3648 *Inorg. Chem.* **1993**, *32*, 3648-3653

# Derivatized Cyclophane Chemistry. Synthesis of New ($\pi$-Benzene)ruthenium(II) Complexes of 2,11-Dithia- and 2,11-Diselena[3.3]orthocyclophane

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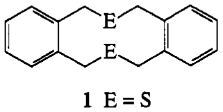
*Received February 2, 1993*

The reactions of $[(\eta^6\text{-}C_6H_6)Ru(acetone)_3][BF_4]_2$ with 2,11-dithia- (**1**) and 2,11-diselena[3.3]orthocyclophane (**2**) were used to prepare the complexes $[(\eta^6\text{-}C_6H_6)Ru(E\text{-}E)(L)][BF_4]_2$ and $[(\eta^6\text{-}C_6H_6)Ru(E\text{-}E)(X)]X$ (E-E = **1**, **2**; L = MeCN, EtCN; X = Cl, Br). The complexes were characterized by microanalysis and $^1H$ and $^{13}C$ NMR and IR spectroscopy. The molecular structure of $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})(EtCN)][BF_4]_2$ (**3**) was determined. Crystals of **3** belong to the space group $P2_1/n$ with $a = 11.670(3)$ Å, $b = 19.893(5)$ Å, $c = 12.038(5)$ Å, $\beta = 104.71(3)°$, $V = 2703(2)$ Å$^3$, and $Z = 4$. The structure was refined to $R = 3.63\%$ and $R_w = 3.91\%$ for 4437 with $I > 2.5\sigma(I)$. The Ru atom is six-coordinate. **1** acts as a chelating ligand via the S donor atoms and adopts a rigid *anti-II* conformation. The Ru–N–C angle is 166.0(3)°, and the bending may reflect $\pi$-donation by EtCN or crystal packing forces. The solid-state structure consists of sheets of $\pi$-interacting cations. Each arene ring of **3** is involved in a $\pi$–$\pi$ interaction with an arene ring on an adjacent cation. The complexes containing MeCN are labile in solution, but those containing EtCN are not. Both nitriles can be displaced by halides. The MeCN complexes can extract low concentrations of EtCN from nitromethane. The complexes of **2** are the first examples of (selenoether)($\pi$-benzene)ruthenium(II) compounds.

## Introduction

The relatively poor $\sigma$-donor and $\pi$-acceptor abilities of thioether ligands have resulted in their coordination chemistry being dominated by either macrocyclic or crown thioether ligands. However, recent studies employing some novel cyclic dithioether ligands have shown that, with attention to ligand design, these species may also have an extensive coordination chemistry.[1,2] Medium-sized cyclic dithioethers are *mesocycles* and as such provide a contrast in properties with those of acyclic and macrocyclic ligand systems. Mesocycles tend to have unusual steric requirements as ligands because of the folding needed to achieve coordination. As a result, the molecular properties of their complexes frequently differ from those of comparable acyclic or macrocyclic ligands.[3]

The 10-membered dichalcogenocyclophanes 2,11-dithia- (**1**) and 2,11-diselena[3.3]orthocyclophane (**2**) offer a number of useful features as mesocyclic ligands. The conformational behaviour of mesocycles is generally complex, but the inclusion of rigid xylyl units may limit the number of available conformations.[4] Molecular mechanical calculations on **1** and **2**[5,6] have shown the energy differences between conformations to be relatively small. The global minimum conformer has an *anti* structure with *exo* oriented heteroatoms and is shown by X-ray crystallography[5] to be present in the solid state. In solution **1** and **2** undergo a dynamic process which involves *anti*/*anti'* interconversion.[5,7] Thus **1**, like many cyclic thioethers, shows a conformational preference for an *exo* arrangement of S atoms both in solution and in the solid state.[8,9] However, unlike many cyclic thioethers the conformational preferences of the free ligand do not dominate the coordination chemistry of **1** or **2**. They have some conformational flexibility which makes available a number of different conformations some of which are potentially capable of chelating to a metal.



1 E = S
2 E = Se

In order for chelation to occur reorientation of the donor atoms from an *exo* to an *endo* arrangement is necessary. Three plausible conformations exist where the donor atoms are arranged for chelation (Figure 1). The *syn* conformation has the highest energy of the three conformations and is therefore the least likely to be observed in metal complexes. The most favoured *endo* conformation *anti-I*, is very sterically demanding, and although it is observed as a chelating ligand in some pseudotetrahedral silver(I) and copper(I) complexes,[10] it is not ideally suited to higher coordination geometries. Other potential coordination sites which exist on a metal would be blocked by the ligand in this conformation. Instead, it is possible for the ligand to raise an arm and assume the alternative conformation, *anti-II*, and thereby allow coordination of a monodentate ligand at the previously

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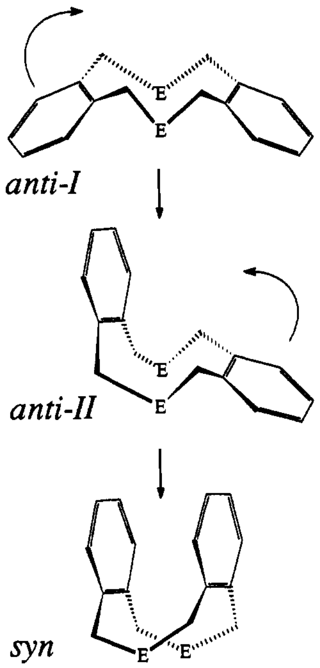

**Figure 1.** Potential chelating configurations of **1** and **2**.

blocked sited. In this way it could be envisaged that these flexible ligands might be used to protect or block certain coordination sites on a metal center.

