*Organometallics* **2005,** *24,* 4265−4273

# Square Planar versus Tetrahedral $NiS_4$ Cores in the Coordination Spheres of (HMB)Ru(II) and Cp*Ru(III) and a Related $CuS_4$ Complex. Synthetic, Single-Crystal X-ray Diffraction, and Magnetic Studies {HMB = $\eta^6$-$C_6Me_6$ and Cp* = $\eta^5$-$C_5Me_5$}

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*Received March 17, 2005*

The reaction of [LRu($\kappa^3$*SSS′*-tpdt)] (L = $\eta^6$-$C_6Me_6$ (HMB), (**1**); L = $\eta^5$-$C_5Me_5$ (Cp*), (**2**); tpdt = $S(CH_2CH_2S^-)_2$) with $Cl_2Ni(PPh_3)_2$ gave diamagnetic trinuclear complexes, [{(HMB)-$Ru^{II}$($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)}$_2$$Ni^{II}$]$^{2+}$ (**3**) and [{Cp*$Ru^{III}$($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)}$_2$$Ni^{II}$]$^{2+}$ (**4**), isolated as hexafluorophosphate salts in 96 and 61% yields, respectively. A similar reaction of **2** with $CuSO_4$ in excess gave a dinuclear species, [Cp*$Ru^{III}$($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)$Cu^{II}$-$(CH_3CN)_2$]$^{2+}$ (**5**) (73% yield, as $PF_6^-$ salt), which further reacted with 1 molar equiv of **2** to give a paramagnetic complex, [{Cp*$Ru^{III}$($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)}$_2$$Cu^{II}$]$^{2+}$ (**6**) (81% yield, as $PF_6^-$ salt), or 1 molar equiv of **1** to give the “mixed-ring” tpdt dithiolate-bridged diamagnetic complex [{Cp*$Ru^{III}$($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)}$Cu^{II}${(HMB)$Ru^{II}$($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt}]$^{2+}$ (**7**) (89% yield, as $PF_6^-$ salt). The molecular structures of complexes **3**−**7** were determined by single-crystal X-ray diffraction analysis. Notably it was observed that the trimetallic array Ru−M−Ru possesses a M−M bond between the central metal atom (Ni(II) or Cu(II)) and terminal Ru atoms in +3 oxidation state, i.e., Ru atoms bearing a Cp* ligand. Thus, while Ni is in a square planar environment in **3**, in the other trinuclear complexes, viz., **4**, **6**, and **7**, Ni/Cu is in a slightly distorted tetrahedral environment with respect to the four thiolate S donors, but is formally five- or six-coordinate, in the presence of one or two M−M bonds, respectively. Variable-temperature magnetic susceptibility studies on neat powders of representative compounds **2**, **3**, **4**, and **6** show $S = {}^1/_2$ Curie-like behavior for mononuclear Ru(III) complex **2**, as expected, and also for the trinuclear {Ru(III)Cu(II)Ru(III)} complex **6**, the behavior of the latter being ascribed either to a 19e electron count on Cu, involving Ru−Cu bonding, or to a strongly antiferromagnetically coupled {Ru(III)($S = {}^1/_2$)Cu(II)($S = {}^1/_2$)Ru(III)($S = {}^1/_2$)} sulfur-bridged moiety. Complexes **3** and **4**, having oxidation states Ru(II)Ni(II)Ru(II) and Ru(III)Ni(II)Ru(III), respectively, are close to being diamagnetic but display very weak paramagnetism between 4.2 and 300 K.

## Introduction

The continuing intense interest in transition metal complexes containing sulfur donor ligands is stimulated by their significant relevance to biological and industrial processes.[1] This area of chemistry abounds with complexes of mono- and bidentate thiolates,[2] as well homo- or hetero-polynuclear compounds containing bridging monothiolates ($RS^-$);[3] but complexes containing dithiolate bridging ligands ($^-SRS^-$) are less common, especially those of the heterometallic variety.[4] Also rare are compounds containing tridentate dithiolate-thioether ligands such as 3-thiapentane-1,5-dithiolate, $S(CH_2CH_2S^-)_2$ (tpdt), in a bridging mode. The literature

