra of the above reaction were carefully examined, and neither olefinic protons nor hydrides were observed. The formation of **2** and n-heptane was further confirmed by IR and GC, respectively.

Reaction of 5 with 2,3-Dimethylvaleraldehyde. 2,3-Dimethylvaleraldehyde (10.3 μL, 0.075 mmol) was mixed with 0.5 mL of 15 mM **5** in C$_6$D$_6$ in an NMR tube. ^{31}P NMR spectra were taken at 40 °C periodically, **5** was completely consumed after ca. 1 h, and Rh(PMe$_3$)$_2$-(CO)Cl was the only product observed. Neither olefinic protons nor hydrides were found from ^{1}H NMR spectra. The formations of Rh-(PMe$_3$)$_2$(CO)Cl and 3-methylpentane were further confirmed by IR and GC, respectively.

Reaction of 1 with t-BuNC. **1** (0.5 mL, 13 mM) in C$_6$D$_6$ was treated with 1.4 μL (0.013 mmol) of t-BuNC in an NMR tube. The color of the solution changed from reddish-purple to bright yellow immediately upon shaking. The ^{31}P NMR spectrum was observed immediately and **1** completely disappeared with the formation of **4** which was confirmed by IR and ^{1}H and ^{31}P NMR. Excess (>2.2 equiv) t-BuNC leads to uncharacterized species.

Reaction of 3 with t-BuNC. **3** (0.45 mL, 25 mM) in C$_6$D$_6$ was treated with 1.5 μL (0.013 mmol) of t-BuNC in an NMR tube. The color of the solution changed from brownish-yellow to bright yellow immediately upon shaking, and evolution of gas was observed. The ^{31}P NMR spectrum was recorded immediately and after ca. 5 min, **3** disappeared completely with the formation of **4**. Free H$_2$ was observed in the ^{1}H-NMR spectrum. As in the reaction of **1**, excess (>1.1 equiv) t-BuNC leads to uncharacterized species.

Appendix: Characterization of [Rh(PCy$_3$)$_2$Cl]$_n$ and [Rh(P^{i}Pr$_3$)$_2$Cl]$_2$ (1)

[Rh(PCy$_3$)$_2$Cl]$_n$. The complex[15] was previously reported to exist in a monomer−dimer equilibrium in benzene as indicated by ^{31}P NMR spectroscopy.[15] The ratio of the two signals, δ 47.5 (d, J_{Rh-P} = 195.3 Hz, dimer) and δ 49.0 (br d, J_{Rh-P} =

210 Hz, monomer),[43] is indeed consistent with a monomer–dimer equilibrium (eq 6; L = PCy₃; 0.5–12 mM; concentrations of the complex are expressed in terms of total rhodium), with K_{eq} = ca. 2.6 × 10⁻³ M in benzene at 25 °C, although precision is somewhat limited by the broadness of the ³¹P NMR signal of the monomer and by fact that the equilibrium lies toward dimer at the higher concentrations (greater than ca. 5 mM) which allow more precise measurements of monomer concentration. In cyclohexane solution (11 mM), however, only dimer (δ 47.9, J_{Rh-P} = 196 Hz) was observed over a wide range of temperatures (25–80 °C; decomposition occurred at higher temperatures).

In accord with the ³¹P NMR spectrum, the UV–visible spectrum of a solution of [Rh(PCy₃)₂Cl]ₙ in cyclohexane was found to be concentration-independent (0.25–4.0 mM), with weak bands at 508 and 378 nm, and intense bands at 334 and 298 nm separated by a minimum at 320 nm (1.0 mm path length). The spectrum of a 4.0 mM benzene solution similarly displayed two weak bands at 510 and 378 nm and an intense maximum at 330 nm. The short wavelength maximum was found at 286 nm with a shoulder at ca. 298 nm, and the minimum between the high energy bands was at 314 nm. When the solution was successively diluted by factors of 2 (ultimately to 0.25 mM), the maxima at 330 and 286 nm gradually shifted to 326 and 282 nm, respectively, with extinction coefficients increased by ca. 20 and 15%, respectively. More distinctive was the loss of the shoulder at ca. 298 nm and a corresponding shift of the local minimum from 314 to 302 nm. Thus the dimer is associated with the band at 298 nm and the monomer with that at 282 nm. Unfortunately, it was not possible to determine the spectrum of the monomer at long wavelengths due to the weakness of any bands it may possess in that region and the low concentrations necessary to shift the equilibrium away from dimer. The UV spectral results were consistent with an equilibrium with the same value of K_{eq}, 2.6 × 10⁻³ M, as determined by ³¹P NMR, although precision was in this case limited by the difficulty in observing *high* concentrations (greater than ca. 4 mM; i.e. predominantly dimer) and by the spectral similarity of the two species.

