Syntheses and Single-Crystal X-ray Diffraction Studies of Acyclic and Macrocyclic Aza Dithiolate (NS_2) Complexes of (Arene)ruthenium(II). Thiolate Alkylation, Base-Promoted Hydroalkylation, and Protonation Reactions

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The complex [(HMB)Ru{η^3-HN($CH_2CH_2S)_2$}] (**2**), synthesized from the reaction of [(HMB)$RuCl_2]_2$ (HMB = η^6-C_6Me_6) with $HN(CH_2CH_2S^-)_2$, undergoes S-alkylation reactions with (i) $Br(CH_2)_nBr$ (n = 2−4), giving [(HMB)Ru{η^3-$S(CH_2)_2NH(CH_2)_2S(CH_2)_n$}]$(PF_6)_2$ (n = 2 (**3**), 3 (**4**), 4 (**5**)), which contain macrocyclic zNS_2 (z = 9−11) ligands, (ii) CH_3I, giving [(HMB)Ru{η^3-$NH(CH_2CH_2SMe)_2$}]$(I{\cdot}PF_6)$ (**6**), and (iii) bromoalkenes $CH_2{=}CH(CH_2)_nBr$ (n = 1, 2), yielding the S-alkenyl derivatives [(HMB)Ru{η^3-$S(CH_2)_2NH(CH_2)_2SCH_2CH{=}CH_2$}]$PF_6$ (**7**), [(HMB)Ru{η^3-$NH((CH_2)_2SCH_2CH{=}CH_2)_2$}]$(Br{\cdot}PF_6)$ (**8**), and [(HMB)Ru{η^3-$S(CH_2)_2NH(CH_2)_2S(CH_2)_2CH{=}CH_2$}]$PF_6$ (**9**). Deprotonation of **3** and **7** results in the formation of arene-tethered complexes, viz. [Ru{η^6:η^3-$C_6Me_5(CH_2)_3S(CH_2)_2NH(CH_2)_2S$}]$PF_6$ (**11**), from **3** via [(HMB)Ru{η^3-$S(CH_2)_2NH(CH_2)_2SCH{=}CH_2$)}]$PF_6$ (**10**), which can be reverted to **3** with acid treatment, and [Ru{η^6:η^3-$C_6Me_5CH_2CH(Me)CH_2S(CH_2)_2NH(CH_2)_2S$}]$PF_6$ (**12**) from **7**. The X-ray crystal structures of **2**, **3**, and **5**−**12** are reported.

Introduction

In recent work we have investigated the chemistry of (HMB)Ru^{II} (HMB = η^6-C_6Me_6) and Cp*Ru^{III} (Cp* = η^5-C_5Me_5) complexes, containing the thiapentanedithiolate ligand ($S(CH_2CH_2S^-)_2$; abbreviated tpdt), and observed a variety of reactivity features, which include ring closure of the acyclic ligand, S-alkylation, and coordination of the complexes as metallodithiolate donors to both main-group and transition metals.[1−5] It would be of interest to examine the effect of replacing the "soft" thioether S atom of tpdt with a "hard" NH group on the chemistry of its (HMB)/Cp*Ru complexes. Indeed, such a study is timely, considering that the organometallic chemistry of bis(2-mercaptoethyl)amine ($HN(CH_2CH_2SH)_2$; abbreviated "$N(SH)_2$") is virtually unexplored. We note that, to date, the metal chemistry of "$N(SH)_2$" has been mainly confined to the coordination of its dianion as an "NS_2" donor ligand to pharmaceutically important metals, viz. Tc-99m and Re for imaging diagnostic purposes in nuclear medicine, with special interest in the fine-tuning of the N substituents and S-alkyl groups to improve lipophilicity of the complexes for use as effective brain imaging agents.[6]

Our subsequent aim was to ring-close the acyclic NS_2 ligand, following the in situ template synthesis developed by Busch for macrocyclic ligands;[7] this methodology was utilized by Sellmann specifically for the ring closure of tpdt at $Mo(CO)_3$,[8] and we have also recently found it to be very effective for converting tpdt at (HMB)Ru^{II} to z-membered (zS_3, z = 8−12) macrocyclic ligands.[1] This would provide a viable route to macrocyclic zNS_2 complexes. Though the first complexes of $9NS_2$ were synthesized by Parker[9] and McAuley[10] more than a decade ago, such compounds still remain scarce.[11] As pointed out by Schröder, the study of such complexes, especially of $9NS_2$, has been hampered by the synthetic difficulties and cost encountered in the synthesis of the ligands.[11−13] However, such macrocyclic complexes are of likely importance, on account of their potential roles

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in metal extraction[14] and metal recognition, sensing, and selectivity[15,16] and, for the N- and S-functionalized derivatives in particular, as models in metalloproteins.[17]

In particular, the organometallic chemistry of zNS$_2$ macrocyclic ligands is only just emerging. The first case is a macrocyclic 10NS$_2$ complex, in which Cu(I) is η^2 bound to the arene ring of an N-appended naphthylethyl group.[18] An example of a different class of organometallics is the μ_2-κC:κN cyanide-bridged disilver complex of 9NS$_2$ synthesized by Schröder's group.[19] This paper will describe the syntheses of a third class of organometallic complexes of macrocyclic zNS$_2$ complexes from an acyclic η^3-"NS$_2$" precursor, together with some reactivity features of the acyclic and macrocyclic compounds, in comparison with those of the trisulfur analogues.

