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Incorporation of Three Phenylacetylene Molecules into an $RhMo_2S_4$ Trinuclear Sulfido Cluster Core, Forming Bridging Metallathiacyclobutene and Dithiolene Moieties

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Summary: The trinuclear sulfido cluster $[\{Rh(PPh_3)_2\}(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{Mo(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$ (***2a***) *reacted readily with three* $PhC{\equiv}CH$ *molecules to afford* $[\{Rh(SCPh{=}CH)Cl(PPh_3)\}\{Mo(SCPh{=}CH)(S_2CNEt_2)\}\{Mo(S_2C_2HPh)(S_2CNEt_2)\}]$*, the structure of which, as well as that of the* $PMePh_2$ *analogue of* ***2a****, have been determined by X-ray analyses.*

Introduction

Transition-metal−sulfur clusters have been studied extensively for the past few decades[1] because of their relevance to the active sites of the sulfur-containing metalloenzymes[2] and industrial catalysts.[3] However, in contrast to much effort that has been devoted to the syntheses of a number of metal−sulfur aggregates, their reactivities toward organic molecules have still been poorly investigated. Activation of various substrate molecules at the multimetallic sites in these clusters might be of particular importance, since it possibly leads to the exploitation of the unique stoichiometric and catalytic transformations of certain substrates that are unattainable by using conventional mononuclear complexes.

Recent studies in this laboratory[4−11] have focused on the pursuit of the rational synthetic pathways toward metal−sulfur clusters with the cores of desired composition and structure. Emphasis has been put on the clusters containing noble metals which can promote many stoichiometric and catalytic reactions, since the reactivities of these metal centers embedded in this metal−sulfur aggregate are of particular interest but still poorly explored. In this context, we have already prepared the new cubane-type $PdMo_3S_4$ cluster and clarified the details of the stereoselective addition of alcohols and carboxylic acids to the activated alkynes which proceeds at the Pd site of this cluster.[4a,12]

Stimulated by these findings, further studies have been undertaken to synthesize a new class of mixed metal−sulfido clusters, which include a series of trinuclear MM'_2S_4 and tetranuclear $M_2M'_2S_4$ clusters (M = Pr, Pt, Rh, Ir; M′ = Mo, W) obtained from the reactions of sulfido-bridged dinuclear complexes $M'_2S_2(\mu_2\text{-}S)_2(S_2CNEt_2)_2$ (M′ = Mo (**1a**), W) with corresponding noble metal complexes.[11] We have examined subsequently the reactions of these clusters with a range of alkynes and found that $[\{Rh(PPh_3)_2\}(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{Mo(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$ (**2a**), prepared from **1a** and $[RhCl(PPh_3)_3]$, reacts with $PhC{\equiv}CH$ to form the $RhMo_2$ cluster $[\{Rh(SCPh{=}CH)Cl(PPh_3)\}\{Mo(SCPh{=}CH)(S_2CNEt_2)\}\{Mo(S_2C_2HPh)(S_2CNEt_2)\}]$ (**3**), having a unique core generated by incorporation of three $PhC{\equiv}CH$ molecules. To compare the X-ray structure of **3** with that of the parent cluster **2a**, preparation of a high-quality single crystal of the latter was also attempted, but this turned out to be unsuccessful. Hence, the $PMePh_2$ analogue $[\{Rh(PMePh_2)_2\}(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{Mo(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$ (**2b**) has been synthesized and fully characterized. Results of these studies are summarized below.

Results and Discussion

When the trinuclear sulfido cluster **2a** was treated with an excess amount of $PhC{\equiv}CH$ (10 equiv) in CH_2-

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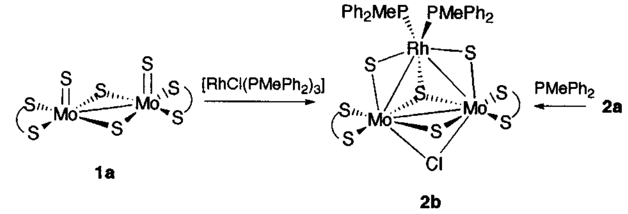
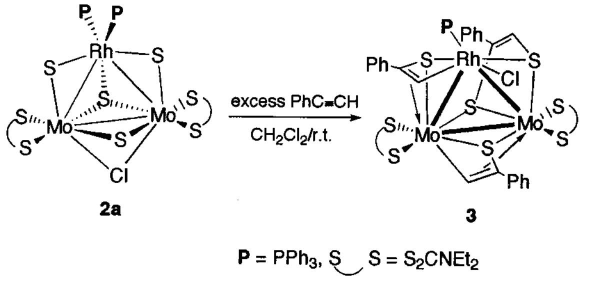
Scheme 1



