Notes

Reactivity of Dinuclear Rhodium(I) Macrocycles Formed via the Weak-Link Approach

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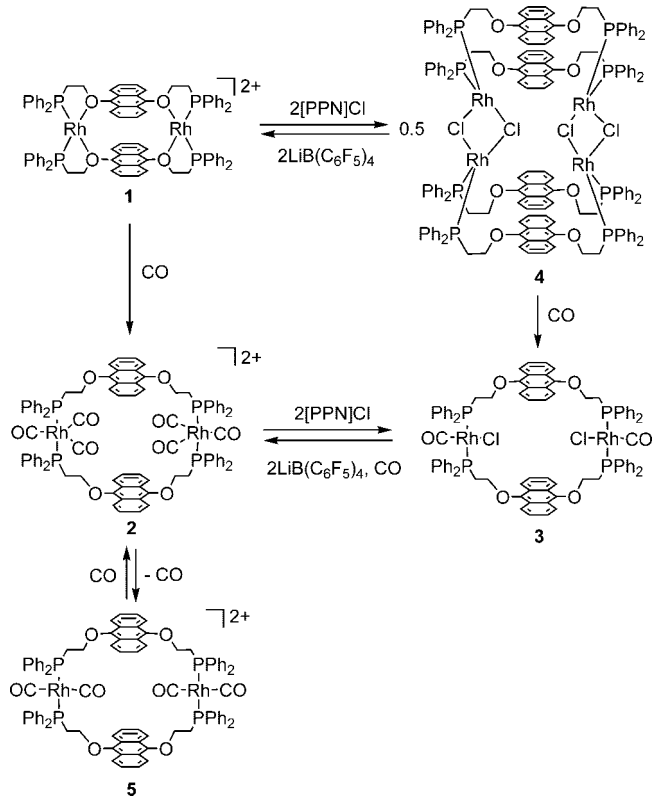
Summary: The reaction of a macrocyclic Rh(I) complex having hemilabile PO ligands with Cl⁻ results in Rh−O bond breakage and yields a Cl-bridged tetranuclear Rh(I) complex, which was characterized by a single-crystal X-ray diffraction study. Reactivity of the complex with CO and halide abstracting agents is described.

Recent developments in the field of supramolecular coordination chemistry have resulted in several new and efficient synthetic strategies for the preparation of two- and three-dimensional structures that possess well-defined shapes, chirality, and function.[1,2] Our group has been developing the weak-link approach (WLA) to provide reliable methods to construct supramolecular but structurally flexible coordination complexes.[1a,3] The WLA allows one to synthesize condensed multimetallic macrocycles with flexible hemilabile ligands that form both strong and weak coordination bonds with a metal center. When the condensed macrocycles are reacted with small molecules or elemental ions that selectively break the weak links, they can be switched between structures with different shapes and charges. These structurally tunable macrocycles have been utilized to realize a new class of allosteric enzyme mimics, which have led to novel amplification systems in chemical sensing.[4]

Scheme 1. Reactivity of the Dinuclear Rhodium(I) Macrocycles 1−5



The starting point for many of these systems is the binuclear Rh(I) complex **1**, assembled via phosphinoalkyl ether hemilabile ligands and a Rh(I) precursor (Scheme 1). One interesting class of structures includes those with bridging anthracene moieties.[5] These structures are fluorescent and allow one to probe the reactions that occur within the macrocycle. While it is well-established that the reactions of rigid condensed macrocycles such as **1** with CO leads to the formation of larger macrocycles with flexible structures **2**[3] and subsequent reactivity with Cl⁻ will lead to macrocycle **3**,[5] the direct reaction between condensed macrocycle **1** and Cl⁻ has not yet been investigated. The

