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The Enigmatic Nature of Rh^{I}Cl(cyclopentadienone) Complexes: Dimers, Trimers, and Tetramers

Dalit Rechavi, Rosario Scopelliti, and Kay Severin*

Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

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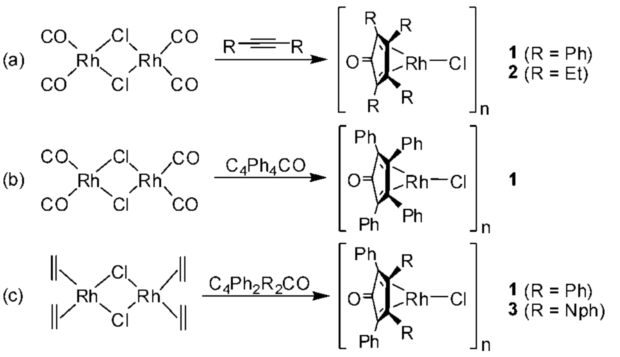
Although Rh^{I}Cl(cyclopentadienone) complexes have been known for more than 40 years, structural data were so far not available. We have investigated the complexes [RhCl(tetraphenylcyclopentadienone)]$_n$ (**1**), [RhCl(2,5-diethyl-3,4-diphenylcyclopentadienone)]$_n$ (**4**), and [RhCl(phencyclone)]$_n$ (**5**) by single-crystal X-ray crystallography. Contrary to what has been observed for simple olefin complexes such as [RhCl(1,5-cyclooctadiene)]$_2$, they crystallize as trimers (**4** and **5**) or tetramers (**1**), in which the RhCl(cyclopentadienone) fragments are aggregated via Rh−(μ-Cl) and Rh−(μ-OC) bonds. When crystallized from acetonitrile, however, complex **4** was found to form the dimeric adduct [Rh(μ-Cl)(CH$_3$CN)(2,5-diethyl-3,4-diphenylcyclopentadienone)]$_2$ (**6**), whereas the phencyclone complex gave an ionic structure (**7**) resulting from chloride transfer. In solution, all complexes form solvent- and concentration-dependent dynamic equilibria.

Introduction

In 1965, Maitlis and McVey reported that the reaction of [RhCl(CO)$_2$]$_2$ with diphenyl- or diethylacetylene resulted in the formation of the cyclopentadienone complexes **1** and **2** (Scheme 1a).[1] Alternatively, complex **1** was obtained from [RhCl(CO)$_2$]$_2$ and tetraphenylcyclopentadienone (Scheme 1b).[1,2] White et al. found that the carbonyl complex [RhCl(CO)$_2$]$_2$ can be replaced by the ethylene dimer [RhCl(C$_2$H$_4$)$_2$]$_2$ without compromising the yield.[3] The latter route was also used to prepare the naphthyl complex **3** (Scheme 1c).[4] Recently, the first catalytic applications of Rh^I(cyclopentadienone) complexes were reported. Heterobimetallic complexes derived from **1** and **3** were successfully employed as catalysts in Oppenauer-type oxidations of primary and secondary alcohols under mild conditions.[5] Furthermore, a tetranuclear complex derived from **1** was shown to act as a very potent catalyst for atom transfer radical addition reactions.[6]

In view of the fact that Rh^{I}Cl(cyclopentadienone) complexes have been known for more than 40 years and that catalytic applications have been developed, it is surprising that the precise nature of these compounds is still not clear. The tetraphenylcyclopentadienone complex **1** was proposed to be a dimer on the basis of molecular weight measurements in chloroform solution.[1] A dimeric, chloro-bridged structure with square-planar Rh^I centers is in line with what has been reported for other Rh^I olefin complexes such as [RhCl(1,5-cyclooctadiene)]$_2$[7] or [RhCl(4-methylpenta-1,3-diene)$_2$]$_2$.[8] For the tetraethylcyclopentadienone complex **2**, on the other hand, molecular weight measurements suggested the presence of a trimeric aggregate, but a proposal for its structure was not made.[1] Below we describe for the first time crystallographic analyses of Rh^{I}Cl(cyclopentadienone) complexes. It is shown that these compounds can aggregate via Rh−(μ-Cl) and Rh−(μ-OC) bonds to give trimeric and tetrameric structures in the solid state. In solution, they form solvent- and concentration-dependent dynamic equilibria.

