reoxidation to the parent cation $[\mathrm{Rh_2}(\mu\text{-}\eta^2\text{-}\mathrm{C_2}\text{-}t\text{-}\mathrm{Bu})(\mathrm{CO})_2(\mu\text{-dppm})_2]^+$ with a comcomitant color change from blue to red.[31] The reoxidation is clean, no other products being discernible. We have been able to eliminate the possibility that the vinylidene complex **6** undergoes oxidation by functioning as a hydride donor to adventitious water. Whether in wet or dry degassed $\mathrm{CH_2Cl_2}$, **6** remains intact until sufficient dry dioxygen is admitted, after which the oxidation proceeds smoothly and rapidly. We are currently attempting to determine the stoichiometry of the oxidation as well as identifying the nature of the dioxygen reduction products.

To us, the most intriguing aspect of this oxidation process concerns whether the interaction of **6** with dioxygen occurs initially at one or both metal centers or whether dioxygen attack occurs directly at the ligand, possibly through some form of electron-transfer process. Our attempts to discern the exact nature of this initial interaction are ongoing.

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**Registry No. 1**, 94294-51-6; **2**, 94323-95-2; **3**, 94294-53-8; **4**, 94294-55-0; **5**, 94294-57-2; **6**, 94294-58-3; **7**, 94294-59-4; **8**, 94294-60-7; $[\mathrm{Rh_2}(\mu\text{-}\eta^2\text{-}\mathrm{C_2Bu}\text{-}t)(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-dppm})_2]\mathrm{ClO_4}$, 94294-62-9; $[\mathrm{Rh_2}(\mu\text{-}\eta^2\text{-}\mathrm{C_2Ph})(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-dppm})_2]\mathrm{ClO_4}$, 94294-64-1; $[\mathrm{Rh_2}(\mu\text{-}\eta^2\text{-}\mathrm{C_2H})(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-dppm})_2]\mathrm{ClO_4}$, 94294-66-3; $[\mathrm{Rh_2}(\mu\text{-}\eta^2\text{-}\mathrm{C_2Bu}\text{-}t)(\mu\text{-}\mathrm{SO_2})(\mathrm{CO})_2(\mu\text{-dppm})_2]\mathrm{ClO_4}$, 94323-97-4; $[\mathrm{Rh_2}(\mu\text{-}\eta^2\text{-}\mathrm{C_2Ph})(\mu\text{-}\mathrm{SO_2})(\mathrm{CO})_2(\mu\text{-dppm})_2]\mathrm{ClO_4}$, 94323-99-6; $[\mathrm{Rh_2}(\mu\text{-}\eta^2\text{-}\mathrm{C_2H})(\mu\text{-}\mathrm{SO_2})(\mathrm{CO})_2(\mu\text{-dppm})_2]\mathrm{ClO_4}$, 94324-01-3; $[\mathrm{Rh_2}(\mu\text{-}\eta^2\text{-}\mathrm{C_2Bu}\text{-}t)(\mathrm{CO})_2(\mu\text{-dppm})_2]^+$, 94294-50-5; $[\mathrm{Rh_2}(\mu\text{-}\mathrm{O_2CCH_3})(\mathrm{CO})_2(\mu\text{-dppm})_2]\mathrm{ClO_4}$, 93646-75-4; $[\mathrm{Rh_2}(\mu\text{-}\mathrm{O_2CCF_3})(\mathrm{CO})_2(\mu\text{-dppm})_2]\mathrm{ClO_4}$, 93646-77-6; $t\text{-}\mathrm{BuC_2H}$, 917-92-0; $\mathrm{PhC_2H}$, 536-74-3; $\mathrm{HC_2H}$, 74-86-2.

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[31] In the $\nu$(CO) region of the infrared, this transformation is characterized by the gradual but complete disappearance of bands at 1943 and 1918 with the concomitant growth of bands at 2022 (w), 1996, and 1982 $\mathrm{cm^{-1}}$ over a period of ca. 30 min. Further monitoring up to 24 h shows no further changes.