As part of our investigations of the coordination chemistry of **1** and **2** with the ($\pi$-benzene)ruthenium(II) moiety, and the likely reactivity of these species, we have prepared a series of cationic complexes which contain potentially labile monodentate ligands. The complexes $[(\eta^6\text{-}C_6H_6)Ru(E\text{-}E)(L)][BF_4]_2$ and $[(\eta^6\text{-}C_6H_6)Ru(E\text{-}E)(X)]X$ (E-E = **1**, **2**; L = MeCN, EtCN; X = Cl, Br) have been prepared and characterized by elemental analysis and $^1H$ and $^{13}C$ NMR and IR spectroscopy. The complex $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})(EtCN)][BF_4]_2$ (**3**) has been further characterized by an X-ray structure determination. It is found that while MeCN is easily substituted from these complexes, EtCN is more difficult to displace. The complexes of **1** are among only a handful of known ($\pi$-arene)ruthenium(II) complexes which contain two bound thioethers[11] and represent the first examples containing a bidentate thioether. The complexes of **2** represent the first examples of (selenoether)($\pi$-benzene)ruthenium(II) compounds.

## Experimental Section

The ligands **1**[6,12] and **2**[13,14] were prepared by literature methods, as were the ruthenium complexes $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$,[15,16] $[(\eta^6\text{-}C_6H_6)Ru(acetone)_3][BF_4]_2$,[17] and $[(\eta^6\text{-}C_6H_6)Ru(MeCN)_3][BF_4]_2$.[17] Nitromethane was purchased from BDH. Propionitrile and deuterated solvents were purchased from Aldrich. NMR spectra were run on a Varian 300- or 200-MHz spectrometer, and IR spectra, on a Diglab FTS60 equipped with a vacuum bench for the far-IR spectra. Analyses were performed by the Campbell Microanalytical laboratory at this university. All preparations were carried out under an atmosphere of dry nitrogen, and all solvents were dried and degassed prior to use.

**$[(\eta^6\text{-}C_6H_6)Ru(1)(MeCN)][BF_4]_2$. Method 1.** To a solution of the tris(acetone) complex $[(\eta^6\text{-}C_6H_6)Ru(acetone)_3][BF_4]_2$ (1.0 mmol) in acetone (25 cm$^3$) was added **1** (0.272 g, 1.0 mmol) and an excess of acetonitrile (*ca.* 1 cm$^3$). The mixture was refluxed for *ca.* 30 min. The solution was then cooled and filtered and the solvent removed under reduced pressure. The resulting yellow-orange solid was recrystallized by slow vapor diffusion of diethyl ether into a solution of the product in nitromethane. Yield = 0.50 g (75%).

**Table I.** Crystallographic Data for **3**

| | | | |
|---|---|---|---|
| chem formula | $C_{25}H_{27}B_2F_8NRuS_2$ | fw | 680.31 |
| $a$, Å | 11.670(3) | space group | $P2_1/c$ (No. 14) |
| $b$, Å | 19.893(5) | $\lambda$, Å | 0.710 69 |
| $c$, Å | 12.038(5) | $\rho_{calcd}$, g cm$^{-3}$ | 1.67 |
| $\beta$, deg | 104.71(3) | $\mu$, cm$^{-1}$ | 7.95 |
| $V$, Å$^3$ | 2703(2) | transm coeff | 0.69–0.72 |
| $Z$ | 4 | $R^a$ | 0.0363 |
| $T$, K | 153 ± 5 | $R_w{}^b$ | 0.0391 |

$^a$ $R = \sum\Delta F/\sum|F_o|$. $^b$ $R_w = \sum w^{1/2}\Delta F/\sum w^{1/2}F_o$; $w = 0.867/[\sigma^2(F_o) + 0.00111(F_o)^2]$.

**Method 2.** A mixture of $[(\eta^6\text{-}C_6H_6)Ru(MeCN)_3][BF_4]_2$ (0.119 g, 0.25 mmol) and **1** (0.068 g, 0.25 mmol) in acetonitrile (40 cm$^3$) was refluxed for 30 min. The solution was cooled, filtered, and then reduced to about half its volume under vacuum. Addition of diethyl ether (50 cm$^3$) precipitated the crude product. Recrystallization by slow vapor diffusion of diethyl ether into a solution of the product in acetonitrile gave orange crystals. Yield = 0.136 g (82%). (Anal. Found: C, 43.1; H, 3.7; N, 2.2; S, 9.8. Calcd for $C_{24}H_{25}B_2F_8NRuS_2$: C, 43.3; H, 3.8; N, 2.1; S, 9.6.) IR: $\nu$(CN) 2292 cm$^{-1}$.

The following compounds were prepared by a procedure analogous to method 1 for the nitrile complexes.

**$[(\eta^6\text{-}C_6H_6)Ru(1)(EtCN)][BF_4]_2$ (3).** Yield = 0.53 g (78%). (Anal. Found: C, 44.3; H, 4.3; N, 2.1; S, 9.7. Calcd for $C_{25}H_{27}B_2F_8NRuS_2$: C, 44.1; H, 4.0; N, 2.1; S, 9.4.) IR: $\nu$(CN) 2290 cm$^{-1}$.

**$[(\eta^6\text{-}C_6H_6)Ru(2)(MeCN)][BF_4]_2$.** Yield = 0.74 g (97%). (Anal. Found: C, 38.0; H, 3.6; N, 2.0. Calcd for $C_{24}H_{25}B_2F_8NRuSe_2$: C, 37.9; H, 3.3; N, 1.8.) IR: $\nu$(CN) 2294 cm$^{-1}$.

**$[(\eta^6\text{-}C_6H_6)Ru(2)(EtCN)][BF_4]_2$.** Yield = 0.67 g (85%). (Anal. Found: C, 38.7; H, 3.4; N, 2.0. Calcd for $C_{25}H_{27}B_2F_8NRuSe_2$: C, 38.8; H, 3.5; N, 1.8.) IR: $\nu$(CN) 2290 cm$^{-1}$.