Scheme 1



Results and Discussion

For our studies, we prepared the new complexes **4** and **5** along with the known compound **1**. The synthesis of **4** and **5** was accomplished following White's methodology by heating a mixture of [RhCl(C$_2$H$_4$)$_2$]$_2$ with 2,5-diethyl-3,4-diphenylcyclopentadienone or phencyclone in toluene at 80 °C (Scheme 2). The products precipitated from solution and were purified by recrystallization. The complexes were not air- or moisture-sensitive and could be handled and kept in ambient atmosphere after their preparation.

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* Corresponding author. E-mail: kay.severin@epfl.ch.

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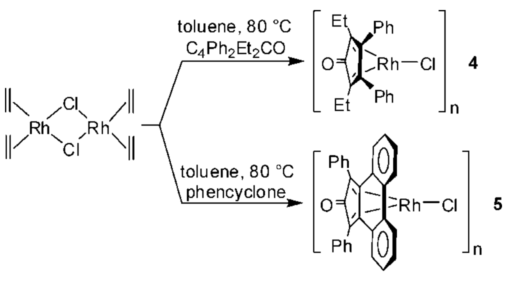
10.1021/om800671x CCC: $40.75

Scheme 2



During the synthesis of complex **5**, we observed a white crystalline material that precipitated from the mother liquor after filtration of the main product. This compound turned out to be the Diels−Alder adduct of phencyclone and ethylene (originating from the rhodium complex).[9]

Single crystals of the complexes **1**, **4**, and **5** were obtained by crystallization from dichloromethane. Both the 2,5-diethyl-3,4-diphenylcyclopentadienone complex **4** and the phencyclone complex **5** were found to display a trimeric structure in the solid state (Figures 1 and 2). The overall geometry of **4** and **5** is similar and can be described as a chloro-bridged (cyclopentadienone)Rh(μ-Cl)$_2$Rh(cyclopentadienone) dimer to which a third RhCl(cyclopentadienone) fragment is connected via a Rh−(μ-Cl) bond and a Rh−(μ-OC) bond. As a consequence, we observe two Rh^I centers with a square-planar geometry and one electronically saturated Rh^I center with a pentacoordinated geometry. The key structural parameters of this core are summarized in Table 1.

For complex **4**, the Rh−Cl bonds of the square-planar metals Rh1 and Rh3 are shorter than those to the electronically saturated Rh2. For complex **5**, on the other hand, the Rh−Cl bonds of Rh1 and Rh3 are similar to those of Rh2. The Rh(μ-Cl)$_2$Rh unit in complex **4** is bent with a fold angle around the Cl1···Cl2 axis of 27.25(12)°. For complex **5**, a fold angle of 54.04(6)° is observed. Such a pronounced deviation from planarity is not unusual for complexes in which two different metal fragments are connected by two chloro-bridges.[10]

At 2.323 (**4**) and 2.356 Å (**5**), the average Rh−C(carbonyl) distances are significantly longer than the average Rh−C(olefin) bonds of 2.101 (**4**) and 2.124 Å (**5**). This indicates that the carbonyl C atoms are not involved in bonding. Accordingly, the carbonyl groups are slightly folded away from the planes defined by the olefinic carbon atoms (dihedral angles: 2−14°).

For both complexes, a number of secondary CH···Cl interactions are observed. Complex **4** displays CH···Cl hydrogen bonds between Cl1 and H40 and between Cl3 and H55. At 2.68 and 2.87 Å, respectively, these H···Cl distances are shorter than the sum of the van der Waals radii for Cl and H (2.95 Å).[11] Similar H···Cl hydrogen bonds are found for two phenyl H atoms and bridging chloro atoms of complex **5** (Cl2···H23 = 2.79, Cl3···H29 = 2.83, Cl3···H81 = 2.80, Cl3···H48 = 2.68 Å).

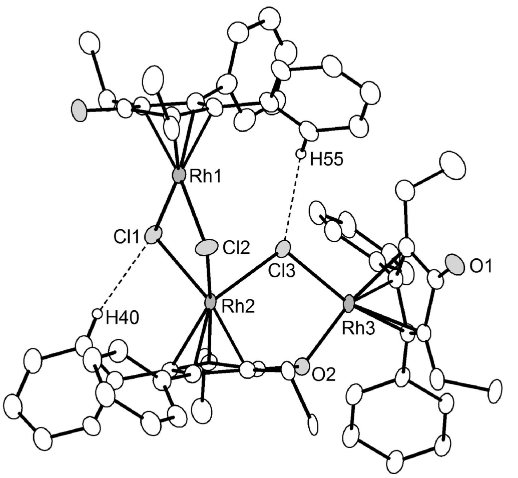


Figure 1. Molecular structure of complex **4** in the crystal. The crystallized solvent molecule (CH_2Cl_2) and the hydrogen atoms, except those involved in secondary interactions, are not shown for clarity. The thermal ellipsoids are set at 50% probability.