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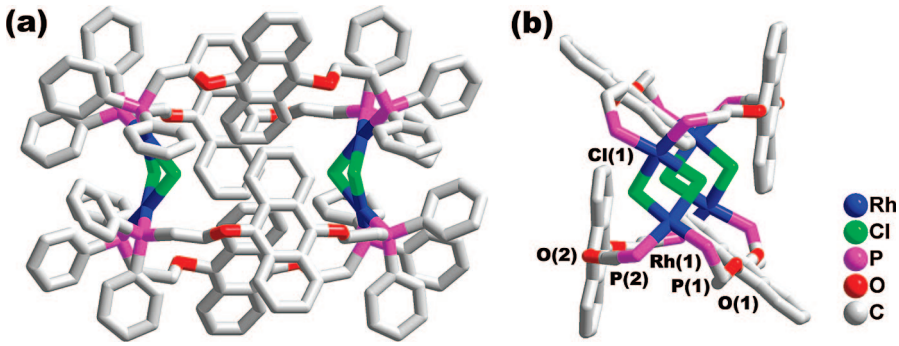


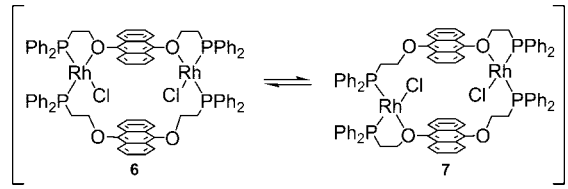
Figure 1. Stick representation for the crystal structure of **4**: (a) front view; (b)side view. Hydrogen atoms, solvent molecules (CH_2Cl_2), and phenyl groups on phosphine in the side view have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−P(1) = 2.214(2), Rh(1)−P(2) = 2.221(2), Rh(1)−Cl(1) = 2.400(2), Rh(1)−Cl(1)* = 2.4040(2); P(1)−Rh(1)−P(2) = 96.14(7), P(1)−Rh(1)−Cl(1) = 169.08(6), P(1)−Rh(1)−Cl(1)* = 89.29(6), P(2)−Rh(1)−Cl(1) = 94.53(7), P(2)−Rh(1)−Cl(1)* = 174.33(7), Cl(1)−Rh(1)−Cl(1)* = 79.99(7), Rh(1)−Cl(1)−Rh(1)* = 85.33(6).

Cl^- anion in this system plays an important role in structure regulation, since it can affect both macrocycle charge and overall structure. Herein, we report the preparation and characterization of the new tetranuclear Rh(I) complex **4**, formed from the reaction between **1** and Cl^-, and its reactivity with CO and halide abstracting agents.

Results and Discussion

The known condensed macrocycle **1** was synthesized from 9,10-bis(2-(diphenylphosphino)ethoxy)anthracene[3c] and a Rh(I) precursor according to literature methods.[5] Addition of 2 equiv of [PPN]Cl (PPN = $[Ph_3P{=}N{=}PPh_3]^+$) to a solution of the condensed macrocycle **1** results in a slight color change from red to orange and the eventual formation of the tetranuclear complex **4**. After 48 h, complex **4**, which is insoluble in CH_2Cl_2, THF, and diethyl ether, is collected as small crystals in the bottom of the reaction vessel (49% yield). A single-crystal X-ray diffraction study of one of these crystals reveals the Cl-bridged tetranuclear Rh(I) structure of **4** (Scheme 1 and Figure 1). The structure consists of two bridging $[Rh(\mu\text{-}Cl)]_2$ units and four flexible 9,10-bis(2-(diphenylphosphino)ethoxy)anthracene ligands. Each Rh(I) center exhibits a distorted-square-planar geometry with cis-Cl and cis-phosphine ligands. The anthracenes located diagonally from each other are parallel to each other, while the angle between the anthracenes that are not parallel is 56.3° (Figure 1b). Although the $[Rh(\mu\text{-}Cl)(PR_3)_2]_2$ (R = alkyl, aryl) motif is quite common,[6] it is rare to see a molecule with $[Rh(\mu\text{-}Cl)]_2$ units that are connected with flexible bidentate P ligands to form a tetranuclear Rh(I) macrocycle.[7] Because of the low solubility of compound **4**, its structure in solution could not be determined.