**$[(\eta^6\text{-}C_6H_6)Ru(1)Cl]Cl$. Method 1.** To a solution of $[(\eta^6\text{-}C_6H_6)Ru(1)(MeCN)][BF_4]_2$ (0.067 g, 0.1 mmol) in nitromethane (5 cm$^3$) was added a 2-fold excess of tetramethylammonium chloride (0.044 g, 0.4 mmol). After being stirred for 16 h, the solution was filtered and the product precipitated by slow addition of diethyl ether. Recrystallization was effected by slow vapor diffusion of diethyl ether into a solution of the product in nitromethane to yield orange/red crystals. Yield = 0.049 g (94%).

**Method 2.** A mixture of **1** (0.272 g, 1.0 mmol) and $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (0.25 g, 0.5 mmol) was refluxed in acetonitrile (35 cm$^3$) for 30 min. The solution was cooled to ambient temperature and the solvent reduced (10 cm$^3$). Slow addition of diethyl ether gave an orange powder, which was recrystallized as in method 1 to yield orange/red crystals. Yield = 0.42 g (80%). (Anal. Found: C, 50.2; H, 4.4; Cl, 13.6; S, 12.0. Calcd for $C_{22}H_{22}Cl_2RuS_2$: C, 50.6; H, 4.2; Cl, 13.6; S, 12.3.) IR: $\nu$(Ru–Cl) 293 cm$^{-1}$.

The following compounds were prepared by a procedure analogous to method 1 for the halide complexes.

**$[(\eta^6\text{-}C_6H_6)Ru(1)Br]Br$.** Yield = 0.24 g (48%). (Anal. Found: C, 43.2; H, 3.7; Br, 26.5; S, 10.4. Calcd for $C_{22}H_{22}Br_2RuS_2$: C, 43.2; H, 3.6; Br, 26.2; S, 10.5). IR: $\nu$(Ru–Br) 214 cm$^{-1}$.

**$[(\eta^6\text{-}C_6H_6)Ru(2)Cl]Cl$.** Yield = 0.36 g (78%). (Anal. Found: C, 42.9; H, 3.5; Cl, 11.7; S, 10.6. Calcd for $C_{22}H_{22}Cl_2RuSe_2$: C, 42.9; H, 3.6; Cl, 11.5; S, 10.4.) IR: $\nu$(Ru–Cl) 289 cm$^{-1}$.

**$[(\eta^6\text{-}C_6H_6)Ru(2)Br]Br$.** Yield = 0.39 g (87%). (Anal. Found: C, 37.7; H, 3.0; Br, 22.7. Calcd for $C_{22}H_{22}Br_2RuSe_2$: C, 37.4; H, 3.1; Br, 22.7.) IR: $\nu$(Ru–Br) 218 cm$^{-1}$.

**X-ray Structure Determination.** Yellow-orange air-stable rhombic crystals were obtained by vapor diffusion of diethyl ether into a nitromethane solution of the product. Preliminary photographic X-ray examination established the space group and approximate cell dimensions. Crystallographic data are given in Table I. A Nicolet P3 diffractometer with graphite-monochromated Mo K$\alpha$ radiation was used. The final unit cell parameters were obtained from 25 centered reflections (6° < 2$\theta$ < 32°). The intensities of three check reflections (400), (060), and (002) measured after every 197 reflections showed isotropic decay <2%,

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**Table II.** Fractional Atomic Coordinates and Isotropic Thermal Parameters ($Å^2$)[a] for **3**

| atom | *x* | *y* | *z* | *U*(eq)[b] |
|---|---|---|---|---|
| Ru(1) | 0.53630(4) | 0.22433(3) | 0.55220(4) | 0.017(1) |
| S(1) | 0.5156(1) | 0.27357(4) | 0.3681(1) | 0.021(1) |
| S(2) | 0.6898(1) | 0.30080(4) | 0.6334(1) | 0.018(1) |
| N(1) | 0.6590(3) | 0.1587(2) | 0.5172(3) | 0.023(1) |
| C(1) | 0.4946(4) | 0.3658(2) | 0.3650(4) | 0.029(1) |
| C(2) | 0.6474(4) | 0.3897(2) | 0.6020(4) | 0.029(1) |
| C(3) | 0.6558(3) | 0.2663(2) | 0.3224(3) | 0.022(1) |
| C(4) | 0.8159(3) | 0.2901(2) | 0.5666(3) | 0.022(1) |
| C(5) | 0.7117(4) | 0.1127(2) | 0.5029(3) | 0.027(1) |
| C(6) | 0.7756(4) | 0.0514(2) | 0.4876(4) | 0.037(1) |
| C(7) | 0.8095(8) | 0.0118(3) | 0.5948(5) | 0.080(3) |
| C(11) | 0.4451(4) | 0.3928(2) | 0.4597(4) | 0.028(1) |
| C(12) | 0.5171(4) | 0.4030(2) | 0.5716(4) | 0.027(1) |
| C(13) | 0.4652(4) | 0.4280(2) | 0.6553(4) | 0.036(1) |
| C(14) | 0.3455(5) | 0.4441(2) | 0.6297(4) | 0.046(2) |
| C(15) | 0.2760(4) | 0.4357(3) | 0.5192(4) | 0.044(2) |
| C(16) | 0.3254(4) | 0.4100(2) | 0.4346(4) | 0.036(1) |
| C(21) | 0.7414(3) | 0.3235(2) | 0.3535(3) | 0.021(1) |
| C(22) | 0.8154(3) | 0.3339(2) | 0.4644(3) | 0.019(1) |
| C(23) | 0.8956(3) | 0.3872(2) | 0.4823(3) | 0.023(1) |
| C(24) | 0.9003(4) | 0.4319(2) | 0.3946(3) | 0.025(1) |
| C(25) | 0.8242(4) | 0.4228(2) | 0.2869(3) | 0.026(1) |
| C(26) | 0.7460(3) | 0.3693(2) | 0.2661(3) | 0.023(1) |
| C(31) | 0.4978(4) | 0.2067(2) | 0.7233(4) | 0.031(1) |
| C(32) | 0.4237(4) | 0.2589(2) | 0.6650(4) | 0.035(1) |
| C(33) | 0.3513(4) | 0.2480(2) | 0.5551(4) | 0.031(1) |
| C(34) | 0.3512(3) | 0.1847(2) | 0.4993(4) | 0.028(1) |
| C(35) | 0.4245(4) | 0.1340(2) | 0.5558(4) | 0.027(1) |
| C(36) | 0.4990(4) | 0.1445(2) | 0.6686(4) | 0.029(1) |
| B(1) | 0.0145(5) | 0.1755(3) | 0.4781(5) | 0.042(2) |
| F(11) | −0.0155(4) | 0.1629(4) | 0.5868(4) | 0.040(2)* |
| F(12) | 0.0696(3) | 0.2364(2) | 0.5022(4) | 0.069(2)* |
| F(13) | −0.0952(2) | 0.1801(1) | 0.3989(2) | 0.043(1) |
| F(14) | 0.041(7) | 0.102(4) | 0.490(9) | 0.149(16)* |
| F(15) | 0.027(5) | 0.128(3) | 0.546(5) | 0.155(25)* |
| F(16) | 0.0869(8) | 0.1619(7) | 0.383(2) | 0.059(5)* |
| F(17) | 0.0854(7) | 0.1302(6) | 0.4553(9) | 0.061(4)* |
| B(2) | 0.4617(5) | 0.0507(2) | 0.2827(4) | 0.033(2) |
| F(21) | 0.3947(2) | 0.0063(1) | 0.2014(2) | 0.037(1) |
| F(22) | 0.3951(3) | 0.1068(1) | 0.2910(2) | 0.044(1) |
| F(23) | 0.5615(3) | 0.0705(1) | 0.2454(2) | 0.045(1) |
| F(24) | 0.5004(3) | 0.0190(1) | 0.3874(2) | 0.048(1) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] An asterisk indicates partial atom occupancy [F(11), 0.66(2), F(12) 0.94(1), F(14) 0.28(6), F(15) 0.24(5), F(16) 0.32(2), F(17) 0.57(3)].

