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New Synthetic Route, X-ray Structure, and Molecular Orbital Analysis for *trans,trans*-Dichlorobis(triphenylphosphine)(phenyl)rhodium(III). Do Agostic Rh···H(PPh$_3$), Hydrogen-Bond (Rh)Cl···H(PPh$_3$), or Steric Intramolecular Interactions Prevail?

Renzo Cini* and Alessandro Cavaglioni[†]

Department of Chemical and Biosystem Sciences and
Technologies, University of Siena, Pian dei Mantellini 44,
I-53100 Siena, Italy

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Introduction

A large amount of experimental and theoretical work has been done in the field of weak metal−hydrogen (M···H) interactions. Just to mention part of the effort devoted to this subject, we note that at least 20 articles about agostic interactions have been published during the last three years in the journals of the American Chemical Society; the papers relevant to compounds of the "platinum group metals" appearing during the last 10 months of 1998 are listed in refs 1−6. The interest in these interactions arises because many fields of inorganic chemistry can be involved: e.g., catalysis, theoretical chemistry, and bioinorganic chemistry.

Coordinatively and electronically unsaturated organometallic and coordination compounds are usually good candidates to have M···H interactions either occurring at the transition states of reaction pathways or "frozen" at the level of agostic interactions.[7] Molecules of kinetically inert metal ions such as Rh(III) (low spin) are particularly suited to have agostic interactions especially when hydrogen atoms proximal to the metal center come from groups such as phenyl which do not easily undergo hydrogen elimination.

In the category of triphenylphosphine derivatives, the compound [RhCl$_2$(Ph)(PPh$_3$)$_2$] was claimed to have two Rh···H agostic interactions.[8] A structurally similar compound however was reported without any agostic hydrogen atom.[9] Therefore, the important question of whether steric repulsion instead of attractive M···H−C interactions brings hydrogen atoms close to the metal center arises in the case of [RhCl$_2$(Ph)(PPh$_3$)$_2$]. Steric interactions related to M···H−C agostic interactions were very recently investigated for Ir(III) complexes by other authors.[6]

Table 1. Selected Crystal Data and Structure Refinement Parameters for [RhCl$_2$(Ph)(PPh$_3$)$_2$], **2**

empirical formula	$C_{42}H_{35}Cl_2P_2Rh$
fw	775.45
temp/K	293(2)
wavelength/Å	0.71073
crystal system	monoclinic
space group	*C*2/*c* (No. 15)
a/Å	12.9060(10)
b/Å	13.861(2)
c/Å	20.106(3)
α/deg	90
β/deg	93.860(10)
γ/deg	90
V/Å^3	3588.6(8)
Z	4
d (calcd)/Mg m^3	1.435
abs coeff/mm^{-1}	0.744
crystal size/mm	0.15 × 0.15 × 0.15
index ranges	$-1 \leq h \leq 17$, $-1 \leq k \leq 18$, $-26 \leq l \leq 26$
no. of reflns collected	5555
no. of indep reflns	4556 ($R_{int} = 0.0230$)
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	4556/0/215
final *R* indices [$I > 2\sigma(I)$; 3062 reflns]	R1 = 0.0499; wR2 = 0.0852
R indices (all data)	R1 = 0.0924; wR2 = 0.0981

The organometallic compound [RhCl$_2$(Ph)(PPh$_3$)$_2$] was reported as prepared from the reaction of [RhHCl$_2$(PPh$_3$)$_3$][10] with diphenylmercury(II), and its crystals were analyzed via X-ray diffraction and assigned to the triclinic system.[8]

Here we report a two-step, high-yield synthesis of [RhCl$_2$(Ph)(PPh$_3$)$_2$] starting from RhCl$_3$·3H$_2$O and SbPh$_3$, through [RhCl$_2$(Ph)(SbPh$_3$)$_3$], an X-ray analysis of the monoclinic crystals, and a density functional analysis with geometry optimization of the model molecule [RhCl$_2$(Ph)(PH$_2$CHCH$_2$)$_2$].

Experimental Section

Materials. RhCl$_3$·3H$_2$O (Janssen or Aldrich), SbPh$_3$ (Fluka), and PPh$_3$ (Erba) were used as purchased without any further purification. Absolute ethanol (EtOH, Erba), CHCl$_3$ (Erba), and CH$_2$Cl$_2$ (Erba) were also used without any further purification.