Experimental Section

Synthesis of [(HMB)Ru{η^3-NH(CH$_2$CH$_2$SH)$_2$}] (2). Into a suspension of sodium methoxide (freshly generated from sodium (36 mg, 1.57 mmol) in MeOH and evacuated to dryness) in THF (15 mL) was injected bis(2-mercaptoethyl)-amine (0.11 mL, 0.88 mmol), and the mixture was stirred for 1 h. To the gel-like suspension was added solid [(HMB)RuCl$_2$]$_2$ (254 mg, 0.38 mmol), and the mixture was stirred at ambient temperature. The color gradually changed to dark red over a period of 3 h, after which the reaction mixture was evacuated to dryness and extracted with acetonitrile (5 × 10 mL). The extracts were filtered through a disk of alumina and concentrated to ca. 40 mL, and ether (15 mL) was added. Cooling at −30 °C for 12 h gave fine deep red crystals of **2** (173 g, 0.43 mmol, 57% yield). ^{1}H NMR (δ, CD$_3$OD): N*H*, 5.44 (br s, 1H); SC*H*$_2$ + HNC*H*$_2$, 2.77−2.70 (7-line m, 2H), 2.54−2.43 (7-line m, 2H), 2.31−2.21 (6-line m, 2H), 1.99−1.93 (6-line m, 2H); C$_6$*Me*$_6$, 2.03 (s, 18H). ^{13}C NMR (δ, CD$_3$CN): *C*$_6$Me$_6$, 92.4; HN*C*H$_2$, 61.1; S*C*H$_2$, 29.1; C$_6$*Me*$_6$, 15.1. IR (ν cm^{-1}, KBr): 3160 s (N−H). FAB$^+$ MS: *m/z* 399 [M]$^+$, 340 [M − S(CH$_2$)$_2$ + 1]$^+$, 296 [M − S(CH$_2$)$_2$NH(CH$_2$)$_2$ + 1]$^+$. FAB-MS: *m/z* 145. Anal. Found: C, 47.8; H, 7.0; N, 3.8; S, 15.9. Calcd for C$_{16}$H$_{27}$NRuS$_2$: C, 48.2; H, 6.8; N, 3.5; S, 16.1.

Reactions of 2 with Haloalkanes. With Dibromoalkanes. Into a stirred solution of **2** (53 mg, 0.13 mmol) in MeOH (8 mL) was injected Br(CH$_2$)$_2$Br (50 μL, 0.72 mmol). A gradual color change from red to yellow occurred over a period of 2 h. Anion metathesis was carried out by stirring with solid NH$_4$PF$_6$ (140 mg, 0.85 mmol) for 1 h. The reaction mixture was then evacuated to dryness and the residue extracted with CH$_3$CN (3 × 3 mL). The yellow extracts were filtered through a disk of Celite and evacuated to dryness, and the residue was redissolved in CH$_3$NO$_2$ (4 mL). Layering with ether gave [(HMB)Ru{η^3-S(CH$_2$)$_2$NH(CH$_2$)$_2$S(CH$_2$)$_2$}](PF$_6$)$_2$ (**3**) as yellow needle-shaped crystals (103 mg, 100% yield) after 3 days at −30 °C. ^{1}H NMR (δ, CD$_3$CN): N*H*, 6.42 (br s, 1H); SC*H*$_2$ + HNC*H*$_2$, 2.90−2.72 (11-line m, 10H), 2.69−2.59 (9-line m, 2H); C$_6$*Me*$_6$, 2.26 (s, 18H). ^{13}C NMR (δ, CD$_3$CN): *C*$_6$Me$_6$, 103.1; HN*C*H$_2$, 52.2; S*C*H$_2$, 36.4, 36.2; C$_6$*Me*$_6$, 16.2. IR (ν cm^{-1}, KBr): 3294 m (N−H), 847 vs and 558 s (PF$_6$). FAB$^+$ MS: *m/z* 572 [M − PF$_6$]$^+$, 426 [M − 2PF$_6$]$^+$, 399 [M − 2PF$_6$ − 2CH$_2$]$^+$, 352 [M − 2PF$_6$ − S(CH$_2$)$_2$NH]$^+$. FAB-MS: *m/z* 145. Anal. Found: C, 29.4; H, 4.5; N, 4.1; P, 7.9; S, 8.7. Calcd for C$_{18}$H$_{31}$F$_{12}$NP$_2$RuS$_2$.MeNO$_2$: C, 29.4; H, 4.4; N, 3.6; P, 8.0; S, 8.3.