which was corrected for during processing. The data were processed[18] and corrected for Lorentz and polarization effects and absorption (empirical $\psi$-scan absorption correction based on six reflections).

The Ru and S atoms were found by direct methods,[18] and subsequent iterative cycles of least-squares refinement and difference Fourier synthesis[18] yielded all non-H atoms. One of the $BF_4^-$ anions displayed a not atypical disorder, as shown by large temperature factors for the F atoms and a number of alternative F positions. The disorder was modeled by allowing partial occupation of sites by some F atoms. The site occupancies account for the required four F atoms. Non-H atoms were refined, by full-matrix least squares, with anisotropic thermal parameters. H atoms were placed in fixed calculated positions. Neutral-atom scattering factors and anomalous dispersion corrections were inlaid[18] or taken from ref 19. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table II, and selected bond lengths and angles, in Table III. Tables of complete bond lengths and angles, hydrogen atom parameters, and thermal parameters are included as supplementary material.

## Results and Discussion

**Preparation and Properties of the Complexes.** Treatment of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with $AgBF_4$ in acetone or acetonitrile provides a convenient source of the $[(\eta^6\text{-}C_6H_6)Ru]^{2+}$ moiety, which will react readily with **1** or **2** to form orange air-stable salts $[(\eta^6\text{-}C_6H_6)Ru(E\text{-}E)(L)][BF_4]_2$ (E-E = **1**, **2**; L = MeCN, EtCN) with **1** or **2** bound in a bidentate fashion. No complexes where L is acetone were detected. Careful manipulation of the reaction conditions can be used to determine the product formed. We have already investigated the reaction of a 0.75:1 mole ratio of **1** and $[(\eta^6\text{-}C_6H_6)Ru]^{2+}$ in refluxing acetone which yields $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})][BF_4]$ (**4**).[2] Under these conditions a hydrogen atom is lost and cyclometalation, involving one of the bridge carbons $\alpha$ to the coordinated sulfur, occurs forming a three-membered ring containing the Ru(II), the carbanion, and a coordinated sulfur. The analogous reaction involving **2** is not seen to occur under these conditions.

The reactions of a 1:1 mole ratio of $[(\eta^6\text{-}C_6H_6)Ru]^{2+}$ and **1** or **2** when carried out in acetonitrile or propionitrile, rather than acetone, gave excellent yields of the four complexes $[(\eta^6\text{-}C_6H_6)Ru(E\text{-}E)(L)][BF_4]_2$ (E-E = **1**, **2**; L = MeCN, EtCN) containing the coordinated alkanenitriles. Alternatively, $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})(MeCN)][BF_4]_2$ can be prepared by reacting **1** directly with the tris(acetonitrile) complex $[(\eta^6\text{-}C_6H_6)Ru(MeCN)_3][BF_4]_2$. The MeCN complexes are labile in solution. Exchange of the bound MeCN with deuteroacetonitrile ($d_3$-MeCN) could easily be achieved by dissolving small amounts of the complexes in $d_3$-MeCN and stirring at room temperature for 16 h. $^1H$ NMR studies clearly showed the appearance of free MeCN accompanied by the virtual removal of the signal due to coordinated MeCN. By contrast, the EtCN complexes are not labile in solution. Dissolution of the EtCN complexes into acetonitrile solution provided only starting material. If the MeCN complexes were recrystallized or heated in nitromethane, the resulting compounds recovered were, without exception, those of the analogous EtCN complexes, formed from the minute impurity contained in the solvent. This is a surprising result considering that acetonitrile and propionitrile are expected to be present in nitromethane in only trace quantities, near the limits of detection.[20] $^1H$ NMR spectra of the nitromethane solvent used for recrystallization confirmed propionitrile to be present in <0.1 mol %. Similarly, if **4** was prepared in nitromethane, a large amount (*ca.* 70%) of the EtCN complex was isolated. Further, prolonged reflux of $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})(MeCN)][BF_4]_2$ in propionitrile-free nitromethane produced significant amounts (*ca.* 25%) of the cyclometalated derivative **4**, identified from $^1H$ NMR, although its production was accompanied by some decomposition. These results confirm that the EtCN–Ru bond is much less labile than the corresponding MeCN–Ru bond. They also demonstrate the inability of **1** or **2** to neutralize the positive charge on the Ru(II) ion,[8] requiring the complex to scavenge for the most effective donor available; thus, the more strongly binding EtCN or a carbanion formed from **1** is preferred over MeCN as a ligand. In the same way "noncoordinating" counterions such as $CF_3SO_3^-$ or $ClO_4^-$ are often found bound in complexes of the thioethers.[8]