Synthesis of [RhCl$_2$(Ph)(SbPh$_3$)$_3$]·C$_2$Cl$_4$, 1·C$_2$Cl$_4$. The starting complex was prepared as reported previously by us.[11−13]

Synthesis of [RhCl$_2$(Ph)(PPh$_3$)$_2$], 2. A 240 mg (0.92 mmol) sample of PPh$_3$ was dissolved in 10 mL of refluxing MeOH (or EtOH); then 340 mg (0.23 mmol) of **1**·C$_2$Cl$_4$ was added, whereupon the color of the suspension turned from orange to red. After a 2 h reflux, the reaction mixture was cooled and the precipitate was filtered off. The collected microcrystalline solid was washed three times with cold MeOH (or EtOH) and then three times with Et$_2$O and finally dried in the air at 25 °C. Yield: 136 mg, 76%. The crude product was recrystallized from CH$_2$Cl$_2$. Anal. Calcd for $C_{42}H_{35}Cl_2P_2Rh$ (MW 775.4): C, 65.05; H, 4.55; P, 7.99. Found: C, 64.58; H, 4.65; P, 7.67. Single red crystals suitable for X-ray diffraction studies were obtained by slowly evaporating a solution of the pure compound in CH$_2$Cl$_2$.

X-ray Structure Determination for [RhCl$_2$(Ph)(PPh$_3$)$_2$], 2. A well-formed red crystal suitable for the X-ray analysis was selected at the polarizing microscope and mounted on a glass fiber. Accurate cell constants (Table 1) were determined by using a Siemens P4 diffrac-

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* Corresponding author. E-mail: cini@cuces.unisi.it.

[†] Present address: ISVEA srl, Laboratorio di Analisi, Via S. Gimignano 92, I-53036 Poggibonsi, Italy. This author contributed to the synthesis and the X-ray structural characterization.

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tometer and full-matrix least-squares refinement of the values of 36 carefully centered randomly selected reflections. The choice of the crystal system, monoclinic, and the space group, *C*2/*c*, was based on the analysis performed on the cell parameters and on the intensities carried out through the XSCAN[14] and PLATON 98[15] packages. The agreement factor for the intensities is $R_{\text{int}} = 0.0230$ over 636 equivalencies. The diffraction data set was corrected for Lorentz−polarization and absorption effects. The structure solution and refinement (based on F^2) was performed through Patterson and Fourier synthesis methods and full-matrix least-squares cycles. All non-hydrogen atoms were refined anisotropically. The H atoms were included and refined through the HFIX 43 and AFIX 43 options of SHELX 97.[16] The final *R* indices converged to R1 = 0.0499 and wR2 = 0.0852.

All the calculations and graphics outputs were performed by using the SHELX 97,[16] PARST 97,[17] and XPMA-ZORTEP[18] and ORTEP 32[19] packages implemented on PC-Pentium machines.

Molecular Orbital Analysis. All the density functional calculations were performed by using the GAUSSIAN94/DFT[20] package implemented on an Origin 2000 SG machine. Geometry optimizations, energy calculations, and population analysis were obtained by using the B3LYP method[21] and the LANL2DZ[20] basis set. The latter consists of 6-31G-like functions for non transition metal atoms and a valence double-ζ basis set for 3s, 3p, 3d, and 4s electrons and orbitals along with an effective core potential (Hay and Wadt[22]) for the metal. All the geometrical parameters were fully optimized without symmetry constraints. Other details are reported in ref 23. The species optimized were $C_2H_3^-$, C_2H_4, $C_6H_5^-$, C_6H_6, $PH_2(CH{=}CH_2)$, $PH_2(C_6H_5)$, and *trans*-$[RhCl_2(C_6H_5)(PH_2CH{=}CH_2)_2]$. The starting structure of the coordination sphere for the optimization of the complex molecule was that found in the solid state for $[RhCl_2(C_6H_5)(PPh_3)_2]$, **2**, except that $PH_2CH{=}CH_2$ was used instead of triphenylphosphine. The orientation of the $CH{=}CH_2$ groups with respect to the Rh−P bonds in the starting structure is exactly that of the phenyl ring proximal to Rh and anti to the phenyl ligand of the experimental solid-state structure.