The complexes [(HMB)Ru{η^3-S(CH$_2$)$_2$NH(CH$_2$)$_2$S(CH$_2$)$_3$}](PF$_6$)$_2$ (**4**), [(HMB)Ru{η^3-S(CH$_2$)$_2$NH(CH$_2$)$_2$S(CH$_2$)$_4$}](PF$_6$)$_2$ (**5**), and [(HMB)Ru{η^3-NH(CH$_2$CH$_2$SMe)$_2$}](I.PF$_6$) (**6**), were similarly obtained as yellow crystalline plates in 76, 78 and 63% yields, respectively, from the reactions of **2** with Br(CH$_2$)$_n$Br (n = 3 or 4) and MeI (see the Supporting Information).

Reactions of 2 with Bromoalkenes. With 1.5 Mol Equiv of Allyl Bromide. Into a stirred solution of **2** (25 mg, 0.063 mmol) in MeOH (8 mL) was injected CH$_2$=CHCH$_2$Br (8 μL, 0.093 mmol), and stirring was continued for 1.5 h. No color change was observed. Subsequent metathesis with NH$_4$PF$_6$ (32 mg, 0.20 mmol) and workup as described above gave hexagonal-shaped crystals of [(HMB)Ru{η^3-S(CH$_2$)$_2$NH(CH$_2$)$_2$SCH$_2$CH=CH$_2$}]PF$_6$ (**7**; 30 mg, 82% yield) from CH$_3$CN−ether after 3 days at −30 °C. ^{1}H NMR (δ, CD$_3$CN): SCH$_2$C*H*=, 5.87−5.73 (symm 14-line m, 1H); =C*H*$_2$ + N*H*, 5.36−5.24 (unres dd, 3H); SC*H*$_2$ + HNC*H*$_2$, 3.67−3.61 (4-line m, 1H), 3.31−3.24 (4-line m, 1H), 2.92−2.84 (7-line m, 1H), 2.71−2.62 (8-line m, 1H), 2.60−2.48 (unres m, 5H), 2.29−2.20 (9-line m, 1H); C$_6$*Me*$_6$, 2.07 (s, 18H). ^{13}C NMR (δ, CD$_3$CN): *C*H=, 131.7; =*C*H$_2$, 122.0; *C*$_6$Me$_6$, 98.1; HN*C*H$_2$, 60.4, 50.9; S*C*H$_2$, 37.2, 36.0, 27.2; C$_6$*Me*$_6$, 15.4. IR (ν cm^{-1}, KBr): 3291 m (N−H), 845 vs and 558 s (PF$_6$). FAB$^+$ MS: *m/z* 440 [M − PF$_6$]$^+$, 399 [M − PF$_6$ − CH$_2$CH=CH$_2$]$^+$. FAB-MS: *m/z* 145. Anal. Found: C, 38.5; H, 5.5; N, 1.9; P, 5.2; S, 10.8. Calcd for C$_{19}$H$_{32}$F$_6$NPRuS$_2$: C, 39.0; H, 5.5; N, 2.4; P, 5.3; S, 11.0.

With Excess Allyl Bromide. [(HMB)Ru{η^3-NH((CH$_2$)$_2$SCH$_2$CH=CH$_2$)$_2$}](Br·PF$_6$) (**8**) was formed in ca. 90% yield and isolated as yellow crystalline plates in 16% yield.

With 4-Bromobutene. Deep red crystals of [(HMB)Ru{η^3-S(CH$_2$)$_2$NH(CH$_2$)$_2$S(CH$_2$)$_2$CH=CH$_2$}]PF$_6$ (**9**) were isolated in 82% yield.

Details on the isolation and data for **8** and **9** are described in the Supporting Information.