Substitution of the alkanenitrile ligands for chloride or bromide to prepare the four complexes $[(\eta^6\text{-}C_6H_6)Ru(E\text{-}E)(X)]X$ (E-E = **1**, **2**; X = Cl, Br) was simply achieved by stirring solutions (nitromethane or acetonitrile) of the nitrile-containing complexes $[(\eta^6\text{-}C_6H_6)Ru(E\text{-}E)(L)][BF_4]$ (E-E = **1**, **2**; L = MeCN, EtCN) in the presence of the appropriate tetraalkylammonium halide. Prolonged exposure to excess bromide resulted in displacement of the coordinated dithiacyclophane as well as the nitrile ligand, to yield a brown, insoluble solid which analyzed as $[(\eta^6\text{-}C_6H_6)RuBr_2]_2$. The chloro complex $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})(Cl)]Cl$ can also

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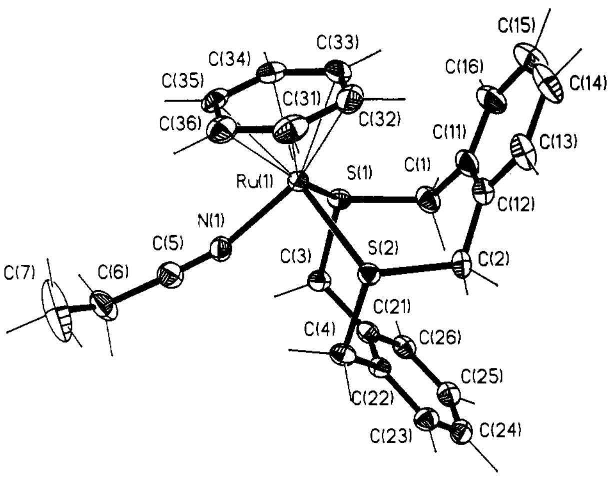

**Figure 2.** View of cation **3** (crystallographic numbering). Thermal ellipsoids are drawn with boundary surfaces at the 50% level.

**Table III.** Selected Bond Lengths (Å) and Angles (deg) for **3**

| | | | |
|---|---|---|---|
| Ru(1)–S(1) | 2.379(1) | N(1)–C(5) | 1.138(5) |
| Ru(1)–S(2) | 2.364(1) | C(1)–C(11) | 1.502(5) |
| R(1)–N(1) | 2.060(3) | C(2)–C(12) | 1.494(5) |
| S(1)–C(1) | 1.850(4) | C(3)–C(21) | 1.497(5) |
| S(1)–C(3) | 1.859(4) | C(4)–C(22) | 1.506(5) |
| S(2)–C(2) | 1.849(4) | C(5)–C(6) | 1.466(6) |
| S(2)–C(4) | 1.858(4) | C(6)–C(7) | 1.477(7) |
| Ru–C | 2.219(4)[a] | | 2.245(4)[b] |
| arene C–C | 1.381(7)[a] | | 1.430(6)[b] |
| B–F | 1.24(3)[a] | | 1.61(2)[b] |
| S(1)–Ru(1)–S(2) | 90.4(1) | C(2)–S(2)–C(4) | 102.8(2) |
| S(1)–Ru(1)–N(1) | 89.0(1) | Ru(1)–N(1)–C(5) | 166.0(3) |
| S(2)–Ru(1)–N(1) | 90.0(1) | S(1)–C(1)–C(11) | 114.5(3) |
| Ru(1)–S(1)–C(1) | 114.1(1) | S(2)–C(2)–C(12) | 115.0(3) |
| Ru(1)–S(1)–C(3) | 110.8(1) | S(1)–C(3)–C(21) | 116.6(3) |
| C(1)–S(1)–C(3) | 101.2(2) | S(2)–C(4)–C(22) | 116.7(3) |
| Ru(1)–S(2)–C(2) | 113.3(1) | N(1)–C(5)–C(6) | 176.9(4) |
| Ru(1)–S(2)–C(4) | 110.3(1) | C(5)–C(6)–C(7) | 111.4(4) |

[a] Minimum. [b] Maximum.

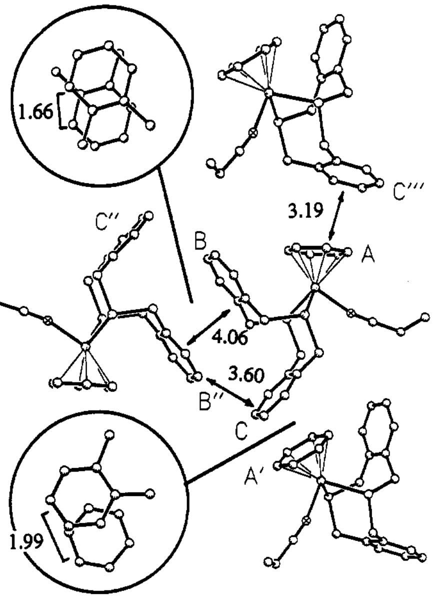

**Figure 3.** Intermolecular $\pi$–$\pi$ interactions observed in the crystal structure of **3**. Distances (Å) are for average contacts between rings. The auxiliary views show the extent of the overlap of arene rings A′, C and B, B″ and give distances (Å) between ring centers.

be prepared by the direct reaction of **1** with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$. Attempts to produce iodo analogues resulted in deep red precipitates of varying compositions.