Molecular drawings were obtained by using XPMA-ZORTEP[18] and ORTEP 32[19] packages implemented on a Pentium machine.

Results and Discussion

Synthesis. The synthesis of $[RhCl_2(Ph)(PPh_3)_2]$, **2**, was carried out by using the new route represented in Scheme 1a. A previous paper by other workers[8] reports the synthesis of **2** through the last step of route b or route c. Route a is easier than route b because it is a two-step synthesis instead of a three-step one. Routes b and c require anaerobic conditions (except for the oxidative addition of HCl to $[RhCl(PPh_3)_3]$), whereas all the operations of route a can be conducted in an air atmosphere. Finally, the overall yield based on $RhCl_3$ is 61% in the present work (route a), whereas the overall yield for route b is 55%.[8,10,24] The overall yield for route c is 32%.[8,10] Therefore, the new preparative route for **2** competes well with the method previously reported.

Scheme 1. Synthetic Routes for $[RhCl_2(Ph)(PPh_3)_2]$, **2**[a]

(a)

$RhCl_3x3H_2O + 4SbPh_3 \rightarrow [RhCl_2(Ph)(SbPh_3)_3] + ClSbPh_2 + 3H_2O$ (EtOH)

$[RhCl_2(Ph)(SbPh_3)_3] + 2\ PPh_3 \rightarrow [RhCl_2(Ph)(PPh_3)_2] + 3\ SbPh_3$ (EtOH)

(b)

$RhCl_3x3H_2O + 4\ PPh_3\ (1{:}6) \rightarrow [RhCl(PPh_3)_3] + OPPh_3 + 2HCl + 2H_2O$ (EtOH/N_2)

$[RhCl(PPh_3)_3] + HCl \rightarrow [RhHCl_2(PPh_3)_3]$ (form-β) (Benzene)

$[RhHCl_2(PPh_3)_3] + HgPh_2 \rightarrow [RhCl_2(Ph)(PPh_3)_2] + C_6H_6 + PPh_3 + Hg$ (Benzene/N_2)

(c)

$RhCl_3x3H_2O + 4PPh_3\ (1{:}4.5) \rightarrow [RhHCl_2(PPh_3)_3]$ (form-α) $+ OPPh_3 + HCl + 2H_2O$ (Acetone/N_2)

$[RhHCl_2(PPh_3)_3] + HgPh_2 \rightarrow [RhCl_2(Ph)(PPh_3)_2] + C_6H_6 + PPh_3 + Hg$ (Benzene/N_2)

[a] Route a: Present work. Route b: step 1, ref 24; step 2, ref 10; step 3, ref 8. Route c: step 1, ref 10; step 2, ref 8.

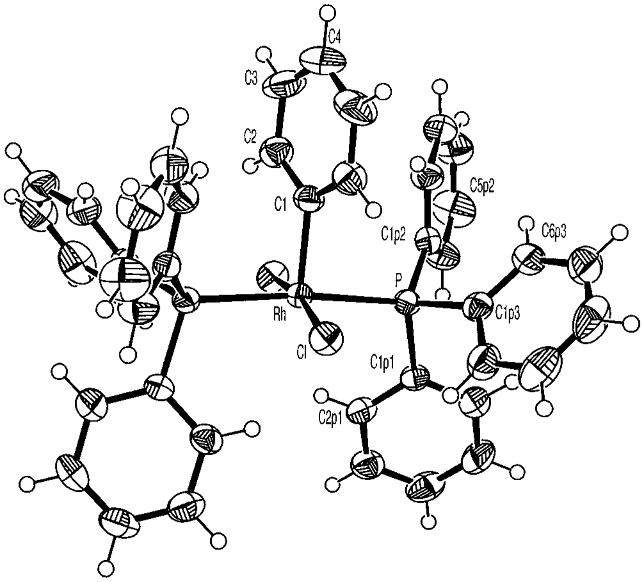

Figure 1. Drawing of the complex molecule $[RhCl_2(Ph)(PPh_3)_2]$, **2**. The ellipsoids enclose 30% probability.