Cl_2 at room temperature for 2 days, three alkyne molecules were incorporated into an $RhMo_2S_4$ core in **2a** to afford **3**, which was isolated as black crystals in 35% yield (eq 1). The ^{31}P NMR spectrum of the reaction mixture showed that one PPh_3 ligand in **2a** was liberated as free PPh_3 along with some $S{=}PPh_3$ during the reaction. Incorporation of three PhC≡CH molecules in **3** was suggested by its ^{1}H NMR spectrum, exhibiting the phenyl resonances arising from PPh_3 and PhC≡CH and the ethyl resonances due to S_2CNEt_2 ligands in an intensity ratio of ca. 3:2, which was finally confirmed by a single-crystal X-ray analysis (vide infra). Reactions of **2a** with several other terminal and inner alkynes at room temperature gave no tractable products, and at higher temperatures decomposition of **2a** took place. Isolation of intermediate clusters in which only one or two alkynes are incorporated were also unsuccessful, since the reactions of **2a** with 2 equiv or less of PhC≡CH resulted in the formation of a mixture of only **3** and unreacted **2a**. The reactions of the closely related clusters $[\{M(PPh_3)_2\}(\mu_3\text{-}S)(\mu_2\text{-}S)_3\{M'(S_2CNEt_2)\}_2(\mu_2\text{-}Cl)]$ (M = Rh, M′ = W; M = Ir, M′ = Mo, W) with PhC≡CH did not occur.



(1)

To confirm the structure of the parent $RhMo_2S_4$ core and collect its pertinent metrical parameters, synthesis and X-ray analysis has been carried out for **2b**, since a single crystal suitable for X-ray diffraction was not available for **2a**. As shown in Scheme 1, **2b** was synthesized by reacting **2a** with $PMePh_2$ or **1a** with $[RhCl(PMePh_2)_3]$. It is to be noted that reactions of **2b** with PhC≡CH did not take place at room temperature, presumably because of the less dissociative nature of the $PMePh_2$ ligand as compared to the PPh_3 ligand. This might suggest that the reaction of **2a** with PhC≡CH involves the dissociation of one PPh_3 ligand on Rh as the initial step.

Figure 1 depicts the ORTEP drawing of **3**, while pertinent bonding parameters in **3** are listed in Table 1. For comparison, results of the X-ray analysis for **2b** are shown in Figure 2 and Table 1.

Cluster **3** has a triangular $RhMo_2$ framework, for which the Mo−Mo distance at 2.628(1) Å is close to that in **2b** (2.660(1) Å) and slightly shorter than those in **1a** (2.814(1)[13] and 2.817(2) Å[14]) and a cubane cluster derived from **1a** $[\{Rh(cod)\}_2\{MoCl(S_2CNEt_2)\}_2(\mu_3\text{-}S)_4]$

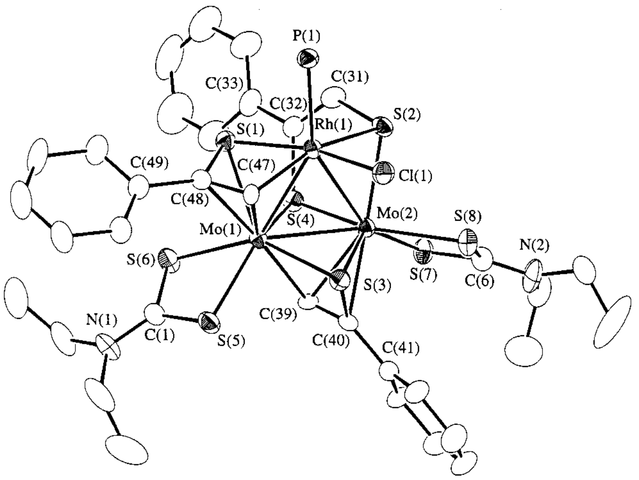


Figure 1. Molecular structure of **3**. Disordered Et carbons with lower occupancies, solvating CH_2Cl_2, and all hydrogen atoms are omitted.