While the halide counterion in the complexes of $[(\eta^6\text{-}C_6H_6)Ru(E\text{-}E)X]X$ (E-E = **1**, **2**; X = Cl, Br) could easily be exchanged by recrystallization in the presence of $NH_4BF_4$, the coordinated halide could not be removed even by employing an excess of $AgBF_4$ in refluxing acetonitrile. Continued reflux (>1 h) did result in some decomposition.

**X-ray Structure of 3.** The single-crystal X-ray structure of **3** (Figure 2) shows the Ru atom to be six-coordinate. The $(\eta^6\text{-}C_6H_6)Ru$ moiety is bound to EtCN and the S atoms of **1** in a "piano stool" configuration. Bond angles about the central Ru, involving **1** and the nitrile, are virtually 90°. EtCN is bound end-on through N. The Ru-N-C angle of 166.0(3)° deviates considerably from that expected for linear coordination (175 ± 5°).[21] This deviation is not inconsistent with increased $\pi$-donation by the nitrile[22] to compensate for the inability of **1** to neutralize the positive charge on the Ru(II) ion.[8] Crystal packing interactions with the rigid nitrile framework may also contribute to this deviation.[23] The ethyl group of EtCN experiences a number of short <2.8-Å nonbonded intermolecular contacts. Previously reported Ru–nitrile bond lengths range from 2.02 to 2.17 Å.[9,24] The Ru–N bond length (2.060(3) Å) is at the short end of this range and is shorter than values found in other Ru–nitrile complexes containing thioethers.[9] The nonlabile nature of coordinated EtCN, in contrast to MeCN, in this complex may reflect the shortness of this bond.

Previously reported Ru–thioether bond distances range from 2.26 to 2.43 Å[8,9] with values being particularly sensitive to the nature and arrangement of the other ligands in the coordination sphere. The Ru–S distances are at the long end of this range but are comparable with those found in $[Ru(12S3)_2]^{2+}$.[25] The distances are, on average, 0.04 Å longer than those in the closely related **4**.[2] The ligand adopts the *anti-II* conformation (Figure 1) in which the benzene rings are 104.6° to each other and fold away from the sulfurs. This is in contrast to an *anti* conformation with benzene rings essentially parallel and exodentate sulfur atoms proposed for **1** in solution[5,6] and found in the solid state.[5] Molecular mechanical calculations[5,6] suggest that of the three *anti* conformations considered most likely for **1**, *anti-II* is the least favored in solution. The *anti-II* conformation is also found, but in more distorted fashion, in **4**; here the benzene rings are 130.6° to each other. That **1** is able to act as an effective ligand in both complexes reflects the relatively low barrier to conformational rearrangement[5,6] and the large ring size, which provide sufficient steric flexibility to allow the donor atoms to be accommodated in the coordination sphere of the metal cation.

In the solid-state the cations are held together by a series of electrostatic interactions involving the arene rings on each cation. There are two distinct types of interactions (Figure 3). The first type of interaction is an offset $\pi$–$\pi$ interaction[26] and involves the $\eta^6$-benzene (ring A) of one cation and a cyclophane arene (ring C‴) on an adjacent cation. Crystal symmetry propagates this

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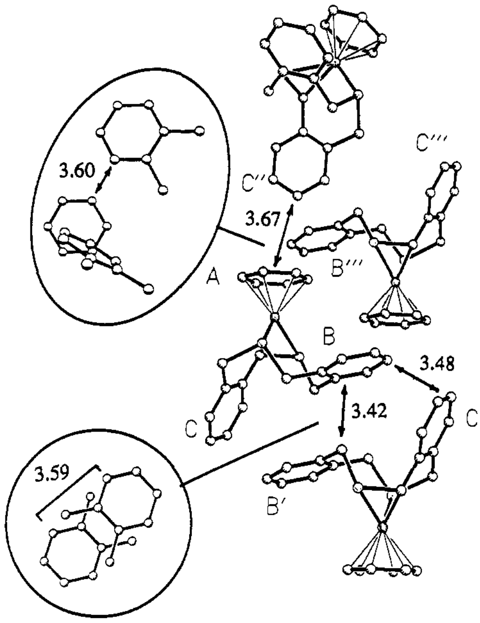

**Figure 4.** Intermolecular $\pi$–$\pi$ interactions observed in the crystal structure of **4**. Distances (Å) are for average contacts between rings. The auxiliary views show the extent of the overlap of arene rings B, B′ and the arrangement of rings C″, B‴ about ring A.

interaction so that chains of identical offset $\pi$–$\pi$ interactions are generated throughout the structure. The distance between the planes of the rings (3.19 Å)[27] and the value of shortest inter-ring contacts (3.07–4.09 Å) are generally much less than expected from the sum of the van der Waals "half-thickness" of the two benzene rings and suggest the presence of strong interactions between the rings of the cations. The second types of interactions are weaker and involve the formation of a cavity with parallel sides formed by the xylyl units rings B and C and symmetry-related units (rings B″ and C″) on an adjacent cation. The cavity is held together by edge-to-face interactions between the arene rings and also interactions between the $CH_2$ hydrogens of the xylyl moieties, which will have small positive charges, and the $\pi$-electrons of the rings. While the close contacts (3.60–3.65 Å) involved in the second types of interactions are longer than those in the first type of interaction, they are consistent with other systems in which weak $\pi$–$\pi$ interactions have been identified.[26]

The solid-state structure of the closely related compound **4**[2] was also investigated for similar $\pi$–$\pi$ interactions. **4** shows an even more extensive series of electrostatic interactions than **3** (Figure 4). All arene rings are involved in more than one interaction. A series of edge-to-face and $CH_2$-to-ring interactions form a cavity similar to that found for **3**. However, in **4** the cavity is capped top and bottom (not shown in Figure 4) by rings related to C″ giving a distorted-octahedral shaped arrangement of cyclophane arene rings. Rings C″, B‴, and C‴ form the trigonal face of a similar distorted-octahedral cavity in the next sheet. Symmetry causes an alternation in the roles of the rings forming the cavities. Thus, rings C and C′ also act as capping rings in forming the two adjacent cavities and the capping rings also adopt the role of rings C and C′ in forming two other adjacent cavities. The rings of type B participate in forming only one cavity and may also interact with the $\eta^6$-benzene rings A. Every $\eta^6$-benzene ring A is involved in a more important edge-to-face interaction with rings of type C″.