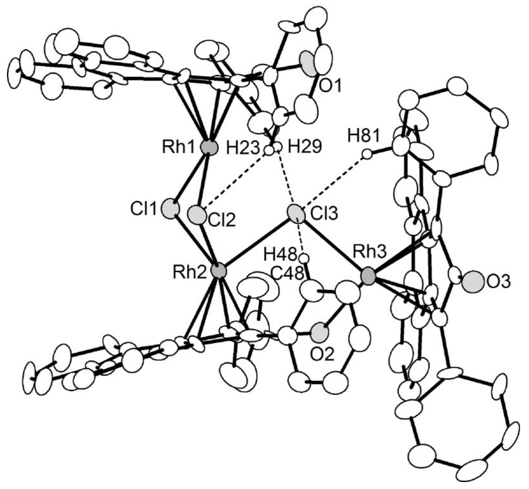
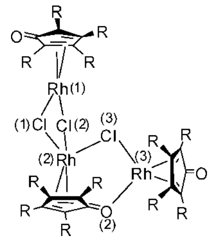


Figure 2. Molecular structure of complex **5** in the crystal. The hydrogen atoms, except those involved in secondary interactions, are not shown for clarity. The thermal ellipsoids are set at 50% probability.

Table 1. Selected Distances (Å) and Angles (deg) for the Complexes 4 and 5



	4	**5**
Rh3−O2	2.071(9)	2.109(5)
Rh3−Cl3	2.349(4)	2.498(2)
Rh3−C(olefin)[a]	2.092	2.119
Rh2−Cl3	2.495(4)	2.509(2)
Rh2−Cl2	2.442(4)	2.444(2)
Rh2−Cl1	2.456(4)	2.418(2)
Rh2−C(olefin)[a]	2.108	2.129
Rh1−Cl2	2.356(4)	2.429(2)
Rh1−Cl1	2.356(4)	2.430(2)
Rh1−C(olefin)[a]	2.103	2.125
O2−Rh3−Cl3	89.1(3)	86.40(15)
Cl2−Rh2−Cl3	89.47(14)	86.12(7)
Cl1−Rh2−Cl3	86.64(13)	87.29(7)
Cl1−Rh2−Cl2	81.63(13)	84.69(7)
Cl2−Rh1−Cl1	85.57(13)	84.75(7)

[a] Averaged values for the four Rh−C(olefin) bonds are given.

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(9) Diels−Alder additions to phencyclone are documented in the literature. See: (a) Yasuda, M.; Harano, K.; Kanematsu, K. *J. Org. Chem.* **1981**, *46*, 3836–3841. (b) Marshall, K.; Rothchild, R. *Spectrosc. Lett.* **2004**, *37*, 469–492. (c) Sklyut, O.; Prip, R.; Azar, N.; Callahan, R.; Rothchild, R. *Spectrosc. Lett.* **2004**, *37*, 493–516.

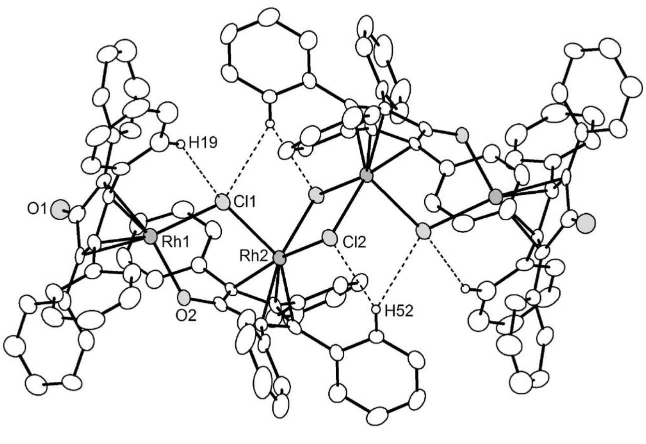
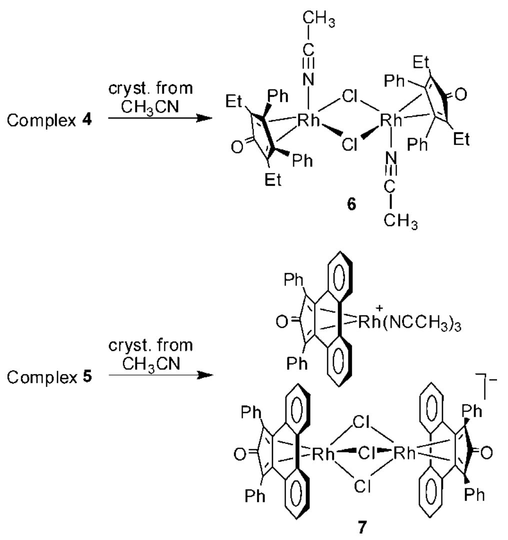