Scheme 2. Possible Intermediates en Route To Form 4



The reaction to form **4** from **1** and Cl^- was monitored by $^{31}P\{^1H\}$ NMR spectroscopy at low temperature. $^{31}P\{^1H\}$ NMR spectroscopy of the reaction mixture shows two well-resolved sets of resonances at 52.3 ppm (dd, J_{Rh-P} = 192, J_{P-P} = 48 Hz) and 35.1 ppm (dd, J_{Rh-P} = 190, J_{P-P} = 48 Hz) at −10 °C, which can be assigned to a phosphine of the chelated κ^2P,O ligand and the unchelated κ^1P,O ligand, respectively, on the basis of previous reports of model Rh−Cl complexes with κ^2P,S and κ^1P,O ligands.[8] The intermediate to form **4** is at least one of two possible isomeric structures (Scheme 2). On the basis of the spectroscopic data of this fleeting intermediate, it is impossible to differentiate the two possibilities. However, both possible intermediates, which may be in dynamic equilibrium with one another, contain weak Rh−O linkages and would be expected to lead to the same observed product **4** upon dimerization through the Cl ligands. The reaction to form **4** can be reversed simply by adding $LiB(C_6F_5)_4 \cdot Et_2O$ under sonication conditions. The sonication is important because of the low solubility of complex **4**.

Interestingly, when **4** is added to CD_2Cl_2 and sonicated in the presence of CO (1 atm), open neutral complex **3** forms in quantitative yield (Scheme 1). In this transformation, the π-acid CO displaces the bridging Cl groups of the tetranuclear complex to form the dinuclear complex **3**.[9] Addition of 2 equiv of $LiB(C_6F_5)_4 \cdot Et_2O$ to compound **3** in CD_2Cl_2 under CO (1 atm) results in the rapid formation of cationic complex **2**. Complex **2** is a known compound and was characterized on the basis of ^1H and $^{31}P\{^1H\}$ NMR, FTIR, and ESI MS and a comparison of that data with literature data. Complex **2** also can be made

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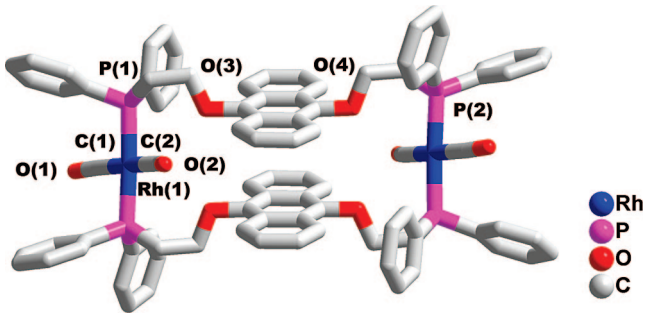

Figure 2. Stick representation for the crystal structure of **5**. Hydrogen atoms, counteranions, and solvent molecules (CH_2Cl_2) have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−P(1) = 2.3223(9), Rh(1)−P(2)* = 2.3517(9), Rh(1)−C(1) = 1.868(4), Rh(1)−C(2) = 1.958(3); P(1)−Rh(1)−P(2)* = 176.58(4), P(1)−Rh(1)−C(1) = 87.0(1), P(1)−Rh(1)−C(2) = 91.0(1), P(2)*−Rh(1)−C(1) = 92.6(1), P(2)*−Rh(1)−C(2) = 89.1(1), C(1)−Rh(1)−C(2) = 173.9(2).

directly from compound **1** via CO addition through literature procedures. Interestingly, bubbling N_2 through the solution of complex **2** results in loss of a single CO ligand at each Rh center and formation of the new complex **5** (Scheme 1). Low-temperature $^{31}P\{^1H\}$ NMR spectroscopy of the reaction mixture allows one to easily follow this transformation. As the single resonance for **2** (26.0 ppm, J_{Rh-P} = 72 Hz) rapidly disappears, a new resonance for **5** (14.9 ppm, J_{Rh-P} = 107 Hz) appears. In addition, the $^{31}P\{^1H\}$ NMR spectrum of complex **5** formed from ^{13}C-labeled CO shows a doublet of triplets, consistent with a complex with two rather than three CO ligands at each Rh center (J_{Rh-P} = 108 Hz and J_{P-C} = 16 Hz). The loss of one carbonyl ligand from each Rh(I) center is consistent with the reactivity observed for related monometallic Rh(I) complexes.[10]