Table 1. Selected Bond Distances (Å) and Angles (deg) in 3 and 2b

Compound **3**			
Rh(1)−Mo(1)	2.769(1)	Rh(1)−Mo(2)	2.932(2)
Mo(1)−Mo(2)	2.628(1)		
Rh(1)−P(1)	2.350(3)	Rh(1)−Cl(1)	2.391(2)
Rh(1)−S(1)	2.316(2)	Rh(1)−C(47)	2.040(8)
C(47)−C(48)	1.37(1)	S(1)−C(48)	1.776(8)
Mo(1)−S(1)	2.450(2)	Mo(1)−C(47)	2.396(8)
Mo(1)−C(48)	2.452(8)		
Mo(1)−S(3)	2.471(2)	Mo(1)−C(39)	2.169(8)
C(39)−C(40)	1.39(1)	S(3)−C(40)	1.774(8)
Mo(2)−S(3)	2.377(2)	Mo(2)−C(39)	2.246(8)
Mo(2)−C(40)	2.313(8)		
Mo(2)−S(2)	2.444(2)	Mo(2)−S(4)	2.362(2)
Rh(1)−S(2)	2.483(2)	S(2)−C(31)	1.764(9)
S(4)−C(32)	1.781(9)	C(31)−C(32)	1.34(1)
Rh(1)−Mo(1)−Mo(2)	65.75(3)	Rh(1)−Mo(2)−Mo(1)	59.44(3)
Mo(1)−Rh(1)−Mo(2)	54.81(3)		
Rh(1)−S(1)−C(48)	68.8(3)	S(1)−Rh(1)−C(47)	69.2(2)
Rh(1)−C(47)−C(48)	103.9(6)	S(1)−C(48)−C(47)	103.6(6)
S(1)−C(48)−C(49)	122.4(7)	C(47)−C(48)−C(49)	133.9(8)
Mo(1)−S(3)−C(40)	83.4(3)	S(3)−Mo(1)−C(39)	65.5(2)
Mo(1)−C(39)−C(40)	105.6(6)	S(3)−C(40)−C(39)	105.2(6)
S(3)−C(40)−C(41)	123.8(7)	C(39)−C(40)−C(41)	131.0(8)
Mo(2)−S(2)−C(31)	104.9(3)	Mo(2)−S(4)−C(32)	109.5(3)
S(2)−Mo(2)−S(4)	82.89(8)	S(2)−C(31)−C(32)	124.7(7)
S(4)−C(32)−C(31)	117.8(7)	S(4)−C(32)−C(33)	116.9(7)
C(31)−C(32)−C(33)	125.2(9)		
Compound **2b**			
Rh(1)−Mo(1)	2.833(1)	Rh(1)−Mo(2)	2.836(1)
Mo(1)−Mo(2)	2.660(1)		
Ph(1)−P(1)	2.306(3)	Rh(1)−P(2)	2.312(3)
Rh(1)−S(1)	2.356(3)	Rh(1)−S(2)	2.368(2)
Rh(1)−S(4)	2.362(3)		
Mo(1)−S(1)	2.206(3)	Mo(2)−S(2)	2.198(3)
Mo(1)−S(3)	2.312(3)	Mo(2)−S(3)	2.315(3)
Mo(1)−S(4)	2.417(3)	Mo(2)−S(4)	2.404(3)
Mo(1)−Cl(1)	2.631(3)	Mo(2)−Cl(1)	2.747(3)
Rh(1)−Mo(1)−Mo(2)	62.07(3)	Rh(1)−Mo(2)−Mo(1)	61.97(3)
Mo(1)−Rh(1)−Mo(2)	55.96(3)		
P(1)−Rh(1)−S(4)	93.73(9)	P(2)−Rh(1)−S(4)	165.84(9)
P(2)−Rh(1)−S(1)	86.08(9)	P(2)−Rh(1)−S(2)	89.09(9)
S(1)−Rh(1)−S(2)	146.57(9)		
S(1)−Mo(1)−Cl(1)	166.10(10)	S(2)−Mo(2)−Cl(1)	168.92(9)
S(3)−Mo(1)−S(6)	148.63(9)	S(3)−Mo(2)−S(8)	150.53(10)
S(4)−Mo(1)−S(5)	160.17(9)	S(4)−Mo(2)−S(7)	155.09(9)