Figure 3. Molecular structure of complex **1** in the crystal. The hydrogen atoms, except those involved in secondary interactions, are not shown for clarity. The thermal ellipsoids are set at 50% probability.

The tetraphenylcyclopentadienone complex **1** has repeatedly been described as a chloro-bridged dimer.[1−6] Surprisingly, however, the solid state structure of single crystals of **1** revealed a tetranuclear complex (Figure 3). The structure of **1** contains a central (cyclopentadienone)Rh(μ-Cl)$_2$Rh(cyclopentadienone) dimer, which is connected to two terminal RhCl(cyclopentadienone) fragments via Rh−(μ-Cl) and Rh−(μ-OC) bonds. The two central Rh^{I} atoms have thus a pentacoordinated geometry, whereas the terminal Rh^{I} atoms have a square-planar geometry. The tetramer has a crystallographic inversion center. Consequently, the Rh(μ-Cl)Rh ring is flat. Similar to what has been observed for crystals of complex **4**, the Rh−Cl bond to the unsaturated metal center Rh1 (2.3769(14) Å) is shorter than the Rh−Cl bonds of the pentacoordinated Rh2 (Rh2−Cl$_{av}$ = 2.462 Å). Overall, the structure is stabilized by six H···Cl hydrogen bonds, all of which are formed with ortho-hydrogens of the phenyl rings (Cl1···H19 = 2.68, Cl1···H52 = 2.80, Cl2···H52 = 2.82 Å).

A driving force for the formation of tri- and tetranuclear aggregates is the apparent tendency of (cyclopentadienone)Rh^{I} to form five-coordinated 18 e^{-} complexes instead of square-planar 16 e^{-} complexes, which are typically observed for Rh^{I} compounds.[12] This prompted us to investigate whether different structures are obtained when RhCl(cyclopentadienone) complexes are crystallized from a coordinating solvent such as acetonitrile. Suitable single crystals were obtained for the complexes **4** and **5**. Whereas complex **4** crystallized from acetonitrile as a chloro-bridged dimer with two coordinated acetonitrile ligands (**6**), complex **5** was transformed into the ionic compound **7** containing the cation [(phencyclone)Rh(CH$_3$CN)$_3$]$^+$ and the dimeric anion [(phencyclone)Rh(μ-Cl)$_3$Rh(phencyclone)]$^-$ (Scheme 3).

Scheme 3



The molecular structure of complex **6** is depicted in Figure 4. Due to the coordination of the two acetonitrile molecules, both Rh^{I} atoms display a pentacoordinated geometry. The Rh(μ-Cl)$_2$Rh unit is nearly planar with a fold angle along the Cl···Cl axis of 2.82(4)°. The Rh−Cl bonds of **6** (Rh1−Cl1 = 2.4541(15), Rh1−Cl2 = 2.5142(13), Rh2−Cl2 = 2.4707(15), Rh2−Cl1 = 2.5347(13) Å) are similar in length to those of the pentacoordinated Rh centers of the complexes **1**, **4**, and **5**. The Rh−N bonds (Rh1−N1 = 2.141(5), Rh2−N2 = 2.143(5) Å) are longer than what has been reported for the pentacoordinated Rh(I)-acetonitrile complex Rh(Tp*i*Pr)(cyclooctene)(CH$_3$CN) (1.968(6) Å).[13] As was observed for **1**, **4**, and **5**, there are hydrogen bonds between the ortho-hydrogens of the phenyl rings and the bridging chloro ligands (Cl1···H19 = 2.74, Cl2···H40 = 2.65 Å).

The structure of the acetonitrile adduct **7** is markedly different from that of **6** (Figure 5). Instead of electronic saturation of the Rh^{I} centers by coordination of acetonitrile ligands, chloride transfer has resulted in a dimeric, triply bridged [(phencyclone)Rh(μ-Cl)$_3$Rh(phencyclone)]$^-$ anion and a [(phencyclone)Rh(CH$_3$CN)$_3$]$^+$ cation.