In addition to the very different behavior in cyclohexane and benzene, markedly different K_{eq} values were observed (by ³¹P NMR) even in solvents as similar as benzene and toluene (2.6 × 10⁻³ vs 5.4 × 10⁻⁴ M, respectively, at 25 °C). The mononuclear Rh(PCy₃)₂Cl complex is thus apparently solvated in benzene. Therefore no clear advantage in terms of absolute BDE information would be obtained by measuring the enthalpy of addition reactions of [Rh(PCy₃)₂Cl]ₙ as opposed to 1, and additional complications would be introduced. To possibly gain some insight into the strength of the halide bridge, however, we obtained Van't Hoff plots for the [Rh(PCy₃)₂Cl]ₙ monomer–dimer equilibrium. The values obtained (eq 6; L = PCy₃) over the temperature range 25–45 °C were ΔH = 12.0 ± 0.8 kcal/mol and ΔS = 28 ± 2 eu in C₆D₆ (11 mM) and ΔH = 14.0 ± 1.1 kcal/mol and ΔS = 32 ± 3 eu in toluene (4 mM).

[Rh(PⁱPr₃)₂Cl]₂ (1). Molecular weight measurements in our own laboratory and elsewhere[44] have indicated that [Rh(PⁱPr₃)₂Cl]ₙ (1) exists as a monomer in solution; however, such measurements, at least in our laboratory, require several days during which significant decomposition occurs in solution. An X-ray crystal structure reportedly shows 1 to be a dimer.[44] Discussed below are several observations that establish that 1

is predominantly dimeric in solution (cyclohexane and benzene) as well as in the solid state.

In contrast with [Rh(PCy₃)₂Cl]ₙ, the UV–visible spectrum of the PⁱPr₃ analog (1) in benzene follows Beer's law in the range 0.25–12 mM. Four bands are found at 498, 380, 334, and 296 nm for a 4 mM solution in benzene, in close resemblance to the spectrum of [Rh(PCy₃)₂Cl]ₙ in *cyclohexane* (508, 378, 334, and 298 nm) in which the dimer is the only observable species. 1 also has a similar spectrum in cyclohexane (4 mM): 496, 378, 334, and 298 nm. Accordingly the ³¹P NMR spectra of 1 in benzene and other solvents including cyclohexane show only one signal and no significant concentration-dependence, indicating firstly that any monomer–dimer equilibrium lies far to one extreme (δ and $^1J_{Rh-P}$ values in C₆D₆ were 57.14, 197 at 100.3 mM, 57.10, 199 at 20.1 mM, and 57.10, 199 at 4.0 mM). In agreement with the UV–visible spectra, the $^1J_{Rh-P}$ value of 1 (198 ± 1 Hz) is closer to that of the dimeric form of Rh(PCy₃)₂Cl (195.3 Hz vs 210 Hz), further suggesting that 1 is exclusively dimeric. This is perhaps not surprising given that PⁱPr₃ is considered slightly less bulky than PCy₃.[45]