Table 2. Selected Bond Lengths (Å) for $[RhCl_2(Ph)(PPh_3)_2]$, **2**

Rh−C(1)	2.014(5)	C(1)−C(2)	1.383(4)
Rh−Cl	2.3458(9)	C(2)−C(3)	1.390(6)
Rh−P	2.3635(9)	C(3)−C(4)	1.367(6)
P−C(1P1)	1.826(3)	Rh···H(2P1)	2.911(2)
P−C(1P2)	1.820(4)	Cl···H(2P1)	2.72(1)
P−C(1P3)	1.823(4)		

X-ray Crystallography for $[RhCl_2(Ph)(PPh_3)_2]$, 2. The molecular structure of **2** is represented in Figure 1, and selected geometrical parameters are reported in Tables 2 and 3. Both the overall molecular structure and intramolecular bond distances and angles found in this work (monoclinic, *C*2/*c*) are almost the same as those previously reported by other workers (triclinic, $P\bar{1}$).[8] The reliability of the symmetry assignment used for the data set collected in this work is in agreement with the lower

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Table 3. Selected Bond Angles (deg) for $[RhCl_2(Ph)(PPh_3)_2]$, **2**

C(1)−Rh-Cl	95.65(2)	C(2)−C(1)-C(2)#1	120.0(5)
Cl#1-Rh−Cl	168.70(5)	C(2)−C(1)-Rh	120.0(3)
Cl−Rh−P#1	84.99(3)	C(1)−C(2)-C(3)	119.2(4)
C(1)−Rh-P	93.03(2)	C(4)−C(3)-C(2)	121.2(5)
Cl−Rh−P	94.41(3)	C(3)−C(4)-C(3)#1	119.1(6)
P#1-Rh−P	173.94(5)	C(2P1)-C(1P1)-P	120.6(3)
C(1P2)-P−C(1P1)	106.05(16)	C(6P1)-C(1P1)-P	121.3(3)
C(1P2)-P−C(1P3)	105.28(17)	C(2P2)-C(1P2)-P	120.2(3)
C(1P1)-P−C(1P3)	101.97(16)	C(6P2)-C(1P2)-P	122.2(3)
C(1P2)-P−Rh	115.07(12)	C(2P3)-C(1P3)-P	118.6(3)
C(1P1)-P−Rh	108.83(12)	C(6P3)-C(1P3)-P	123.3(3)
C(1P3)-P−Rh	118.26(12)		

[a] Symmetry transformation used to generate equivalent atoms: (#1) $-x + 1, y, -z + {}^1/_2$.

conventional agreement factor R1 (0.0499) when compared to that of ref 8 (0.0541). It must be noted that the data/parameter ratio is 14.2 (15.8 for ref 8). A search for additional symmetry carried out by using PLATON 98[15] on the cell parameters and atomic coordinates only from ref 8 as retrieved from the CSD suggests the *C*2/*c* space group.

The pentacoordinate rhodium center is linked to two symmetrically equivalent trans chloride anions (trans to each other), to two symmetrically equivalent phosphorus atoms (trans to each other) from PPh_3 molecules, and to the carbon atom of a Ph ligand. The Rh, C(1), C(4), and H(4) atoms sit on a crystallographic C_2 axis. The metal is exactly on the planes defined by the atoms C(1)/C(2)/C(3)/C(4) and by the atoms P(1)/P1#/C(1). The Rh−Cl bond distance (2.346(1) Å) is a little shorter than that reported in ref 8 (2.359(1 Å). The Rh−P and Rh−C bond distances (2.363(1) and 2.014(5) Å) are almost the same those previously reported (2.369(1) and 2.013(3) Å).[8] The Rh−Cl and Rh−P bond vectors are bent away from the Ph ligand so that the Cl−Rh−Cl and P−Rh−P bond angles are 168.70(5) and 173.94(5)°, respectively.

The intramolecular contact distance between Rh and two ortho hydrogen atoms from the phenyl groups of PPh_3 which are anti with respect to the Ph ligand is 2.911(2) Å (2.854 Å is the mean value from ref 8). This short contact was reported as indicative of an agostic Rh···H(C) interaction.[8] The analysis of other geometrical parameters is in agreement with this hypothesis. In fact, the Rh−P−C(1P1) bond angle (108.8(1)°) is smaller than Rh−P−C(1P2) (115.1(1)°) and Rh−P−C(1P3) (118.3(1)°). The existence of short intramolecular C(2P1)−H···Cl($-x + 1$, y, $-z + 0.5$) contacts should be noted: C···Cl, 3.396(4) Å; H···Cl, 2.72(1); C−H···Cl, 130(2)°. This suggests the presence of Cl···H−C hydrogen bonds.