Reactions with Base. Solutions of **3** and **7** in CH$_3$CN were treated with solid base (details are given in the Supporting Information). The reaction of **3** with 1 mol equiv of KOH gave red crystals of [(HMB)Ru{η^3-S(CH$_2$)$_2$NH(CH$_2$)$_2$SCH=CH$_2$)}]PF$_6$ (**10**) in 63% yield. ^{1}H NMR (δ, CD$_3$CN): SC*H*=, 6.61 (dd, J = 16.5, 9.1 Hz, 1H); =CH*H*$_{cis}$, 5.78 (d br, J = 8.2 Hz, 1H); =CH*H*$_{trans}$, 5.82 (d br, J = 15.7 Hz, 1H); N*H*, 5.36 (s, 1H); SC*H*$_2$ + HNC*H*$_2$, 2.87 (broad m, 1H), 2.69 (c unres m, 6H), 2.57−2.46 (symm 7-line m, 1H); C$_6$*Me*$_6$, 2.07 (s, 18H). ^{13}C NMR (δ, CD$_3$CN): S*C*H=, 128.4; =*C*H$_2$, 125.0; *C*$_6$Me$_6$, 97.7; HN*C*H$_2$, 61.5, 52.0; S*C*H$_2$, 39.1, 27.8; C$_6$*Me*$_6$, 15.3. IR (ν cm^{-1}, KBr): 3308 m (N−H), 840 vs and 558 s (PF$_6$). FAB$^+$ MS: *m/z* 572 [M]$^+$, 426 [M − PF$_6$ − 1]$^+$, 399 [M − PF$_6$ − 2CH$_2$]$^+$, 323 [M − PF$_6$ − S(CH$_2$)$_4$NH + 1]$^+$. FAB− MS: *m/z* 145. Anal. Found: C, 38.1; H, 5.3; N, 2.7; P, 5.4; S, 11.0. Calcd for C$_{18}$H$_{30}$F$_6$NPRuS$_2$: C, 37.9; H, 5.3; N, 2.5; P, 5.4; S, 11.2. The use of excess KOH or 1 mol equiv of KOBu^t led to isolation of orange needle-shaped crystals of [Ru{η^6:η^3-C$_6$Me$_5$(CH$_2$)$_3$S(CH$_2$)$_2$NH(CH$_2$)$_2$S}]PF$_6$ (**11**) in 99% yield (for data, see the Supporting Information). Similar reactions of **4** and **5** only led to recovery of the starting complexes.

The reaction of **7** with 1 mol equiv of KOH gave orange crystalline solids of [Ru{η^6:η^3-C$_6$Me$_5$CH$_2$CH(Me)CH$_2$S(CH$_2$)$_2$NH(CH$_2$)$_2$S}]PF$_6$ (**12**) in 76% yield. For a 1:1 mixture of diastereoisomers, the data are as follows. ^{1}H NMR (δ, CD$_2$Cl$_2$): N*H*, 5.10 (br s, 2H); C*H*, 3.31−3.24 (unres. m, 1H), 3.08−3.00 (unres m, 1H); SC*H*$_2$ + HNC*H*$_2$ + C$_6$Me$_5$C*H*$_2$, 2.90−2.33 (unsymm m, 15H), 2.30−1.99 (overlapping m, 7H), 1.89−1.78 (11-line m, 2H); C$_6$*Me*$_5$, 2.27, 2.23, 2.21, 2.16, 2.15, 2.12, 2.06, 2.05, 1.94, 1.93 (s, each 3H; total 30H); SCH$_2$CH(*Me*)CH$_2$, 1.32 and 1.28 (d, J = 6.4 and 6.8 Hz, each 3H). ^{13}C NMR (δ, CD$_3$CN): *C*$_6$Me$_5$, 102.6, 101.6, 99.6, 98.6, 98.2, 98.1, 97.6, 97.5, 95.0, 94.9, 88.2, 86.5; CH$_2$*C*H(Me)CH$_2$, 39.1, 32.5; HN*C*H$_2$, 64.6, 62.5, 56.0, 53.5; S*C*H$_2$ + C$_6$Me$_5$*C*H$_2$, 40.4, 38.7, 38.5, 37.5,

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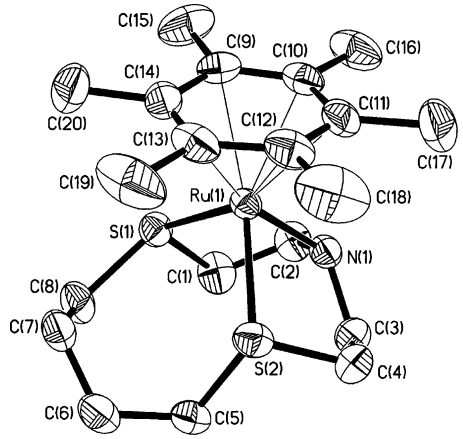
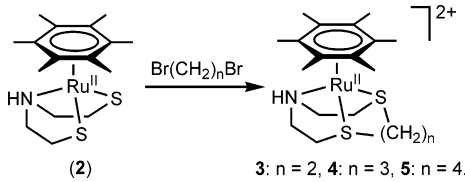


Figure 1. ORTEP plot for the molecular structure of the dication of **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme 1



33.6, 32.5, 28.0, 26.9; $CH_2CH(Me)CH_2$, 23.0, 21.6; C_6Me_5, 17.4, 16.5, 15.8 (overlapping s), 15.7, 15.5, 14.9, 14.7. IR ν (cm^{-1}, KBr): 3309 w (N−H), 842 vs and 558 s (PF_6). FAB^+ MS: *m/z* 440 $[M - PF_6]^+$. FAB-MS: *m/z* 145. Anal. Found: C, 39.5; H, 5.4; N, 2.8; S, 10.7. Calcd for $C_{19}H_{32}F_6NPRuS_2$: C, 39.0; H, 5.5; N, 2.4; S, 11.0.