The solid-state structures of **3** and **4** taken together illustrate the variety of $\pi$–$\pi$ interactions possible in metal complexes containing cyclophane ligands. While the two structures have features in common, for example, the edge-to-face and $CH_2$-to-ring interactions which produce similar shaped cavities in both compounds, they also display one of the two extremes of attractive $\pi$–$\pi$ interactions, namely, offset $\pi$-stacking interactions in **3** and edge-to-face interactions in **4**. Clearly, the type of $\pi$-interactions found in a structure is very sensitive to the way in which the cyclophane ligand is folded.

**Spectroscopic Properties.** The NMR data indicate that in solution all of the complexes have a similar structure to **3**, with the cyclophane ligands adopting an *anti-II* conformation.

**$^1$H NMR Spectra.** Data are presented in Table IV. All the cyclophane complexes show a strong singlet in the region $\delta$ = 5.3–5.7 ppm which can be assigned to the $\pi$-bound benzene ring. Other aromatic protons appear in the 7.4–7.5 ppm region. Of most interest are the signals due to the protons in the methylene bridges. The cyclophane is rigidly bound in the *anti-II* conformation with $C_s$ symmetry and so has two distinct methylene types; type 1 methylene carbons are those which are analogous to C(1) and C(2), while type 2 carbons are those analogous to carbons C(3) and C(4) of **3** (Figure 2). Each type contains nonequivalent protons which are axial and equatorial with respect to the cyclophane ring. The resulting spectrum in this region, then, consists of two pairs of AB doublets. The large range of chemical shifts (2.7–5.5 ppm) reflects the widely differing environments of these protons. Models based on the crystal structures of **3** and **4** show that for all the complexes axial protons of type 1 point toward the opposing aromatic ring of the cyclophane and hence are more shielded than the other protons: chemical shifts range from 3.09 to 3.13 ppm (E-E = **1**) and from 2.75 to 2.77 ppm (E-E = **2**). Axial protons of type 2 point toward the sixth ligand, L, and hence are highly sensitive to the nature of this ligand. This is conveniently illustrated by the inclusion of the highly electronegative halide ligands which result in considerable deshielding as evidenced by the marked shift of these signals to higher frequency. The equatorial protons are less affected by these types of steric and electronic influences. Their chemical shifts lie in the range 3.87–4.2 ppm (E-E = **1**) and 4.17–4.35 ppm (E-E = **2**). Assignments of the equatorial protons are based on matching the $^2J_{H-H}$ coupling constants with the axial protons and are confirmed by HETCOR NMR experiments. Complexes of **2** exhibited $^2J_{Se-H}$ coupling in the form of satellites. These were sometimes difficult to measure but where seen were *ca.* 11–15 Hz.

**$^{13}$C NMR Spectra.** The spectra are unexceptional, and chemical shift data are reported in Table V. A singlet due to the $\pi$-bound benzene ring occurs between 76 and 88 ppm. Other aromatic carbons lie in the range 125–132 ppm. Two signals due to the methylene bridges occur in the regions 28.8–33.9 (E-E = **1**) and 26.2–28.0 ppm (E-E = **2**). These are assigned using HETCOR experiments. The bridge carbons remote from the sixth ligand L are little affected by it, and their chemical shifts vary only by ±1ppm whereas those in close proximity to L can vary by as much as 5 ppm. This can have the effect of changing the relative positions of the two signals; *i.e*, the bridge carbons closest to the ligand L can appear to high or low frequency of the remote bridges, depending upon the nature of L. In the nitrile complexes the chemical shift of the nitrile carbon moves to higher frequency upon coordination compared to the free nitrile. The shifts are fairly uniform (*ca.* 12 ppm) for the MeCN and EtCN complexes.

**IR Spectra.** The spectra are similar for all the complexes and so give no indication as to why the MeCN complexes are more labile than the EtCN complexes. The values of the $\nu$(CN) stretches for all the nitrile complexes are quite similar and lie in the narrow range 2290–2294 cm$^{-1}$. The $\nu$(CN) values have all increased by *ca.* 42 cm$^{-1}$ from that of the uncomplexed nitrile. The $\Delta\nu$(CN) values do not seem to be directly related to the donor strength of the nitrile. Such an observation has been found previously.[23] The far-IR spectra of the halide complexes show

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(27) The planes are inclined by 17° to each other, and the value was obtained by averaging the two distances between each center of the least-squares plane defined by one benzene ring and the least-squares plane of the other ring.