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# A Stable 16-Electron Rhodium(III) Rhodacarborane Derived from an Intermediate Containing an Agostic Hydrogen Atom. Molecular Structure of *closo*-3-($\eta^3$-$\mathrm{C_8H_{13}}$)-1,2-$(\mathrm{CH_3})_2$-3,1,2-$\mathrm{RhC_2B_9H_9}$

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*Summary:* Protonation of [PPN][*closo*-3,3-($\eta^4$-1,5-cyclooctadiene)-1,2-$(\mathrm{CH_3})_2$-3,1,2-$\mathrm{RhC_2B_9H_9}$] with trifluoroacetic acid in dichloromethane at −73 °C results in the formation of an unstable intermediate that exhibits an agostic hydrogen interaction and that rearranges at 7 °C to produce an unusually stable 16-electron rhodium(III) metallacarborane, *closo*-3-($\eta^3$-$\mathrm{C_8H_{13}}$)-1,2-$(\mathrm{CH_3})_2$-3,1,2-$\mathrm{RhC_2B_9H_9}$, which, as determined from an X-ray crystal structure study, is not stabilized via any apparent M–H–C interactions.

The importance of the formation of transient 16-electron metal species in organometallic catalytic reactions has been widely recognized for a great many years, and attention has recently focused upon the ability of such unsaturated transition metal species to activate aliphatic C–H bonds of both coordinated and uncoordinated organic moieties.[1] There have now been several reported examples of stable 16-electron transition-metal complexes containing organic ligands whose stability has been attributed to a unique mode of interaction between the metal center and a proximal C–H bond of the bound ligand; the C–H bond shares its $\sigma$ electrons with the metal to provide a two-electron, three-center M–H–C interaction, thus providing the metal with a formal 18-electron configuration.[2] We wish to report here the formation of a surprisingly stable, 16-electron rhodium(III) ($\eta^3$-cyclooctenyl)rhodacarborane species that is unusual in that, unlike other electron-deficient $\eta^3$-cycloalkenyl organotransition-metal complexes,[2] it exhibits no apparent distortion of the cyclooctenyl or carborane ligands due to M–H–C interactions, yet its formation occurs via an intermediate that appears to contain such an M–H–C interaction. We also wish to report evidence which indicates that the stability of the ($\eta^3$-cyclooctenyl)rhodacarborane appears to be due to the substituents on the carbon atoms of the carborane ligand.

Protonation in vacuo of a dichloromethane solution of the (1,5-cyclooctadiene)rhodacarborane anion [*closo*-3,3-($\eta^4$-1,5-cyclooctadiene)-1,2-$(\mathrm{CH_3})_2$-3,1,2-$\mathrm{RhC_2B_9H_9}]^-$ (**1**)[3] using 2 equiv of trifluoroacetic acid at −73 °C was found to result in the formation of a thermally unstable intermediate, **1a**, which exhibits broad resonances in the 200-MHz $^1$H FT NMR spectrum at 3.99, 2.95, 2.31, 2.08, and −3.94 ppm. The unusual resonance at −3.94 ppm was found to represent a single proton via integration. Due to the broadness of the signals, combined with a lack of response to decoupling, it appears that this unstable species is fluxional in solution. By comparison of the $^1$H NMR spectrum for **1a** with that of complex **1**,[4] the resonances at 3.99, 2.31, and 2.08 ppm can be attributed to vinyl, methylene, and carboranyl methyl protons, respectively, and based upon chemical shift, the resonance at 2.95 ppm appears to be representative of aliphatic protons. However, the broad upfield resonance observed at −3.94 ppm was not readily identifiable. In order to determine the nature of this unique proton, we chose to examine potential sites of interaction between complex **1** and the acid source.