Protonation with HPF_6. Proton NMR spectral observations were made on the effect of protonation with HPF_6 on solutions of **7**, **9**, and **10** in CD_3CN (details are given in the Supporting Information).

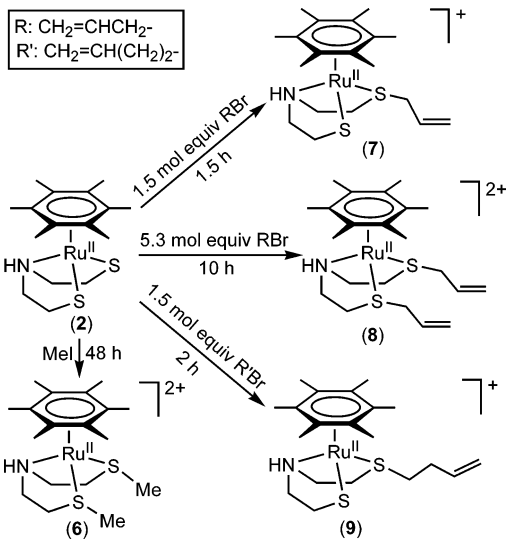
Results and Discussion

Synthesis. The ambient-temperature reaction of $[(HMB)RuCl_2]_2$ with the sodium salt of bis(2-mercaptoethyl)amine, $HN(CH_2CH_2SNa)_2$, led to the isolation of $[(HMB)Ru\{\eta^3\text{-}HN(CH_2CH_2S)_2\}]$ (**2**) as deep red crystals in 57% yield.

Ring closure reactions with α,ω-dibromoalkanes, $Br(CH_2)_nBr$ ($n = 2-4$), led to high yields of complexes **3**−**5**, containing the macrocyclic (zNS_2) ligands, viz. nine-membered 1-aza-4,7-dithiacyclononane ($9NS_2$), 10-membered 1-aza-4,8-dithiacyclodecane ($10NS_2$), and 11-membered 1-aza-4,9-dithiacycloundecane ($11NS_2$), respectively (Scheme 1). These constitute the first η^6-arene metal complexes of these macrocyclic ligands.

The complexes **2** and **3**−**5** have all been spectroscopically characterized. The molecular structure of **5** is shown in Figure 1 and those of **2** and **3** in Figure S1 (Supporting Information). In **3** and **5**, Ru is coordinated to η^6-HMB and a η^3-azadithia macrocycle of ring sizes 9 and 11, respectively. Selected metric data are listed in Table S3 (Supporting Information), in which the significant parameters are compared with those of the corresponding $9S_3$ and $11S_3$ analogues.[1] The bond parameters of **2** are given in Table S4 (Supporting Information), where they are compared with those of its tpdt analogue, $[(HMB)Ru\{\eta^3\text{-}S(CH_2CH_2S)_2\}]$ (**1**). In all these data, the effect of the relative sizes of N and S is reflected.

Scheme 2



S-Alkylation. The thiolate S atoms of complex **2** are susceptible to alkylation. Thus, a prolonged reaction with excess MeI gave the dicationic complex **6** in 63% yield, a finding analogous to that of the tpdt analogue (**1**) of **2**.[1] With 3-bromopropene (allyl bromide) in slight excess, the mono-*S*-allyl complex **7** (82% yield) was obtained, while the use of 5 mol equiv of the bromide for an extended reaction time gave the bis-*S*-allyl complex **8** in 90% crude yield, of which 16% was isolated as crystals. Using 4-bromo-1-butene, the mono-S-alkylated product **9** was obtained in 82% yield; however, a bis-S-alkylated derivative was not formed with excess bromobutene, even at prolonged reaction time (Scheme 2). Complexes **6**−**9** were all characterized by spectroscopy and by single-crystal X-ray diffraction analyses. The molecular structures of **8** and **9** are shown in Figure 2 and those of **6** and **7** in Figure S2 (Supporting Information), together with that of the S-vinyl complex **10**. The metric data of **6** are given in Table S4 (Supporting Information), while the metric data of **7**−**9** are given in Table S5 (Supporting Information), together with those of **10** and its tpdt analogue.[20]

Spectral characteristics (NMR, IR, and MS) of these complexes are consistent with their molecular structural features.