At 2.472 Å, the average Rh−Cl bond length of the anion [(phencyclone)Rh(μ-Cl)$_3$Rh(phencyclone)]$^-$ is slightly shorter than what has been observed for the neutral, mixed-valence complex [(tetraphenylcyclopentadienone)Rh(μ-Cl)$_3$RhCp*] (2.486 Å)[4] but longer than those of the cation [Cp*Rh(μ-Cl)$_3$RhCp*]$^+$

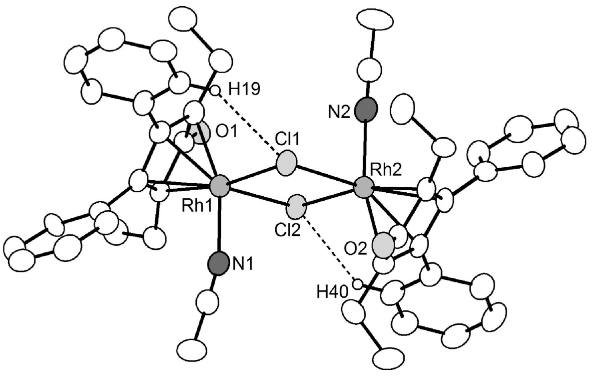


Figure 4. Molecular structure of complex **6** in the crystal. The hydrogen atoms, except those involved in secondary interactions, are not shown for clarity. The thermal ellipsoids are set at 50% probability.

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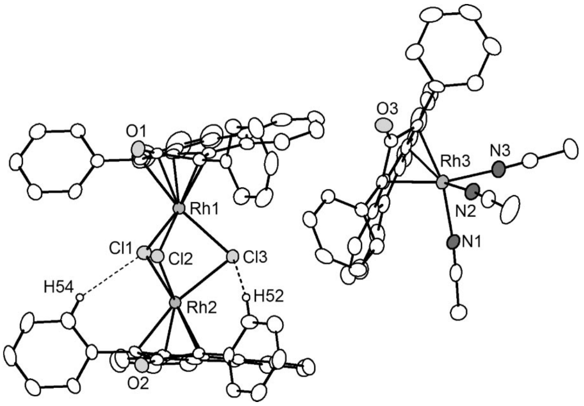

Figure 5. Molecular structure of complex **7** in the crystal. The cocrystallized solvent molecules (3 CH_3CN) and the hydrogen atoms, except those involved in secondary interactions, are not shown for clarity. The thermal ellipsoids are set at 50% probability.

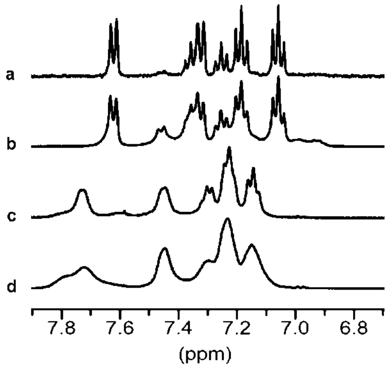

Figure 6. Aromatic region of the ^1H NMR spectra of complex **1** in CD_2Cl_2 at 0.2 mM (a), in CD_2Cl_2 at 7.1 mM (b), in CD_3CN at 0.9 mM (c), and in CD_3CN at 8.0 mM (d).

(2.459[14] or 2.458[15] Å). As for **1**, **4**, and **5**, intramolecular hydrogen bonds between the ortho-hydrogens of the phenyl rings and the bridging chloro ligands are observed (Cl1···H54 = 2.75, Cl3···H52 = 2.69 Å).

To obtain additional information about the structures in solution, we have recorded NMR spectra at variable concentrations in different solvents. First, we investigated the known complex **1**, for which molecular weight measurements in chloroform had predicted a dimeric structure. In CD_2Cl_2 at a concentration of $[RhCl(C_4Ph_4CO)] = 0.2$ mM, we observed a single set of signals in the ^1H NMR spectrum (Figure 6a). When the concentration was increased to 7.1 mM, however, peaks of a new species were clearly visible (Figure 6b). The relative amount of this new species was determined by integration of selected signals for a series of ^1H NMR spectra at concentrations between 2.38 and 14.15 mM of Rh. These data could best be fitted to a dimer−trimer equilibrium. We therefore conclude that complex **1** exists in dichloromethane at low concentrations predominantly as a dimer, but at concentrations >1 mM there are significant amounts of a trimeric species. The latter has likely a structure that is similar to what has been observed for complexes **4** and **5** in the solid state. The fact that complex **1** crystallizes as a tetramer is evidence that higher aggregates than trimers are also possible. We assume that the tetramer is formed at the very high concentrations that are present during the crystallization process.