The analysis shows that attractive interactions should occur also between H(2P3) and Cl (C···Cl, 3.256(4) Å; H···Cl, 2.85(1); C−H···Cl, 108(1)°) and between H(2)($-x + 1$, y, $0.5 - z$) and Cl (C···Cl, 3.225(4) Å; H···Cl, 2.66(1); C−H···Cl, 120(1)°).

The crystal packing does not have any appreciable stacking interaction involving the π-system of the Ph moieties. The complex molecules are held together by weak C−H···Cl attractions such as H(4P1)($x - 0.5$, $y + 0.5$, z)···Cl (C···Cl, 3.798(5) Å; H···Cl, 3.17(1) Å; C−H···Cl, 126(2)°) and H(3P2)($x - 0.5$, $y - 0.5$, z)···Cl (C···Cl, 3.911(4) Å; H···Cl, 3.05(1); C−H···Cl, 155(3)°) and C−H···π-Ph interactions such as H(2P2)($-x + 1$, y, $-z + 0.5$)···C(1) (C···C, 3.283(4) Å; H···C, 2.65(1) Å; C−H···C, 126(4)°), H(5P2)($-x + 1.5$,$-y + 0.5$,$-z + 1$)···C(4P3) (C···C, 3.736(7) Å; H···C, 2.93(1) Å; C−H···C, 146(4)°). No remarkable repulsive intermolecular interaction involving phenyl groups of PPh_3 could be found.

Table 4. Selected Bond Distances (Å) for the Species Computed through the Density Functional Theory (B3LYP/LANL2DZ Level, Unless Otherwise Specified), Along with Selected Intramolecular Contact Distances for the Rhodium Complex

		ethene		benzene												
species	H−C(1)	H−C(2)	C(1)−C(2)	H−C(1)/ H−C(6)	H−C(3)/ H−C(5)	H−C(4)	C1−C(2)/ C1−C(6)	C(2)−C(3)/ C(5)−C(6)	C(3)−C(4)/ C(4)−C(5)	H−P	C−P	C−Rh	P−Rh	Cl−Rh	H···Cl	H···Rh
$C_2H_3^-$	1.140	1.110	1.388													
$C_2H_3^-$/6-31G**	1.135	1.114	1.357													
C_2H_4	1.088	1.088	1.348													
C_2H_4/6-31G**	1.087	1.087	1.330													
$C_6H_5^-$				1.100	1.097	1.092	1.445	1.418	1.413							
$C_6H_5^-$/6-31G**				1.103	1.096	1.091	1.424	1.405	1.400							
C_6H_6				1.088	1.088	1.088	1.409	1.409	1.409							
C_6H_6/6-31G**				1.086	1.086	1.086	1.396	1.396	1.396							
PH_2CHCH_2	1.090	1.089	1.349							1.451	1.887					
PH_2CHCH_2/6-31G**	1.089	1.087	1.335							1.427	1.843					
$PH_2C_6H_5$				1.088	1.088	1.088	1.412	1.409	1.408	1.449	1.901					
$PH_2C_6H_5$/6-31G**				1.086	1.086	1.086	1.402	1.395	1.396	1.425	1.855					
$[RhCl_2(C_6H_5)(PH_2CHCH_2)_2]$	1.088	1.088	1.348	1.084	1.088	1.087	1.413	1.411	1.407	1.428	1.864	2.031	2.406	2.441	2.828	3.691

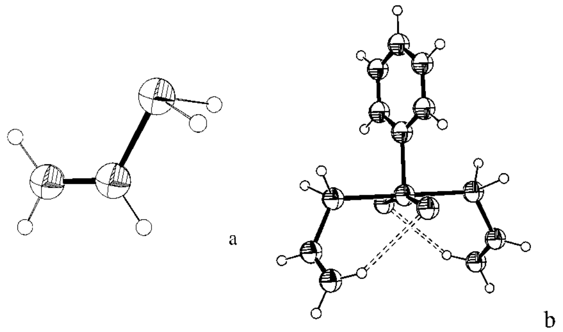

Figure 2. Drawings of selected molecules optimized at the DFT-B3LYP/LANL2DZ level: (a) PH_2CHCH_2; (b) $[RhCl_2(Ph)(PH_2CHCH_2)_2]$.