Base-Promoted S−C Cleavage in Azadithia Macrocyclic Ligands and Arene Tethering in *S*-Allyl/Alkenyl Derivatives. Treatment of **3** with 1 mol equiv of KOH resulted in S−C cleavage, giving **10** in 63% yield. Excess KOH and a longer reaction time gave the arene-tethered compound **11** in 99% yield (Scheme 3). Such S−C cleavages are well-documented in thia macrocyclic ligands in complexes of group 9 metals[21] and Ru.[22] These reactivity features parallel those previously observed by Bennett and Goh for the $9S_3$ analogue of **3**,[20] except that in this present case a second deprotonation step to give **10A** is not feasible. It appears that

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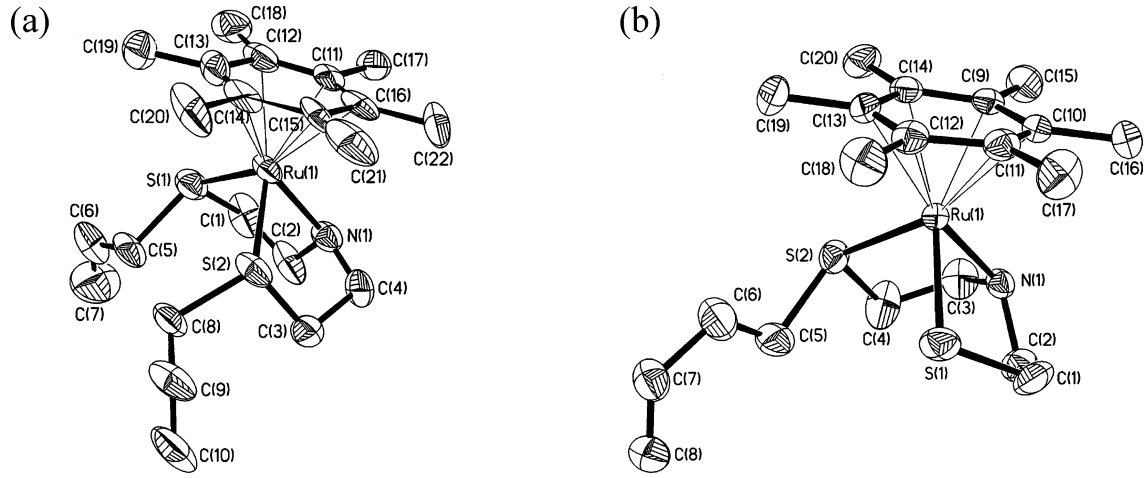
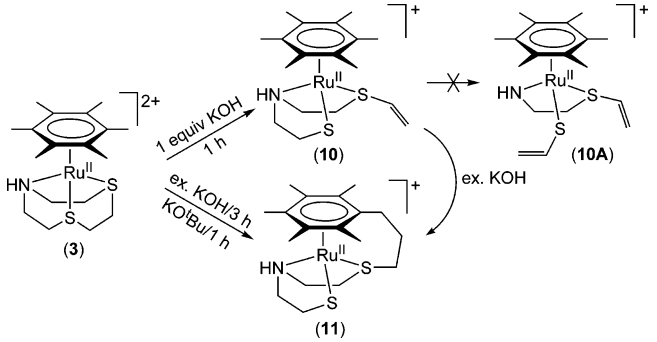


Selected metric data (Å) -
C(5)–C(6) 1.49(3), C(6)–C(7) 1.26(4),
C(8)–C(9) 1.45(3), C(9)–C(10) 1.31(4)

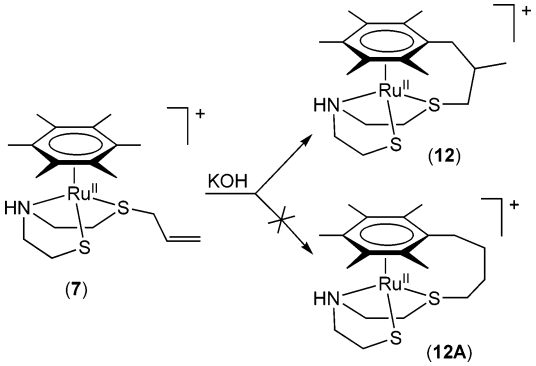
Selected metric data (Å) -
C(5)–C(6) 1.507(6), C(6)–C(7) 1.499(7),
C(7)–C(8) 1.296(8)/1.25(2)

Figure 2. ORTEP plots for the molecular structures of the S-alkenyl complexes (a) dication of **8** and (b) monocation of **9**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme 3



Scheme 4



S−C cleavage cannot occur in the $NH(CH_2)_2S$ linkages of **3**. However, analogous to the $9S_3$ complex, further deprotonation can occur at a Me group of HMB in **10**, giving rise to the tethered species **11** via an intramolecular Michael addition of the resulting carbanion to the terminal ethene carbon of the thioether vinyl appendage of the "open" NS_2 ligand.

Unexpectedly, similar S−C cleavage was not observed in **4** and **5**. Treatment of these complexes with base resulted in color changes from yellow to orange, but subsequent workup led to recovery of the starting materials. An in situ proton NMR experiment in CD_3CN with pulverized KOH showed an immediate shift and broadening of all the resonances of **4** and **5**, with loss of the NH proton resonance but no sign of alkenyl protons of **7** or **9**, the expected products from S−C cleavage. It thus appears that base treatment only abstracted the NH proton in these cases.