The solid-state structure of complex **5** was confirmed by a single-crystal X-ray diffraction study (Figure 2). The Rh(I) center exhibits a distorted-square-planar geometry with trans-CO and trans-P coordination environments. The two anthracenyl rings in **5** are parallel with each other with a 3.79 Å separation, consistent with a $\pi-\pi$ stacking interaction.[11] Similar $\pi-\pi$ stacking interactions have been observed in other metallamacrocycles,[12] but one sees a much larger distance (e.g., >6 Å) in analogous binuclear Rh(I) macrocycles, where there are three CO ligands per trigonal-bipyramidal Rh center.[3] The extra CO ligand may inhibit the $\pi-\pi$ stacking interactions observed for the complexes with square-planar Rh centers and only two CO ligands.

Experimental Section

General Methods and Instrument Details. All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques or an inert-atmosphere glovebox unless otherwise noted. Diethyl ether, CH_2Cl_2, and hexanes were purified by published methods.[13] All solvents were deoxygenated with nitrogen prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc. and used as received. $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) was purchased from Strem Chemicals and used as received. 9,10-Bis(2-(diphenylphosphino)ethoxy)-anthracene)[3c] and $[(\mu_2$-9,10-bis(2-(diphenylphosphino)ethoxy)-anthracene$)_2Rh_2Cl_2(CO)_2]$ (**3**)[5] were synthesized according to literature methods. All other chemicals were used as received from Aldrich Chemical Co. ^1H NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer and referenced relative to residual proton resonances in CD_2Cl_2. $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 300 MHz FT-NMR spectrometer at 121.53 MHz and referenced relative to an external 85% H_3PO_4 standard. All chemical shifts are reported in ppm. FT-IR spectra were obtained using a Thermo Nicolet Nexus 670 FT-IR. Electrospray ionization mass spectra (ESI-MS) were recorded on a Micromas Quatro II triple quadrupole mass spectrometer. Elemental analyses were performed by Quantitative Technologies Inc. Whitehouse, NJ.

Synthetic Methods. Synthesis of $[(\kappa^2:\mu_2:\kappa^2$-9,10-bis(2-(diphenylphosphino)ethoxy)anthracene$)_2Rh_2][B(C_6F_5)_4]_2$ (1). Complex **1** was synthesized in a manner similar to that used for $[(\kappa^2:\mu^2:\kappa^2$-9,10-bis(2-(diphenylphosphino)ethoxy)anthracene$)_2Rh_2][B(3,5-C_6H_3(CF_3)_2)_4]_2$[5]using 9,10-bis(2-(diphenylphosphino)ethoxy)-anthracene) (31.8 mg, 0.050 mmol), $[RhCl(cod)]_2$ (12.6 mg, 0.025 mmol), and $LiB(C_6F_5)_4(Et_2O)$ (38.0 mg, 0.050 mmol) in 92% yield (65.2 mg). ^1H NMR (CD_2Cl_2): δ 8.11 (m, $C_{14}H_8$, 4H), 7.73 (m, PC_6H_5, 8H), 7.52 (m, PC_6H_5, 4H), 7.43 (m, PC_6H_5, 8H), 7.32 (m, $C_{14}H_8$, 4H), 3.97 (m, OCH_2, 4H), 2.88 (m, CH_2PPh_2, 4H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 62.5 (d, J_{Rh-P} = 213 Hz). ESI-MS (*m/z*): $[M - 2B(C_6F_5)_4]^{2+}$ 738.1 (calcd for $[C_{84}H_{72}O_4P_4Rh_2]^{2+}$ 737.6). Anal. Calcd for $C_{132}H_{72}B_2F_{40}O_4P_4Rh_2$: C, 55.96; H, 2.56. Found: C, 56.08; H, 2.55.