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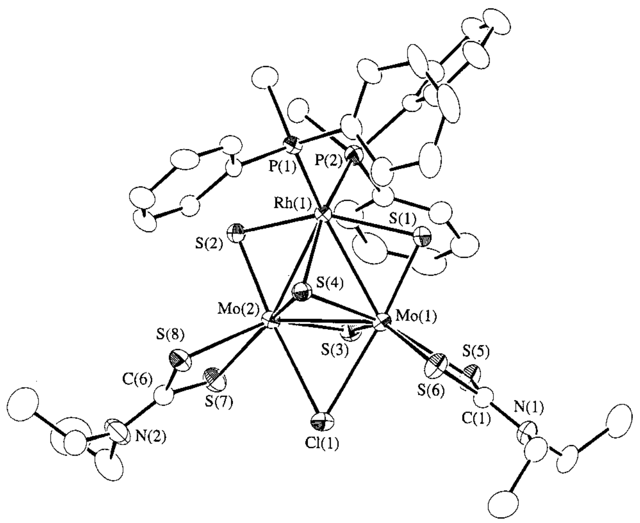

Figure 2. Molecular structure of **2b**. All hydrogen atoms are omitted.

(2.760(2) and 2.771(2) Å).[11b] As for the Rh−Mo bonds, the Rh(1)−Mo(1) distance at 2.769(1) Å is slightly shorter and the Rh(1)−Mo(2) distance at 2.932(2) Å is slightly longer than those in **2b** (2.833(1) and 2.836(1) Å). These metal−metal bond distances in **3** and **2b** are all within the range of the bond order of unity. The most significant difference between the $RhMo_2S_4$ core structures in **3** and in **2b** is that all of the four S atoms in the former bridge two metals, in contrast to the presence of three μ_2-S atoms and one μ_3-S atom in the latter. The separations of Rh(1) from S(3) and S(4) by 3.17 and 3.64 Å, respectively, observed in **3** indicate the change of the μ_3-sulfido ligand in **2a** into the μ_2-S atom in **3**: i.e., formation of **3** is accompanied by the cleavage of the Rh−μ_3-S bond in **2a**, whose length observed in **2b** is 2.362(3) Å. For other metal−sulfur interactions in **3**, six Mo−S distances varying from 2.377(2) to 2.517(2) Å and two Rh−S lengths at 2.316(2) and 2.483(2) Å are all unexceptional for those with single-bond interactions.

Figure 1 clearly shows that three PhC≡CH molecules are bound to the $RhMo_2S_4$ core in **3**. Two alkynes add to the metal−sulfido bonds, each forming metallathiacyclobutene moieties. Thus, the addition of alkyne to one of the Mo−S bonds gives the Mo(1)−C(39)═C(40)−S(3) moiety, which further coordinates to Mo(2) by S(3) and the two C atoms. The other alkyne adds to the Rh(1)−S(1) bond, forming the Rh(1)−C(47)═C(48)−S(1) moiety, which is bound further to Mo(1) by S(1), C(47), and C(48). In these metallathiacyclobutene moieties, the C atoms having the Ph substituent occupy the position adjacent to the S atom. The torsion angle observed for the Mo(1)−C(39)−C(40)−S(3) linkage is 6.1(6)°, and that for the Mo(1)−C(39)−C(40)−C(41) linkage is 171.6(7)°. These as well as the C(39)−C(40) bond length at 1.39(1) Å are consistent with the sp^2 character of the C(40) atom. Similar feature is observed for the rhodathiacyclobutene ring, having the Rh(1)−C(47)−C(48)−S(1) and Rh(1)−C(47)−C(48)−C(49) torsion angles of 10.6(6) and 165.7(8)° along with the C(47)−C(58) distance at 1.37(1) Å.