Base treatment of **7** caused a slow color change to orange via an intermediate dark blue species, which appeared paramagnetic from the nature of its proton NMR spectrum. From the final resultant solution was isolated in 76% yield complex **12**, which carries a three-carbon tether with a Me substituent (Scheme 4). The alternative complex **12A**, with a four-carbon tether, was not detected. Additionally, it was found that arene tethering cannot be effected in **9**.

It appears that arene∼$S_{n=4,5}$ (where n = number of carbons on the tethered chain) derivatives are thermodynamically unstable. Indeed, "straps" of four or more methylene carbons are rare, there being only one such case reported up to 2000 of a Cp∼$P_{n=4}$ four-carbon tether in a $CpRu^{II}$ species.[23] In contrast, the literature contains numerous examples of arene/Cp∼$X_{n=2,3}$ complexes of Ru(II) for X = P, O, N, as well as for X = S.[24,25]

The ^1H and ^{13}C NMR spectra of **11** and **12** provide clear evidence for the presence of an arene-tethered ligand. Thus, these spectra show five peaks for the Me substituents on the arene ring of **11**. In the case of **12**, 2 sets of such resonances of equal intensity, together with 2 signals each for CH and Me on the tether strap and 12 ^{13}C signals for arene rings, are indicative of a 1:1 diastereoisomeric mixture, arising from chirality at C6 and Ru. However, the crystal structure analysis shows the predominance of the S_{Ru},S_C or R_{Ru},R_C diastereoisomer (85%) with a 15% presence of the second (S_{Ru},R_C or R_{Ru},S_C) isomer.

The molecular structures of **11** and **12** are illustrated in Figure 3. They differ only in a Me substituent at C6 for **12**, a consequence of the preferential formation of a SC_3 rather than a SC_4 tether chain, as noted above.

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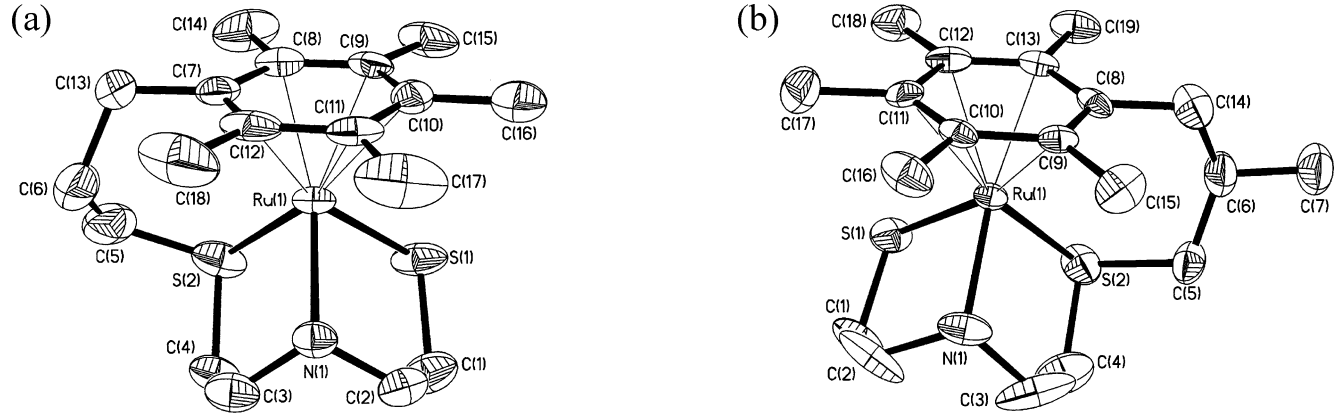


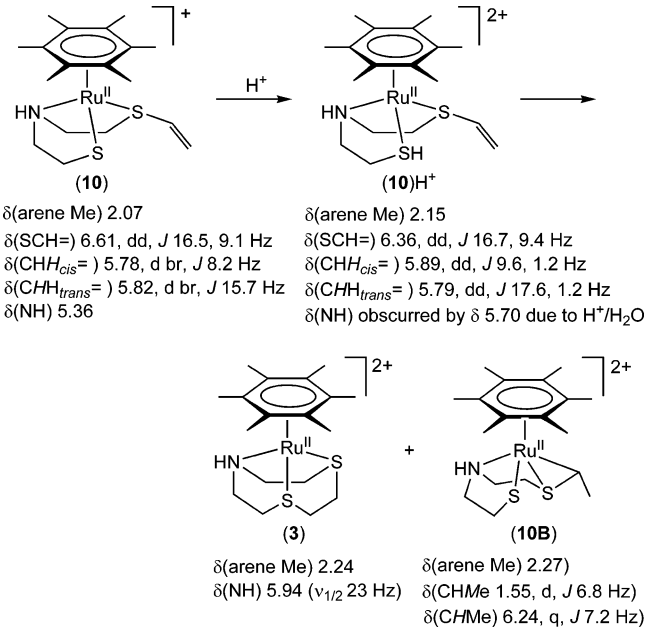
Selected metric data (Å) -
C(7)–C(13) 1.519(11) ± 0.002

Selected metric data (Å) -
C(8)–C(14) 1.518(8) ±0.005

Other C–C distances in the tethers average 1.521(11) ± 0.05 Å. The tethered arene rings are planar.