Since a chemical shift of −3.94 ppm is not unusual for a hydrogen involved in a bridging B–H–B bonding interaction, the possibility that the protonation of **1** occurs at the carborane ligand to produce an exo-nido species[5] containing a B–H–B bridging bond was considered. Examination of this protonation reaction via low-temperature 127-MHz $^{11}\mathrm{B}\{^1\mathrm{H}\}$ FT NMR spectroscopy ruled out this possibility by revealing only resonances due to an apparently symmetric (six resonances) *closo*-metallacarborane species and displaying no signals due to boron atoms involved in either B–H–B or M–H–B bonding interactions.[6]

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[1] Janowicz, A. H.; Bergman, R. *J. Am. Chem. Soc.* **1983**, *105*, 3929 and references therein.

[2] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395 and references therein.

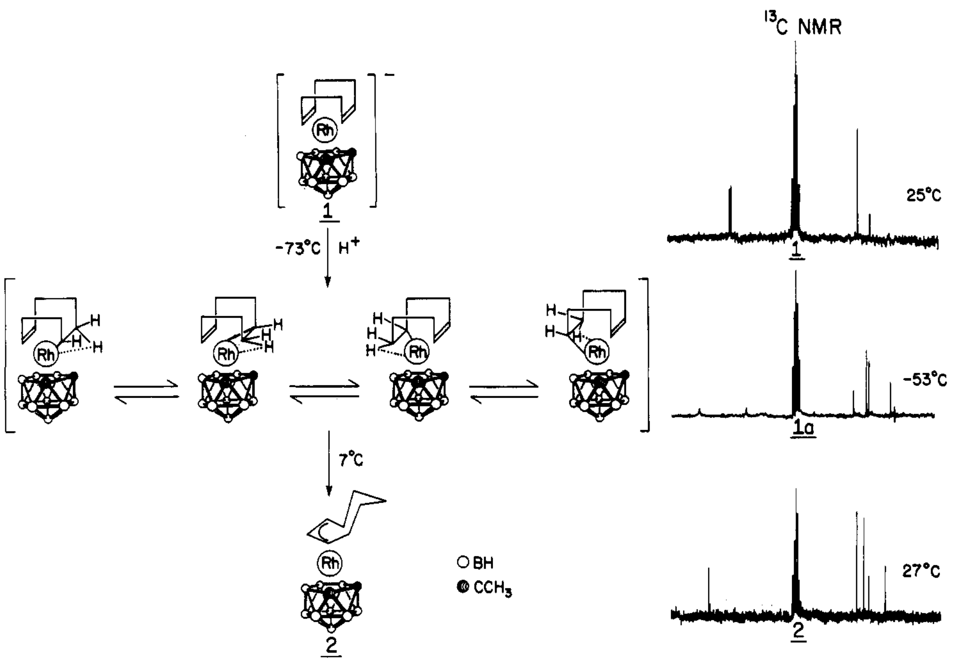
[3] Analytically pure complex **1** was prepared by reaction of the disubstituted monoanion Cs[*nido*-7,8-$(\mathrm{CH_3})_2$-7,8-$\mathrm{C_2B_9H_{10}}$] with 4 equiv of sodium isopropoxide and 1 equiv of $[\mathrm{Rh(1,5\text{-}C_8H_{12})Cl}]_2$ in 2-propanol, followed by precipitation of the $\mathrm{PPN^+}$ salt by addition of (PPN)Cl.

[4] **1**: $^1$H NMR ($\mathrm{CD_2Cl_2}$, 25 °C, $\delta$) 3.95 (s, br, 4 H, vinylic CH), 2.38 (m, br, 8 H, methylene CH), 2.08 (s, 6 H, carboranyl methyl CH).

[5] Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2979.

0276-7333/85/2304-0426\$01.50/0

**Scheme I**



The upfield $^1$H NMR chemical shift of the unique proton in **1a** might also be attributed to an interaction with the rhodium atom. However, the possible identity of this proton as a metal hydride was also ruled out. It was found that the deuteration of **1** using $CF_3CO_2D$ resulted in no observable reduction of the upfield proton resonance at −3.94 ppm in the $^1$H NMR spectrum, indicating that protonation must occur at the COD ligand. Additionally, the resonance at −3.94 ppm is located unusually downfield for a typical rhodacarborane hydride species.[7] Finally, the $^{13}C\{^1H\}$ NMR spectrum of **1a**,[8] shown in Scheme I, indicates that protonation of **1** results in the disappearance of the olefinic resonances of the COD ligand at 76.5 and 76.2 ppm found in complex **1**,[9] with the corresponding formation of two new aliphatic carbon resonances at 29.9 and 21.3 ppm. This spectrum conclusively demonstrates that protonation occurs at the olefinic carbon atoms and consequently rules out the formation of a (COD)-rhodacarborane hydride species.