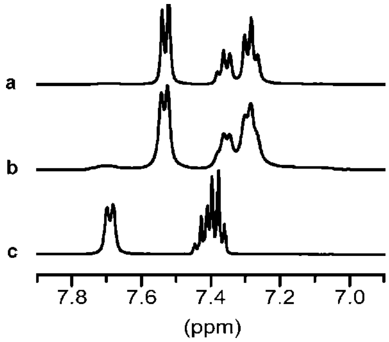

Figure 7. Aromatic region of the ^1H NMR spectra of complex **4** in CD_2Cl_2 at 8.7 mM (a), in CD_2Cl_2 at 51.4 mM (b), and in CD_3CN at 15.9 mM (c).

The ^1H NMR spectra of complex **1** in CD_3CN were very broad and showed strong concentration dependence (Figure 6c,d). This suggests that dynamic aggregates of different size are present in solution. These aggregates may consist of chloro-bridged dimers such as **6** or salts such as **7**, but the quality of the NMR data impeded further conclusions.

For CD_2Cl_2 solutions of the new complex **4**, the situation was similar to what has been observed for **1**. At low concentrations, a single set of signals was observed, but a second complex was formed at higher concentrations, accompanied by peak broadening (Figure 7a,b). In CD_3CN, however, complex **4** gave very distinct spectra compared to what had been observed for complex **1**. The ^1H NMR spectra showed a single set of sharp signals, and the spectra were not concentration dependent (Figure 7c). From the NMR spectra, it can be concluded that a single species is present in acetonitrile. This is likely the dimer **6**, which was characterized crystallographically.

The naphthyl-substituted complex **3** and the phencyclone complex **5** were only sparingly soluble in dichloromethane and acetonitrile. NMR studies with variable concentrations were therefore not performed.

Conclusion

Ru^{II} complexes with cyclopentadienone ligands have been used extensively as catalysts for organic transformations.[16] The chemistry of Rh^I complexes with cyclopentadienone ligands is less developed, but recent results demonstrate that interesting catalytic transformations can be observed as well.[5,6] The present study was performed to obtain more information about the key starting materials for this type of chemistry. Although Rh^I-Cl(cyclopentadienone) complexes have been known since 1965, structural data were so far not available. We demonstrate that from noncoordinating solvents these complexes can crystallize as trimers or tetramers, in which the Rh^ICl(cyclopentadienone) fragments aggregate via Rh−(μ-Cl) and Rh−(μ-OC) bonds. In CD_2Cl_2 solution, they form dynamic equilibria with dimers. A driving force for the formation of higher aggregates is the

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Table 2. Crystallographic Data for the Complexes 1, 4, and 5

	1 × 6 CH_2Cl_2	**4** × CH_2Cl_2	**5** × 2 CH_2Cl_2
empirical formula	$C_{122}H_{92}Cl_{16}O_4Rh_4$	$C_{64}H_{62}Cl_5O_3Rh_3$	$C_{89}H_{58}Cl_7O_3Rh_3$
mol weight/g mol^{-1}	2600.80	1365.12	1732.23
cryst size/mm^3	0.27 × 0.24 × 0.18	0.10 × 0.07 × 0.06	0.13 × 0.12 × 0.06
cryst syst	monoclinic	triclinic	monoclinic
space group	$C2/c$	$P\bar{1}$	$P2_1/n$
a/Å	24.3100(7)	12.1598(9)	11.6158(6)
b/Å	17.7651(6)	13.6567(12)	24.7527(13)
c/Å	27.4450(8)	20.194(2)	24.7806(12)
α/deg	90	90.772(8)	90
β/deg	105.813(3)	97.825(8)	91.395(5)
γ/deg	90	111.784(8)	90
volume/Å^3	11404.1(6)	3077.5(5)	7122.9(6)
Z	4	2	4
density/g cm^{-3}	1.515	1.473	1.615
temperature/K	140(2)	140(2)	140(2)
absorp coeff/mm^{-1}	0.996	1.055	1.004
θ range/deg	2.85 to 25.03	2.69 to 22.99	2.89 to 25.03
index ranges	$-28 \rightarrow 28, -21 \rightarrow 20, -32 \rightarrow 32$	$-12 \rightarrow 11, -13 \rightarrow 15, -22 \rightarrow 22$	$-12 \rightarrow 12, -29 \rightarrow 29, -29 \rightarrow 29$
reflns collected	33 663	15 687	42 508
data/restraints/params	9716/6/666	7583/438/676	11 749/18/919
goodness-of-fit on F^2	1.028	0.842	0.818
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0506$, $wR_2 = 0.1178$	$R_1 = 0.0696$, $wR_2 = 0.1460$	$R_1 = 0.0571$, $wR_2 = 0.0842$
R indices (all data)	$R_1 = 0.0913$, $wR_2 = 0.1178$	$R_1 = 0.1569$, $wR_2 = 0.1667$	$R_1 = 0.1664$, $wR_2 = 0.1035$