Figure 3. ORTEP plots for the molecular structures of the monocationic arene-tethered complexes (a) **11** and (b) **12**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Scheme 5



Protonation of Ethenethiolate Complexes. Acidification of red solutions of **7**, **9**, and **10** in CD_3CN at 0 °C resulted in an immediate color change to pale orange, that of **10** gradually converting to yellow over 2−3 h. The resultant proton NMR spectral changes are illustrated in Figures S3−S5 (Supporting Information) and are further elaborated on for **10** in Scheme 5. In all three cases, the proton NMR resonances of the vinylic protons remained, though slightly shifted. The protonated solution of **10** showed new arene Me signals at δ 2.15, 2.24, and 2.27 (relative intensity 54:3:1, assigned to the S-protonated species (**10**)H$^+$, **3**, and **10B**, respectively), an extremely weak doublet at δ 1.55 (J = 6.8 Hz), δ(NH) probably under the intense proton peak of the acid at δ 5.70, and multiplets for $SCH_2/HNCH_2$ at δ 2.49−2.33 (2H) and δ 2.86−2.61 (8H) with fine structure entirely different from those of **10** (see Figure S3). After 2 days at room temperature, the Me resonance of the species (**10**)H$^+$ had disappeared, as did all the resonances pertaining to the vinylic protons; the Me singlets of **3** and **10B** then possessed the relative intensity ca. 6:1. Also observed were a doublet at δ 1.55 (J = 6.8 Hz, Me) and a quartet at δ 6.24 (J = 7.2 Hz, CH), possessing relative intensity correlating well with the HMB signal (δ 2.27), assigned to species **10B**. A broad resonance at δ 5.94 was assigned to the NH group. It was observed that, after 5 days, **10B** had undergone ca. 20% isomerization to a like species, reaching ca. 40% after 9 days, indicated by new peaks assigned to HMB at δ 2.18, an Me doublet at δ 1.63 (J = 7.2 Hz), and a CH quartet at δ 6.11 (J = 6.8 Hz). These observations suggest there had occurred an instantaneous protonation, most likely at thiolate S, since vinylic protons still persist, followed by two slow processes: viz., (i) a cyclization process to re-form **3** as was found for the analogous $9S_3$ system, in which case the process was completely reversible, and (ii) protonation at the terminal CH_2 of the ethane moiety to generate the thioacetaldehyde complex **10B**, as was also observed for analogous ethenethiolate complexes derived from $[(HMB)Ru(9S_3)]^{2+}$.[20b]

Likewise, protonation of **7** and **9** initiated an immediate replacement of the arene Me resonance, shifts of all other resonances, and drastic changes in the fine structure and coupling patterns of the $SCH_2/HNCH_2$ resonances (see Figures S4 and S5). However, unlike in the case of **10**, no further changes were observed up to 5 days. It may be inferred that the S-protonated derivatives of **7** and **9** had persisted for this period and did not undergo cyclization to form **4** and **5**, respectively. It will be recalled that neither **7** nor **9** can be obtained from deprotonation of **4** and **5** with base. Attempts at isolation of the protonated derivatives of **7** and **9** only led to recovery of the original compounds, indicating that the protonated species are only stable in the presence of acid.

Conclusions

Analogous to $S(CH_2CH_2S^-)_2$ (tpdt), the acyclic η^3-$HN(CH_2CH_2S^-)_2$ dianion ligated to $[(HMB)Ru]^{2+}$ undergoes (i) ring closure with α,ω-dibromoalkanes, producing macrocyclic zNS_2 (z = 9−11) complexes, and (ii) mono- and bis-S-alkylation with bromoalkenes, forming S-alkenyl derivatives. For z = 9, the C−S linkage in the

macrocyclic ligand undergoes reversible base/acid cleavage/formation. The *S*-vinyl derivative formed can be further deprotonated to give an arene-tethered complex. Likewise, the base treatment of the *S*-allyl complex also leads to an analogous arene−three-carbon-tether complex. Treatment of these alkenyl complexes with acid results in instantaneous protonation at the thiolate donor atom. In the case of the *S*-vinyl complex, this is followed by a slow rearrangement to generate the original macrocyclic complex as the major product.

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Supporting Information Available: Table S1, giving crystal data collection and processing parameters, Table S2, giving IR spectral data, Tables S3−S5, giving selected bond parameters of the complexes, Figures S1 and S2, giving ORTEP diagrams of **2** and **3** and of **6**, **7**, and **10**, respectively, Figures S3−S5, giving proton NMR spectral changes which illustrate the immediate effect of protonation of complexes **10**, **7**, and **9**, respectively, text giving experimental details for the syntheses and characterization of some of the complexes, and crystallographic data as CIF files for complexes **2**, **3**, and **5**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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