The upfield shift of the unique proton in **1a** thus probably best represents an agostic hydrogen involving the interaction of a hydrogen atom on the protonated COD ligand with the rhodium center via a two-electron, three-center M–H–C bond. This bonding interaction would be formed following the protonation of one olefinic bond of complex **1** as shown in Scheme I. Due to the broadness of the $^1$H NMR spectral signals of complex **1a**, combined with the apparent symmetry of the $^1$H, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra of this complex, it also appears that this intermediate is fluxional in solution, even at −73 °C, and subsequently appears symmetrical on the NMR time scale. This fluxionality can be accounted for by a series of extremely rapid 1,2- and 1,4-hydrogen shifts involving the agostic hydrogen as illustrated in Scheme I (the disappearance of both olefinic carbon resonances in the $^{13}C\{^1H\}$ NMR spectrum of **1a** implies that this fluxionality must involve all four olefinic carbon atoms).

As further support for the proposed agostic hydrogen interaction in **1a**, the protonation of two analogous (1,5-cyclooctadiene)rhodacarborane anions [*closo*-3,3-($\eta^4$-1,5-cyclooctadiene)-1-($C_6H_5$)-3,1,2-$RhC_2B_9H_{10}$]$^-$ (**3**) and [*closo*-3,3-($\eta^4$-1,5-cyclooctadiene)-3,1,2-$RhC_2B_9H_{11}$]$^-$ (**4**)[10] was carried out in both dichloromethane and acetonitrile solvents at low temperature. In dichloromethane, both of the corresponding protonation intermediates **3a** and **4a**, respectively, exhibited upfield proton resonances (−4.5 ppm) analogous to that observed in complex **1a**, but in contrast, the protonation intermediates derived from **3** and **4** in acetonitrile (**3b** and **4b**, respectively) no longer exhibited any resonances upfield of 1 ppm. These results are consistent with the presence of agostic hydrogen interactions in complexes **1a**, **3a**, and **4a**, since an agostic hydrogen would be expected to be displaced by a stronger electron donor, such as acetonitrile in forming **3b** and **4b**.[2]

It is interesting to note that the protonation of **1** to produce **1a** differs significantly from the protonation of an analogous, isoelectronic system, $C_5H_5Rh$(1,5-cyclooctadiene), as reported by Lewis and coworkers.[11] These researchers found that protonation of $C_5H_5Rh$(1,5-cyclooctadiene) at room temperature in neat $CF_3CO_2H$ initially results in the formation of an asymmetric rhodium species containing an unconjugated $\sigma$–$\pi$ cyclooctenyl ligand. However, no M–H–C interactions are observed via $^1$H NMR.

Allowing the dichloromethane solution of **1a** to warm to 7 °C results in the quantitative formation of the title compound *closo*-3-($\eta^3$-$C_8H_{13}$)-1,2-$(CH_3)_2$-3,1,2-$RhC_2B_9H_9$, **2**, via a series of rapid 1,2-hydrogen shifts. The $^1$H NMR of complex **2**[12] is consistent with its formulation: a quartet (5.86 ppm) and a triplet (4.69 ppm) are observed for the

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[6] **1a**: $^{11}B\{^1H\}$ NMR ($CD_2Cl_2$, −23 °C, $\delta$) −0.02 (1), −0.99 (1), −2.65 (2), −8.40(2), −11.40 (1), −4.14 (2).

[7] Rhodacarborane hydride resonances generally are observed in the region of $\delta$ −6 to −10.