Formation of $[(\mu_2$-9,10-bis(2-(diphenylphosphino)ethoxy)-anthracene$)_2Rh_2(CO)_6][B(C_6F_5)_4]_2$ (2). An NMR tube was loaded with a CD_2Cl_2 solution (0.5 mL) of $[(\kappa^2:\mu_2:\kappa^2$-9,10-bis(2-(diphenylphosphino)ethoxy)anthracene$)_2Rh_2][B(C_6F_5)_4]_2$ (**1**; 14.2 mg, 5 μmol) and charged with CO (1 atm). The resulting solution changed from red to yellow. ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data of the solution are consistent with the quantitative formation of $[(\mu_2$-9,10-bis(2-(diphenylphosphino)ethoxy)anthracene$)_2Rh_2(CO)_6][B(C_6F_5)_4]_2$ (**2**). ^1H NMR (CD_2Cl_2, −76 °C): δ .8–7.0 (m, PC_6H_5 and $C_{14}H_8$, 24H), 6.92 (m, $C_{14}H_8$, 4H), 3.96 (br, OCH_2, 4H), 3.56 (br, CH_2PPh_2, 4H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −76 °C): δ 6.0 (d, J_{Rh-P} = 72 Hz). ESI-MS (*m/z*): $[M - 4CO - 2B(C_6F_5)_4]^{2+}$ 766.0 (calcd for $[C_{86}H_{72}O_6P_4Rh_2]^{2+}$ 765.6). FTIR (CH_2Cl_2): ν_{CO} 2039 cm^{-1}(s). The lability of the CO ligands made it impossible to obtain an elemental analysis for the complex.

Synthesis of $[(\mu_2$-9,10-bis(2-(diphenylphosphino)ethoxy)-anthracene$)_2Rh_2Cl_2]_2$ (4). [PPN]Cl (22.8 mg, 40 μmol) in CH_2Cl_2 (3 mL) was added to a solution of $[(\kappa^2:\mu_2:\kappa^2$-9,10-bis(2-(diphenylphosphino)ethoxy)anthracene$)_2Rh_2][B(C_6F_5)_4]_2$ (**1**; 56.8 mg, 20 μmol) in CH_2Cl_2 (3 mL). After 48 h, the crystals were collected and washed with CH_2Cl_2 (3 mL × 2). The red crystals of **4** were obtained in 49% yield (15.3 mg). Due to its low solubility, the product was characterized only by single-crystal X-ray diffraction and elemental analysis. Anal. Calcd for $C_{168}H_{144}Cl_4O_8P_8Rh_4 \cdot 4CH_2Cl_2$: C, 60.20; H, 4.46. Found: C, 60.14; H, 4.19. Crystals of $\mathbf{4} \cdot 7CH_2Cl_2$ suitable for X-ray diffraction analysis were directly obtained by the reaction in CH_2Cl_2. Although the structure determined from the crystallographic data has seven CH_2Cl_2 solvent molecules, the elemental analysis shows four solvated CH_2Cl_2 molecules for the compound. This difference is likely due to the drying of the sample under reduced pressure prior to EA.

Synthesis of $[(\mu_2$-9,10-bis(2-(diphenylphosphino)ethoxy)-anthracene$)_2Rh_2(CO)_4][B(C_6F_5)_4]_2$ (5). A CD_2Cl_2 solution of $[(\mu_2$-9,10-bis(2-(diphenylphosphino)ethoxy)anthracene$)_2Rh_2(CO)_6]$-$[B(C_6F_5)_4]_2$ (**2**; 5 μmol) was bubbled with N_2 gas for several minutes. The solution changed from yellow to pale orange. ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data show the quantitative formation

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Table 1. Crystallographic Data