The third alkyne molecule reacts with the two sulfido atoms in **2a** to afford a dithiolene ligand, in which the S(2) atom bridges Rh(1) and Mo(2), while the S(4) atom is bound to two Mo atoms. It is not clear which S atom of S(3) and S(4) in **3** corresponds to μ_3-S in the parent **2a**. The five-membered ring defined by Mo(2), S(2), S(4), C(32), and C(31) is almost planar, with the torsion angles for the linkages S(2)−Mo(2)−S(4)−C(32) and S(4)−Mo(2)−S(2)−C(31) being 0.4(3) and 2.1(3)°, respectively. Bond lengths in this Mo−dithiolene moiety are comparable to those in the typical η^2-dithiolene ligands bound to Mo.[15] It should also be noted that the Cl ligand bridging two Mo atoms in **2a** migrates to the Rh site.

Shibahara et al. have recently reported the reaction of the incomplete cubane-type cluster $[Mo_3(\mu_2\text{-}S)_3(\mu_3\text{-}S)(H_2O)_9]^{4+}$ with HC≡CH,[16] where only one acetylene reacts with the two μ_2-S ligands to afford a bridging dithiolene ligand, but further reaction does not occur. This presents a sharp contrast to the reaction of **2a** with PhC≡CH, in which three alkyne molecules are incorporated into a related M_3S_4 core to generate rhodathiacyclobutene, molybdenathiacyclobutene, and dithiolene moieties at one time. Hence, the reaction reported here seems quite unique, although each of the reactions to form metallathiacyclobutene[17] and dithiolene chromophores[6c,15,18] from mono- and dinuclear metal−sulfur complexes with alkynes has already been demonstrated.

Experimental Section

General Considerations. All reactions were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques. Compounds **1a**,[19] **2a**,[11b] and $[RhCl(PMePh_2)_3]$[20] were prepared according to the literature methods, while other chemicals were obtained commercially and used without further purification. NMR spectra were recorded on a JEOL EX-270 or LA-400 spectrometer, while elemental analyses were done by a Perkin-Elmer 2400 series II CHN analyzer.

Preparation of [{Rh(SCPh═CH)Cl(PPh_3)}{Mo(SCPh═CH)(S_2CNEt_2)}{Mo(S_2C_2HPh)(S_2CNEt_2)}] (3·CH_2Cl_2). Into

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Table 2. Crystal Data for 3·CH$_2$Cl$_2$ and 2b

	3·CH$_2$Cl$_2$	**2b**
formula	$C_{53}H_{55}N_2PS_8$-Cl_3Mo_2Rh	$C_{36}H_{46}N_2P_2S_8$-$ClMo_2Rh$
fw	1408.63	1155.44
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	12.801(6)	12.141(5)
b, Å	13.972(3)	17.136(6)
c, Å	17.610(3)	22.599(3)
α, deg	88.60(2)	90
β, deg	77.63(3)	97.23(2)
γ, deg	72.83(3)	90
V, Å^3	2937(1)	4664(2)
Z	2	4
μ(Mo Kα), cm^{-1}	11.81	13.90
no. of unique rflns	13 249	11 197
no. of data used ($I > 3\sigma(I)$)	12 632	10 698
R	0.057	0.049
R_w	0.064	0.059

a CH$_2$Cl$_2$ solution (20 mL) of **2a** (60 mg, 0.047 mmol) was added PhC≡CH (52 μL, 0.47 mmol), and the mixture was stirred at room temperature for 2 days. Volatiles were removed from the reaction mixture in vacuo, and a residual black solid was washed with ether (5 mL × 3). Crystallization of the residue from CH$_2$Cl$_2$-hexane (4 mL/8 mL) gave **3**·CH$_2$Cl$_2$ as black crystals (23 mg, 35% yield). ^{1}H NMR (CDCl$_3$): δ 0.74, 0.83, 0.88, 0.90 (dd, $^3J_{H-H} = 7.2$ Hz, 3H each, NCH$_2$C*H*$_3$), 3.08 (dq, 1H, $^3J_{H-H} = 7.2$ Hz, $^2J_{H-H} = 14$ Hz, NC*H*$_2$CH$_3$), 3.20−3.27 (m, 5H, NC*H*$_2$CH$_3$), 3.47 (dq, 1H, $^3J_{H-H} = 7.2$ Hz, $^2J_{H-H} = 14$ Hz, NC*H*$_2$CH$_3$), 3.67 (dq, 1H, $^3J_{H-H} = 7.2$ Hz, $^2J_{H-H} = 14$ Hz, NC*H*$_2$CH$_3$), 6.74−7.71 (m, 32H, Ph and two CH), 8.95 (s, 1H, CH). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 43.2 (d, $J_{Rh-P} = 136$ Hz, PPh$_3$). Anal. Calcd for $C_{53}H_{55}N_2PS_8Cl_3Mo_2Rh$: C, 45.19; H, 3.94, N, 1.99. Found: C, 45.07; H, 3.95; N, 1.93.