[8] **1a**: $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, −53 °C, $\delta$) 34.17, 29.93, 28.98 (2 C, carboranyl methyl C), 21.34.

[9] **1**: $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 25 °C, $\delta$) 76.46 (2 C, olefinic C), 76.22 (2 C, olefinic C), 32.62 (4 C, methylene C), 28.35 (2 C, carboranyl methyl C).

[10] Analytically pure samples of **3** and **4** were prepared in the same manner as for complex **1**, using the monoanions Cs[*nido*-7-($C_6H_5$)-7,8-$C_2B_9H_{11}$] and Cs[*nido*-7,8-$C_2B_9H_{12}$], respectively.

[11] Evans, J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1971**, 1252. Evans, J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 510.

[12] **2**: $^1$H NMR ($CD_2Cl_2$, 25 °C, $\delta$) 5.85 (q, $J$ = 8 Hz, 2 H, allylic CH), 4.68 (t, $J$ = 8 Hz, 1 H, allylic CH), 2.54 (m, br, 2 H, methylene CH), 2.20 (s, 6 H, carboranyl methyl CH), 1.80 (m, br, 4 H, methylene CH), 1.43 (m, br, 2 H, methylene CH), 1.08 (m, br, 2 H, methylene CH).

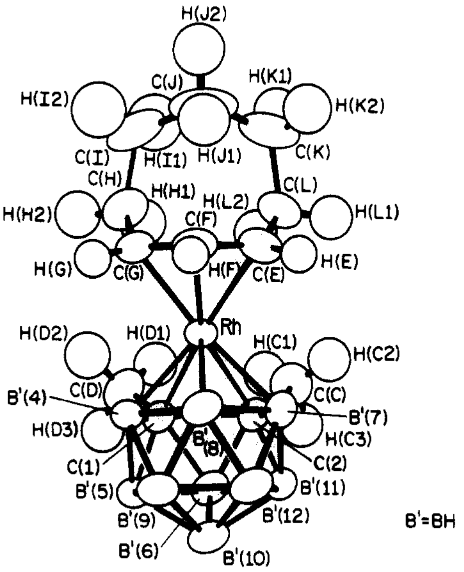

**Figure 1.** ORTEP projection of *closo*-3-($\eta^3$-$C_8H_{13}$)-1,2-$(CH_3)_2$-3,1,2-$RhC_2B_9H_9$ (2).

two types of allylic protons and a sharp singlet (2.20 ppm) representing the two carboranyl methyl groups indicates the symmetric nature of the $\eta^3$-cyclooctenyl rhodium moiety.[13] There are no proton resonances upfield of $\delta$ 1.0, which indicates that there are no M–H–C interactions involving the ligand and the metal. The X-ray crystal structure of complex 2 (obtained by using a single red crystal grown from vapor diffusion of pentane into a dichloromethane solution of complex 2) supports these data. It should also be noted that Lewis' $C_5H_5Rh(COD)$ protonation intermediate rearranges via 1,2-hydrogen shifts very slowly and the $\eta^3$-cyclooctenyl rhodium cyclopentadienide product is only formed in small amounts after several hours.[11]

The structure of 2 was determined by single-crystal X-ray diffraction.[14] An ORTEP projection of complex 2 is shown in Figure 1. The rhodium atom is symmetrically bound to all five atoms of the $C_2B_3$ pentagonal face at distances ranging from 2.12 to 2.20 Å, and the carborane cage exhibits expected bond angles and distances. The carboranyl methyl groups are likewise found at normal positions, precluding the possibility for any Rh–$\beta$(C–H) interactions.[15] The $\eta^3$-cyclooctenyl ligand is symmetrically bound to the rhodium atom via the three allylic carbon atoms C(E), C(F), and C(G). The hydrogen atoms on these allylic carbons and on the adjacent carbons C(H) and C(L) were among those located on the difference map, and they did not exhibit any interaction with the rhodium center.[16] It can thus be concluded that there are no M–H–C interactions present in complex 2, and therefore this species indeed represents a stable 16-electron rhodium(III) rhodacarborane.