Table 3. Crystallographic Data for the Complexes 6 and 7

	6	**7** × 3 CH_3CN
empirical formula	$C_{46}H_{46}Cl_2N_2O_2Rh_2$	$C_{99}H_{72}Cl_3N_6O_3Rh_3$
mol weight/g mol^{-1}	935.57	1808.71
cryst size/mm^3	0.47 × 0.38 × 0.19	0.40 × 0.39 × 0.24
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a/Å	18.823(2)	11.7647(3)
b/Å	9.3966(17)	18.6753(7)
c/Å	23.578(5)	20.0806(6)
α/deg	90	69.319(3)
β/deg	95.544(14)	89.865(2)
γ/deg	90	81.665(3)
volume/Å^3	4150.7(12)	4078.3(2)
Z	4	2
density/g cm^{-3}	1.497	1.473
temperature/K	140(2)	140(2)
absorp coeff/mm^{-1}	0.963	0.755
θ range/deg	2.72 to 27.48	2.63 to 26.02
index ranges	$-24 \rightarrow 24, -12 \rightarrow 12, -30 \rightarrow 28$	$-14 \rightarrow 11, -23 \rightarrow 23, -24 \rightarrow 24$
reflns collected	32 350	36 729
data/restraints/params	9494/0/487	15 953/0/1033
goodness-of-fit on F^2	0.917	0.854
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0504$, $wR_2 = 0.1111$	$R_1 = 0.0354$, $wR_2 = 0.0565$
R indices (all data)	$R_1 = 0.1044$, $wR_2 = 0.1365$	$R1 = 0.0693$, $wR_2 = 0.0605$

tendency of the Rh^I centers to form electronically saturated 18 e^- complexes. This is reflected by the structures of the complexes **6** and **7**, which were obtained from the coordinating solvent acetonitrile. The high propensity of Rh^ICl(cyclopentadienone) complexes to form pentacoordinated, electronically saturated complexes via aggregation (as observed for **1**, **3**, and **4**), solvent addition (as observed for **6**), or chloride transfer (as observed for **7**) should be considered for future studies in this area.

Experimental Section

General Procedures. $[RhCl(C_2H_4)_2]_2$ was purchased from Acros and tetraphenylcyclopentadienone from Aldrich. Phencyclone was purchased from Alfa Aesar and was purified by crystallization from CH_2Cl_2/CH_3OH before use. 2,5-Diethyl-3,4-diphenylcyclopentadienone was purchased from Alfa Aesar and was purified by column chromatography before use. NMR spectra: Bruker Avance-DPX-400 spectrometer, protonated solvents as internal standards, δ in ppm, J in Hz. If integration ratios were not correct, a d1 = 10 s was used.

Complex 1. This complex was prepared by a modification of the method previously described.[3] Tetraphenylcyclopentadienone (0.7197 g, 1.872 mmol) and $[RhCl(C_2H_4)_2]_2$ (0.3025 g, 0.7800 mmol) were heated in toluene (30 mL) at 80 °C under nitrogen for 48 h. The solution was then concentrated on a rotary evaporator to ca. 5 mL and cooled to room temperature, and the resulting wine-red crystals were filtered from the solution and washed with pentane. The product was further purified by dissolving it in dichloromethane and precipitation with pentane (71%). IR: 1651, 1511, 1494 cm^{-1}. Concentration-dependent NMR experiments: the ratio between the peaks at 7.63 ppm (d) and at 7.46 ppm (br, d) was measured at 15 different concentrations between 2.38 and 14.15 mM of Rh. The results were fitted to several possible equilibrium cases (dimer−tetramer, dimer−trimer, trimer−tetramer, and trimer−monomer). The best fit was obtained for a dimer−trimer case, where K_{eq} was very little dependent on concentration ($R^2 = 0.226$) and stayed constant over the range of concentrations, with only 6.1% standard deviation. For the other cases, K_{eq} correlated linearly with the concentrations, with R^2 between 0.806 and 0.915.