Further evidence for the dimeric nature of 1 is offered by the $^2J_{P-P}$ coupling value. This was obtained by exploiting the markedly different ³¹P chemical shifts which result not only from deuteration at a given phosphine position but also, to a lesser extent, from deuteration of a *different* phosphine ligand on the same metal center. Thus, when solutions of perdeuterio- and perprotio-[Rh(PMe₃)₂Cl]₂ were mixed, phosphine scrambling resulted and a statistical distribution of isotopomers was observed (see Experimental Section for details): two doublets attributable to RhP₂ and RhP*₂ centers (P and P* = perprotio- and perdeuteriophosphine) and two doublets of doublets attributable to a RhPP* center with a $^2J_{P-P}$ value of 60 Hz consistent with the *cis*-phosphines[7] expected of the halide-bridged dimer and observed crystallographically.[46] This contrasts with much greater $^2J_{P-P}$ values (>300 Hz) found for numerous Rh(I)[47] and other[48] with *trans*-phosphines. When solutions of perdeuterio- and perprotio-1 were mixed, the pattern of the resulting spectrum was essentially identical to that obtained in the analogous [Rh(PMe₃)₂Cl]₂ experiment, revealing a $^2J_{P-P}$ value of 55 Hz.

The ³¹P-NMR spectra of 1 reveal no significant differences in either δ or $^1J_{Rh-P}$ values across a fairly wide range of solvents: (δ, $^1J_{Rh-P}$) benzene (57.1, 198.3), THF (57.3, 198.7), toluene (57.2, 198.4), mesitylene (57.2, 197.1), 2,2,5,5-Me₄-THF (57.3, 197.8), methylcyclohexane (57.4, 197.5), and cyclohexane (57.5, 196.8). This suggests the absence of any significant metal–solvent interactions in support of the dimeric nature of the complex. A priori, an alternative explanation for the absence of solvent effects could be the formation of an agostic (C–H coordinated) monomer. This explantation, however, is in conflict with the above spectral data, including the similarities to [Rh(PCy₃)₂Cl]₂ and [Rh(PMe₃)₂Cl]₂. Further-

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(46) A crystal structure of [Rh(PMe₃)₂Cl₂][46a] reveals it to be dimeric, with essentially the same, folded, Rh₂Cl₂ bridge geometry first found for [Rh(CO)₂Cl]₂[46b] and subsequently for several related dimers.[46c] (a) Emge, T.; Goldman, M. E.; Goldman, A. S. To be submitted for publication. (b) Dahl, L. F.; Martell, C.; Wampler, D. L. *J. Am. Chem. Soc.* **1961**, *83*, 1761–1762. (c) Curtis, M. D.; Butler, W. M. *Inorg. Chem.* **1978**, *17*, 2928–2931.

(47) For example, the complex *cis*-Rh(PPh₃)₂(PMe₃)Cl has a trans $^2J_{PP}$ coupling constant of 365 Hz (trans) and *cis*-phosphine coupling constants of 44 Hz (PMe₃–PPh₃) and 38 Hz (PPh₃–PPh₃). The trans $^2J_{PP}$ coupling of *cis*-Rh(PMe₃)₂(PⁱPr₃)Cl is 345 Hz compared with 49.3 and 38.7 Hz for the *cis* couplings. Wang, K.; Goldman, A. S. Unpublished results.

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more, the expected spectroscopic indications of agostic interactions[49] were *absent*, including (i) a C—H stretch in the 2250—2800 cm^{-1} region of the IR spectrum, (ii) an upfield signal in the ^{1}H NMR spectrum, even at temperatures down to −130 °C, and (iii) inequivalence of the phosphines in the ^{31}P NMR spectrum, also down to −130 °C. Note that it was apparently possible to freeze out free rotations of the phosphine ligand (around Rh—P and/or P—C bonds) at low temperatures (methylcyclohexane-d_{14} or toluene-d_8), probably due to the crowded cis configuration of the bulky ligands; thus the ^{1}H NMR spectrum of **1** changes from a simple pattern attributable to 24 equivalent methyl and 12 equivalent methine groups to a complex pattern indicative of a highly unsymmetrical complex at temperatures below ca. −70 °C. The ^{13}C spectrum behaves similarly, with several peaks resolved below ca. −80 °C. (By comparison, the corresponding signals in the ^{1}H and ^{13}C spectra of the *trans*-phosphine complex Rh(P^{i}Pr$_3$)$_2$Cl(CO) remain unresolved at −100 °C). Nevertheless, even with rotations frozen out no evidence for agostic interactions was observed in either the ^{1}H or ^{13}C spectra of **1** and the ^{31}P spectrum contained only one signal.

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