	$\mathbf{4}\cdot 7CH_2Cl_2$	$\mathbf{5}\cdot 4CH_2Cl_2$
empirical formula	$C_{175}H_{162}Cl_{18}O_8P_8Rh_4$	$C_{140}H_{80}B_2Cl_8F_{40}O_8P_4Rh_2$
formula wt	3690.55	3284.96
temp (K)	153(2)	293(2)
wavelength (Å)	0.710 73	0.710 73
cryst syst, space group	monoclinic, *C*2/*m*	triclinic, $P\bar{1}$
a (Å)	24.845(3)	11.439(1)
b (Å)	25.051(3)	16.356(2)
c (Å)	16.168(2)	18.746(2)
α (deg)		90.305(2)
β (deg)	127.172(2)	100.456(2)
γ (deg)		105.572(2)
V (Å^3)	8018.0(16)	3317.3(7)
Z, calcd density (Mg/m^3)	2, 1.529	1, 1.644
abs coeff (mm^{-1})	0.844	0.574
F(000)	3764	1640
cryst size (mm)	0.13 × 0.13 × 0.04	0.28 × 0.15 × 0.10
θ range for data collecn (deg)	1.31−28.83	1.11−28.81
no. of collected/unique rflns	37 143/9951 (*R*(int) = 0.0941)	30 627/15 378 (*R*(int) = 0.0921)
abs cor	numerical	
max, min transmission	0.9761, 0.9122	0.9531, 0.8687
refinement method	full-matrix least squares on F^2	
no. of data/restraints/params	16 168/0/949	15 378/2/893
goodness of fit on F^2	1.078	0.818
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0887, wR2 = 0.2296	R1 = 0.0546, wR2 = 0.1294
R indices (all data)	R1 = 0.1444, wR2 = 0.2500	R1 = 0.0930, wR2 = 0.1444
largest diff peak, hole (e/Å^{-3})	1.373, −0.814	1.246, −0.814

of [(μ_2-9,10-bis(2-(diphenylphosphino)ethoxy)anthracene)$_2$Rh$_2$(CO)$_4$]-[B(C_6F_5)$_4$]$_2$ (**5**). ^{1}H NMR (CD_2Cl_2, −76 °C): δ 7.8–7.0 (m, PC$_6H_5$ and C$_{14}H_8$, 24H), 6.92 (m, C$_{14}H_8$, 4H), 3.96 (br, OCH_2, 4H), 3.56 (br, CH_2PPh$_2$, 4H). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, −76 °C): δ 14.9 (d, J_{Rh-P} = 107 Hz). ESI-MS (*m*/*z*): [M − 6CO − 2B(C_6F_5)$_4$]$^{2+}$ 737.0 (calcd for [$C_{84}H_{72}O_4P_4Rh_2$]$^{2+}$ 737.1). FTIR (KBr): ν_{CO} 2039 (s), 2005 cm^{-1} (w). Anal. Calcd for $C_{136}H_{72}B_2F_{40}O_8P_4Rh_2$: C, 55.46; H, 2.46. Found: C, 55.77; H, 2.70. Crystals of $\mathbf{5}\cdot 4CH_2Cl_2$, suitable for single crystal X-ray diffraction analysis, were obtained by recrystallization of the product from 2:1 CH_2Cl_2−hexane. Although the structure determined from the crystallographic study has four CH_2Cl_2 solvent molecules, the elemental analysis shows no CH_2Cl_2 in the compound. This difference is likely due to the drying of the sample under reduced pressure prior to EA.

X-ray Crystallography. Crystals of $\mathbf{4}\cdot 7CH_2Cl_2$ and $\mathbf{5}\cdot 4CH_2Cl_2$, suitable for single-crystal X-ray diffraction studies, were mounted on a glass fiber using oil (Infineum V8512). All measurements were made on a CCD area detector with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation on a Bruker SMART-1000 diffractometer. The raw data collected were processed to produce conventional intensity data by the program SAINT. The intensity data were corrected for Lorenz and polarization effects. Absorption correction was also applied using the numerical method. The structures were solved by direct methods provided by the program package SHELXTL. All of the non-hydrogen atoms were refined anisotropically. CH_2Cl_2 solvent molecules are highly disordered and were treated by SQUEEZE.[14] The electron count from the SQUEEZE model converged to electron 353 count/cell ($\mathbf{4}\cdot 7CH_2Cl_2$) and 72 count/cell ($\mathbf{5}\cdot 4CH_2Cl_2$). Hydrogen atom positions were calculated and included in the final cycle of refinement (see Table 1 for crystallographic data).

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Supporting Information Available: CIF files giving X-ray crystallographic data for the structure determinations of $\mathbf{4}\cdot 7CH_2Cl_2$ and $\mathbf{5}\cdot 4CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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