Preparation of [{Rh(PMePh$_2$)$_2$}(μ_3-S)(μ_2-S)$_3${Mo(S$_2$CNEt$_2$)}$_2$(μ_2-Cl)] (2b). Method 1. Into a CH$_2$Cl$_2$ solution (12 mL) of **2a** (100 mg, 0.0781 mmol) was added PMePh$_2$ (58 μL, 0.31 mmol), and the mixture was stirred at room temperature for 17 h. The resultant reddish purple solution was dried in vacuo, the residue being washed with ether (5 mL × 2) and then extracted with benzene (20 mL). Addition of hexane (16 mL) to a concentrated extract (8 mL) gave **2b** as black crystals (41 mg, 45% yield). ^{1}H NMR (CDCl$_3$): δ 1.03 (d, $J_{P-H} = 9.2$ Hz, 3H, PMe), 1.34, 1.43 (dd, 6H each, $^3J_{H-H} = 6.8$ Hz, NCH$_2$C*H*$_3$), 2.08 (d, $J_{P-H} = 9.6$ Hz, 3H, PMe), 3.86−4.14 (m, 8H, NC*H*$_2$CH$_3$), 7.03−7.41 (m, 20H, PPh). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 18.0 (dd, 1P, $J_{Rh-P} = 116$, $J_{P-P} = 52$ Hz, PMePh$_2$), 42.0 (dd, 1P, $J_{Rh-P} = 175$, $J_{P-P} = 52$ Hz, PMePh$_2$). Anal. Calcd for $C_{36}H_{46}N_2P_2S_8ClMo_2Rh$: C, 37.42; H, 4.01; N, 2.42. Found: C, 37.59; H, 4.09; N, 2.43.

Method 2. A mixture of **1a** (62 mg, 0.10 mmol) and [RhCl(PMePh$_2$)$_3$] (74 mg, 0.10 mmol) in CH$_2$Cl$_2$ (15 mL) was stirred at room temperature for 17 h. Volatiles were removed in vacuo, and the remaining solid was washed with ether. Crystallization of the residue from CH$_2$Cl$_2$/hexane (3 mL/10 mL) gave **2b** as black crystals (73 mg, 63% yield).

X-ray Diffraction Studies. Single-crystal X-ray analyses of **3** and **2b** were carried out using a Rigaku AFC7R diffractometer equipped with a Mo Kα source at room temperature. Details of crystal and data collection parameters are summarized in Table 2.

Structure solution and refinements were performed with the use of the teXsan program package.[21] The positions of non-hydrogen atoms determined by DIRDIF PATTY[22] were refined anisotropically. For **3**·CH$_2$Cl$_2$, two C atoms of one Et group were disordered over two positions, whose refinements were based upon the occupancy of 0.55 for C(9) and C(10) and 0.45 for C(11) and C(12). One Cl atom of the solvating CH$_2$Cl$_2$ was also located at the two disordered positions Cl(3) and Cl(4), which were both refined with an occupancy of 0.50. With respect to hydrogen atoms, H(37) and H(43), attached to C(31) and C(39), respectively, were found in the Fourier map and refined isotropically. Other hydrogen atoms except for those bonded to C(9), C(11), and C(47) were placed at the calculated positions and included at the final stage of refinements with fixed parameters. For **2b**, all non-hydrogen atoms were refined anisotropically, while all hydrogen atoms placed at the ideal positions were treated with fixed parameters.

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Supporting Information Available: Listings of atomic coordinates, anisotropic thermal paameters, and extensive bond lengths and angles for **3** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] teXsan: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985 and 1992.

[22] PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System; Technical Report of the Crystallography Laboratory: University of Nijmegen, Nijmegen, The Netherlands, 1992.