**Table IV.** $^1$H NMR Data for the Complexes[a]

| compd | $\eta^6$-$C_6H_6$ | RCN | $CH_2$ type 1[b] ax, eq [$^2J_{H_a\text{-}H_e}$ (Hz)] | $CH_2$ type 2[b] ax eq [$^2J_{H_a\text{-}H_e}$ (Hz)] | $C_6H_6$ |
|---|---|---|---|---|---|
| $[(\eta^6\text{-}C_6H_6)Ru(MeCN)_3](BF_4)_2$ | 6.28 | 2.53 (s) | | | |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})(MeCN)](BF_4)_2$ | 5.71 | 2.74 (s) | 3.13 (d), 4.17 (d) [12.8] | 4.44 (d), 4.22 (d) [14.5] | 7.49 (s), 7.51 (s) |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})(EtCN)](BF_4)_2$ (**3**) | 5.71 | 1.40 (t) ($CH_3$), 3.11 (q) ($CH_2$), $^3J_{H\text{-}H} = 7.5$ Hz | 3.13 (d), 4.17 (d) [12.8] | 4.44 (d), 4.20 (d) [14.6] | 7.49 (s), 7.51 (s) |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})Cl]Cl$ | 5.40 | | 3.09 (d), 4.07 (d) [12.9] | 5.30 (d), 3.87 (d) [13.8] | 7.42 (s), 7.47 (s) |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})Br]Br$ | 5.45 | | 3.10 (d), 4.12 (d) [12.8] | 5.47 (d), 4.09 (d) [13.9] | 7.44 (s), 7.49 (s) |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{2})(MeCN)](BF_4)_2$ | 5.63 | 2.75 (s) | 2.76 (d), 4.17 (d) [11.8] | 4.50 (d), 4.35 (d) [12.7] | 7.46 (s), 7.48 (s) |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{2})(EtCN)](BF_4)_2$ | 5.63 | 1.41 (t) ($CH_3$), 3.11 (q) ($CH_2$), $^3J_{H\text{-}H} = 7.5$ Hz | 2.77 (d), 4.17 (d) [11.8] | 4.52 (d), 4.32 (d) [12.6] | 7.45 (s), 7.48 (s) |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{2})Cl]Cl$ | 5.31 | | 2.71 (d), 4.06 (d) [11.8] | 5.31 (d), 3.99 (d) [11.9] | 7.40 (s), 7.43 (s) |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{2})Br]Br$ | 5.36 | | 2.75 (d), 4.08 (d) [11.9] | 5.51 (d), 4.15 (d) [12.2] | 7.39 (s), 7.45 (s) |

[a] $CD_3NO_2$ solution, $\delta$, ppm. [b] Type 1 and type 2 refer to the two distinct methylene types when **1** or **2** adopt an *anti-II* conformation (see text); ax = axial, and eq = equatorial.

**Table V.** $^{13}$C NMR Data for the Complexes[a]

| compd | $\eta^6$-$C_6H_6$ | RCN | CN | $CH_2$ type 1[b] | $CH_2$ type 2[b] | $C_6H_6$[c] |
|---|---|---|---|---|---|---|
| $[(\eta^6\text{-}C_6H_6)Ru(MeCN)_3](BF_4)_2$ | 83.96 | −1.65 | 123.96 | | | |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})(MeCN)](BF_4)_2$ | 88.35 | −0.09 | 125.01 | 33.03 | 33.90 | 126.53, 126.71, *127.62*, 129.12, *130.47*, 131.71 |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})(EtCN)](BF_4)_2$ (**3**) | 88.43 | 4.05, 9.44 | 133.75 | 33.04 | 33.77 | 126.55, 126.72, *127.54*, 129.13, *130.43*, 131.73 |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})Cl]Cl$ | 85.70 | | | 32.88 | 28.86 | 125.72, 126.22, 128.88, 131.43 |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{1})Br]Br$ | 85.76 | | | 33.33 | 31.90 | 125.63, 126.20, 129.03, 131.49 |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{2})(MeCN)](BF_4)_2$ | 86.56 | −0.27 | 130.09 | 27.94 | 26.40 | 126.08, 126.26, *128.60*, 128.72, *130.29*, 130.88 |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{2})(EtCN)](BF_4)_2$ | 86.64 | 4.19, 9.32 | 133.22 | 27.97 | 26.24 | 126.10, 126.26, *128.54*, 128.72, *130.25*, 130.89 |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{2})Cl]Cl$ | 84.06 | | | 27.37 | 22.55 | 125.32, 125.77, 128.53, 130.77 |
| $[(\eta^6\text{-}C_6H_6)Ru(\mathbf{2})Br]Br$ | 84.15 | | | 27.93 | 25.09 | 125.32, 125.84, 128.68, 130.83 |

[a] $CD_3NO_2$ solution, $\delta$, ppm. [b] Type 1 and type 2 refer to the two distinct methylene types when **1** or **2** adopt an *anti-II* conformation (see text). [c] When observed the ipso carbons are given in italics.

many common features confirming the NMR-based assessment that all of the complexes are isostructural. The $\nu$(RuX) stretch is readily assigned by a comparison of the spectra and is not particularly sensitive to the nature of the cyclophane ligand.

## Conclusion

Eight new ($\pi$-benzene)ruthenium(II) dichalcogenoether compounds have been prepared. They demonstrate the ability of dithio- and diselenoethers to act as effective ligands. This work has shown that labile complexes can be prepared which involve loss of a ligand L rather than loss of a thio- or selenoether ligand as is usually the case in $\pi$-arene–Ru(II) thioether complexes.[11] The complexes display a range of Ru–L bond lability, illustrating how sensitive the electronic properties of the Ru center are to the nature of the ligand L in these systems. This sensitivity is brought about by the poor donor abilities of the dichalcogenoethers, which are not able to provide for electrical neutrality at the Ru center, and this in turn exaggerates the donor properties of ligand L. Finally, this work has shown that metal complexes of the derivatized cyclophanes, like cyclophane systems themselves,[28] may display considerable and important $\pi$–$\pi$ interactions. It further suggests that metal moieties may be able to be used to modify and control the nature of $\pi$-stacking in such systems. These complexes of the derivatized cyclophanes will provide useful synthetic precursors as their chemistry and reactivity is further investigated by us.

**Acknowledgment.** We thank the New Zealand University Grants Committee for a postdoctoral fellowship (T.K.) and the University of Otago for financial support. We are grateful to Dr. Ward T. Robinson (University of Canterbury) for X-ray data collection and to Dr. Chris A Hunter (University of Sheffield) for helpful discussions.

**Supplementary Material Available:** Tables of data collection and refinement details, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters (5 pages). Ordering information is given on any current masthead page.

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