At this point, a question arises as to the cause of the short Rh−H and Cl−H intramolecular contacts. The relationships between H atoms and Rh and Cl atoms can be due to agostic Rh···H−C interactions, to Cl···H−C hydrogen bonds, to intramolecular steric interactions within the PPh_3 ligands, or eventually to a combination of two or three of these contributions. To shed some light on the matter, we carried out the density functional analysis that is discussed below.

Density Functional Analysis. The computed molecules and selected bond distances are listed in Table 4. Selected optimized molecules are represented in Figure 2. The comparison between the computed bond distances at the B3LYP/LANL2DZ and B3LYP/6-31G** levels for $C_2H_3^-$, C_2H_4, $C_6H_5^-$, C_6H_6, $PH_2(CHCH_2)$, and $PH_2(C_6H_5)$ shows that the values relevant to the corresponding H−C vectors are practically equal. In the case of the C−C vectors, the largest difference between the two levels of theory is that relevant to the $C_2H_3^-$ anion (0.031 Å). The values computed without any polarization function (LANL2DZ) are in all the cases higher than those obtained using the 6-31G** basis set. The computed H−P and C−P bond distances using the LANL2DZ basis set are 0.024 and 0.045 Å larger than those from 6-31G**. Therefore, the analysis shows that the B3LYP/LANL2DZ level of computation is sufficient for the purpose of reproducing the ligand moieties of the complex molecule. The starting structure for $[RhCl_2(Ph)(PH_2CHCH_2)_2]$ was based on the X-ray structure of **2**. In other words, the geometry for the $RhCl_2(C_6H_5)P_2$ moiety was exactly the same as that at the solid state. The starting orientation of the P−CH═CH_2 groups of the model ligand was exactly like that of the P−CH═CH− groups proximal to the Rh and Cl atoms in the structure of **2**.

The comparison between the computed model molecule $[RhCl_2(Ph)(PH_2CHCH_2)_2]$ and the experimental structure of **2** has interesting findings. The computed C−Rh bond distance (2.031 Å) is in excellent agreement with the experimental value (2.014(5) Å). The computed P−Rh distance (2.406 Å) is in good agreement with the experimental value (2.364(1) Å). The computed Rh−P−C bond angle is 117.7°, much larger than the corresponding value found for **2**. Very interestingly, the shortest Rh···H contact distance for the optimized structure is 3.691 Å (found 2.911(2) Å) and the shortest Cl···H contact distance is 2.828 Å (found 2.72(1) Å). (It has to be noted that a good agreement exists also between the computed and experimental (Rh−Ph)H···Cl contact distances, 2.663 and 2.591 Å, respectively.) In other words the $-CHCH_2$ groups rotate away from Rh, around the P−C vector and toward Cl. This observation excludes the existence of any Rh···H agostic interaction or it says that Cl···H intramolecular H-bonds prevail. Therefore, intramolecular steric repulsion can force one of the phenyl rings of the PPh_3 ligand toward the metal center in molecule **2**. It has to be noted that the significance of steric repulsion in weak agostic interactions was very recently shown for Ir(III) complexes.[6]

In conclusion, this work presents a new efficient synthetic route to stable organometallic compounds which can serve as starting materials for several preparative strategies. The removal of three $SbPh_3$ groups from $[RhCl_2(Ph)(SbPh_3)_3]$ by reaction with PPh_3 produces a coordinatively and electronically unsaturated compound because of the larger hindrance of PPh_3 as compared to $SbPh_3$ and because of the presence of a stable and highly trans-influencing Rh−C bond.

The molecular orbital investigation showed that agostic Rh···H−C interactions are not present or, at best, are weaker than Cl···H−C interactions and if they exist, they are probably assisted by steric repulsion within the bulky ligand in the structure of **2**.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of $[RhCl_2(Ph)(PPh_3)_2]$ and tables listing detailed crystallographic data, atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, and the atomic positional parameters of the selected optimized structure at the DFT-B3LYP/LANL2DZ level. This material is available free of charge via the Internet at http://pubs.acs.org.

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