Complex 4. 2,5-Diethyl-3,4-diphenylcyclopentadienone (0.3694 g, 1.281 mmol) and $[RhCl(C_2H_4)_2]_2$ (0.2070 g, 0.5337 mmol) were heated in toluene (21 mL) at 80 °C under nitrogen for 48 h. The toluene was then evaporated on a rotary evaporator, the solid was dissolved in a minimal amount of dichloromethane, pentane was added, and wine-red crystals were obtained upon prolonged chilling at −18 °C (87%). Single crystals for crystallography were obtained by slow evaporation of a solution of complex **4** in CH_2Cl_2. Anal. Calcd: C 59.10, H 4.72. Found: C 59.34, H 4.62. IR: 1639, 1507, 1498 cm^{-1}. Red crystals of complex **6** were obtained by slow evaporation of an acetonitrile solution of complex **4**. IR: 1646, 1501 (w) cm^{-1}.

Complex 5. Phencyclone (0.2449 g, 0.6404 mmol) and $[RhCl(C_2H_4)_2]_2$ (0.2669 g, 0.1035 mmol) were heated in toluene (10 mL) at 80 °C under nitrogen for 48 h. The toluene was then evaporated on a rotary evaporator, and the wine-red crystals were filtered off on a #4 glass sinter and washed with pentane. A second crop of crystals was obtained upon slow evaporation of the mother liquor (88%). Single crystals for crystallography were obtained by slow evaporation of a solution of complex **5** in CH_2Cl_2. Anal. Calcd for a trimer with one cocrystallized CH_2Cl_2: C 64.16, H 3.43. Found: C 64.03, H 3.44. IR: 1663, 1648, 1634, 1600, 1535, 1495 cm^{-1}. Orange-red crystals of complex **7** were obtained by slow evaporation of an acetonitrile solution of complex **5**. IR: 1618, 1599 cm^{-1}.

Phencyclone Diels−Alder Adduct with Ethylene. Transparent crystals of the ethylene Diels−Alder adduct of phencyclone were observed after slow evaporation of almost all the mother liquor of complex **4**. They were filtered off, and their structure was determined by single-crystal crystallography and by NMR. Yield: 31% (based on phencyclone, not optimized). ^{1}H NMR in CD_2Cl_2: δ 8.75 (1H, d, $J = 8.32$), 7.72 (1H, d, $J = 7.82$), 7.65 (1H, dt, $J_t = 7.46$, $J_d = 1$), 7.55 (1H, dt, $J_t = 7.34$, $J_d = 1.48$), 7.51 (1H, tt, $J = 7.34$, $J = 1.48$), 7.441 (1H, dt, $J_t = 7.585$, $J_d = 1.48$), 7.27 (1H, d, $J = 7.82$), 7.21 (1H, dt, $J_t = 7.34$, $J_d = 1.48$), 7.09 (1H, dd, $J = 8.31$, $J = 0.48$), 2.98 (1H, ddd, $J = 6.85$, $J = 4.16$, $J = 0.5$), 2.21 (1H, ddd, $J = 6.84$, $J = 4.17$, $J = 0.5$).

Crystallographic Investigations. The relevant details of the crystals, data collection, and structure refinement can be found in Tables 2 and 3. Diffraction data were collected using Mo Kα radiation on different equipment and at different temperatures: a four-circle kappa goniometer equipped with an Oxford Diffraction KM4 sapphire CCD (**1**, **4**, **5**, and **7**) or a Marresearch mar345 IPDS (**6**). Data were reduced by CrysAlis PRO 1.7.1.[17] Absorption correction was applied to all data sets using a semiempirical method.[18] All structures were refined using full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the "riding model" with $U_{iso} = aU_{eq}$ (where a is 1.5 for methyl hydrogen atoms and 1.2 for others). Structure refinement and geometrical calculations were carried out on all structures with SHELXTL.[19] Some restraints have been applied to the structures **1**, **2**, and **3**. In the case of **1**, a disordered CH_2Cl_2 was treated by means of DFIX (C−Cl distances), and EADP cards were applied to the displacement parameters of the chlorines. In the case of **2**, the crystal was very small and weak, and a SIMU card was applied to all light atoms (C, O) in order to have reasonable displacement parameters. In the case of **3**, some restraints (ISOR card) were applied to three carbon atoms (C2, C33, C82) that failed to behave anisotropically.

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Supporting Information Available: X-ray crystallographic file in CIF format is available free of charge via the Internet at http://pubs.acs.org.

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