These results are surprising in light of the thermal stability and resistance to air oxidation of complex 2. The influence of the carboranyl substituents of 2 on this stability was examined by comparing the thermal rearrangement products of **3a** and **4a** with 2. Warming dichloromethane solutions of **3a** and **4a** in vacuo to 7 °C results in the formation of the corresponding $\eta^3$-cyclooctenyl products *closo*-3-($\eta^3$-$C_8H_{13}$)-1-$(C_6H_5)$-3,1,2-$RhC_2B_9H_{10}$ (**5**) and *closo*-3-($\eta^3$-$C_8H_{13}$)-3,1,2-$RhC_2B_9H_{11}$ (**6**), but these 16-electron species are thermally unstable and decompose rapidly upon formation. Interestingly, the low-temperature intermediates **3b** and **4b** in acetonitrile produce analogous $\eta^3$-cyclooctenyl products as acetonitrile adducts at 7 °C (*closo*-3-($\eta^3$-$C_8H_{13}$)-3-$(CH_3CN)$-1-$(C_6H_5)$-3,1,2-$RhC_2B_9H_{10}$ (**7**) and *closo*-3-($\eta^3$-$C_8H_{13}$)-3-$(CH_3CN)$-3,1,2-$RhC_2B_9H_{11}$ (**8**), respectively), and these 18-electron complexes are stable for extended periods of time. The stability of the 16-electron rhodium(III) complex 2 thus appears to be a sensitive function of the methyl substituents of the carborane ligand.

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**Supplementary Material Available:** Tables of atomic positions, thermal parameters, bond lengths and angles, and structure factor data for 2 (22 pages). Ordering information is given on any current masthead page.

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(13) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151.

(14) **Crystal data:** $C_{12}H_{28}RhB_9$, $M_r$ = 372.560, monoclinic, space group $P2_1/c$; $a$ = 7.303 (3) Å, $b$ = 13.768 (4) Å, $c$ = 17.943 (4) Å, $\beta$ = 94.96 (3)°, $V$ = 1797.4 (9) Å$^3$, $Z$ = 4, $D$(calcd) = 1.38 g cm$^{-3}$; $R$ = 0.030 for 2562 unique reflections having $I > 3\sigma(I)$ (Syntex P$\bar{1}$ four-circle diffractometer, Mo K$\alpha$ radiation, $\lambda$ = 0.7107 Å). The structure of complex 2 was solved by the heavy-atom method. All hydrogen atoms were either located on the difference map or generated at reasonable positions. In the final least-squares cycle based on $F$, 247 parameters were refined, including positional and anisotropic thermal parameters for 1 Rh, 9 B, and 12 C (those of the cyclooctenyl ligand and those of the icosahedron), and positional parameters for 16 of the 28 hydrogen atoms. The final least-squares cycle converged at $R$ = 0.030 and $R_w$ = 0.044; $w = {}^1/\sigma^2(F_o)$. The goodness-of-fit was 1.624 as defined by $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ with $N_o$ (number of observations) = 2562 and $N_v$ (number of variables) = 247. On the final difference map, the highest peak was 0.53 e Å$^{-3}$.

(15) (a) Angles Rh–C(1)–C(D) and Rh–C(2)–C(C) are both normal (110.53° and 110.03°, respectively), which indicates an absence of any $\beta$(C–H) interactions.[15b] (b) Carmona, E.; Sanchez, L.; Poveda, M. L.; Marin, J. M.; Atwood, J. L.; Rogers, R. D. *J. Chem. Soc., Chem. Commun.* **1983**, 161.

(16) Significant rhodium–hydrogen distances (Å): Rh–H(E) = 2.81 (7), Rh–H(F) = 2.68 (6), Rh–H(G) = 2.74 (6), Rh–H(H1) = 2.76 (9), Rh–H(H2) = 3.46 (8), Rh–H(L1) = 3.48 (7), Rh–H(L2) = 2.59 (7).