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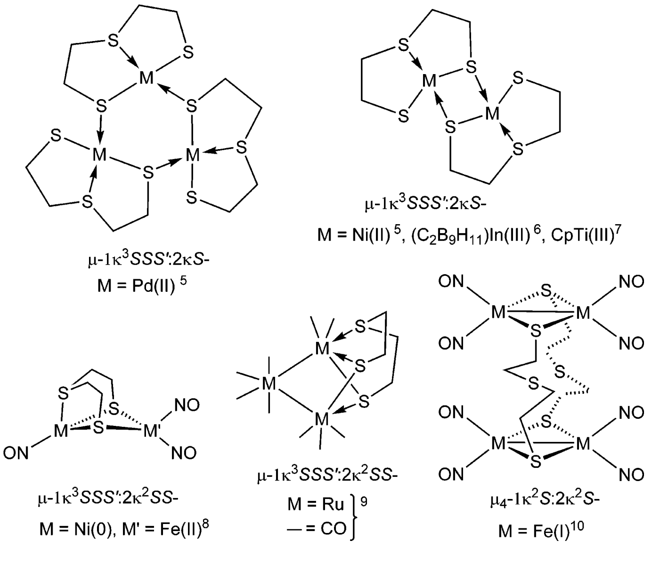
(1) See, for instance, the following and the references therein: (a) Rauchfuss, T. B. *Inorg. Chem.* **2004**, *43*, 14. (b) *Transition Metal Sulfur Chemistry−Biological and Industrial Significance*; Stiefel, E. I.; Matsumoto, K., Eds.; ACS Symposium Series 653; 1996. (c) Howard, J. B.; Rees, D. C. *Chem. Rev.* **1996**, *96*, 2965. (d) Sellman, D.; Sutter, J. *Acc. Chem. Res.* **1997**, *30*, 460. (e) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983. (f) Dubois, M. R. *Chem. Rev.* **1989**, *89*, 1. (g) Curtis, M. D.; Druker, S. H. *J. Am. Chem. Soc.* **1997**, *119*, 1027. (h) Bianchini, C.; Meli, A. *Acc. Chem. Res.* **1998**, *31*, 109. (i) Sánchez-Delgado, R. A. *J. Mol. Catal.* **1994**, *86*, 287. (j) Holm, R. H.; Ciurli, S.; Weigel, J. A. *Prog. Inorg. Chem.* **1990**, *38*, 1.

10.1021/om050200p CCC: \$30.25

**Chart 1. Tpdt-Bridged Compounds**



shows only a few examples of such compounds with bonding modes illustrated in Chart 1.

Our previous studies have shown that the $\eta^3$-tpdt complexes of Ru, viz., [(HMB)Ru$^{II}$($\kappa^3$*SSS*′-tpdt)] (**1**)[11] and [Cp*Ru$^{III}$($\kappa^3$*SSS*′-tpdt)] (**2**),[12] readily function as metallodithiolate ligands, with tpdt bridging via the two dithiolate sulfur atoms in $\mu$-1$\kappa^3$*SSS*′:2$\kappa^2$*SS*-bonding mode. Thus, the thiolate sulfur donors in both complexes can initiate nucleophilic displacement of chloro ligands in their respective precursor complexes $[LRuCl_2]_2$ (**1A**: L = $\eta^6$-$C_6Me_6$ (HMB); **2A**: L = $\eta^5$-$C_5Me_5$ (Cp*), respectively)[11,12] and a similar $\mu$-dichoro ruthenium dimer [Ru$^{II}$(COD)$Cl_2$]$_n$,[13] forming dithiolate-bridged diruthenium complexes **A**, **B**, and **C** (see Chart 2). A notable difference lies in the presence of a metal−metal bond for those complexes containing a Cp*Ru(III) moiety, in agreement with the demands of the 18e rule. It was also observed that in the reaction between **1** and **2A** the participation of redox processes between the Ru(II) center of **1** and the Ru(III) center of **2A** gave rise to trinuclear species **D** and **E**.[13] These reactivity features had suggested to us the probable role of **1** and **2** in the generation of thiolate-bridged heterobimetallic complexes. In view of general interest in heterometallic complexes for several reasons, which include variety in their patterns of bonding modes, and solid state and catalytic applications,[14] we have explored that possibility, since bridging by thiolate-thioether ligands is virtually unknown in heterometallic chemistry. Indeed, we have found that nucleophilic displacements of chloro ligands at metal centers of groups 14 and 10 have generated di- and tri-heteronuclear species of types **F**[15] and **G**,**H**.[16]

This paper describes comparative results with Ni(II) and Cu(II) systems and a magnetic study of the new complexes formed.

## Results and Discussion

**Syntheses. Reaction with $Cl_2Ni(PPh_3)_2$.** The reaction of [LRu($\kappa^3$*SSS*′-tpdt)] {L = HMB (**1**), Cp* (**2**), tpdt = $S(CH_2CH_2S^-)_2$} with 1.0 molar equiv of $Cl_2Ni(PPh_3)_2$ gave the trinuclear cationic complexes [{LRu($\mu$-1$\kappa^3$*SSS*′:2$\kappa^2$*SS*-tpdt)}$_2$Ni]$^{2+}$ (L = HMB (**3**), L = Cp* (**4**)), which were isolated as black crystals of their $PF_6$ salts in 96 and 61% yields, respectively, after $PF_6$ metathesis. The thiolate S atoms of **1** and **2** act as effective nucleophiles for the displacement of *all* the $PPh_3$ and chloride ligands of Ni, as shown in Scheme 1; in contrast, the $PPh_3$ ligands in $Cl_2Pt(PPh_3)_2$ cannot be displaced, thus resulting in the dinuclear complexes, **J**.[16] This observation is in agreement with the much higher lability of Ni(II) versus Pt(II).

For reasons not immediately clear to us at present, there exist both the *cis* and *trans* isomers for the Pd and Pt analogues;[16] only the *trans* orientation of the arene rings is found in **3**. For the trinuclear Cp*Ru(III) compounds, the tetrahedral configuration of the $NiS_4$ moiety in **4** was found also for Pd, but not for Pt, which contains a square planar $MS_4$ core.

**Reaction with $CuSO_4$.** The reaction of **2** with an excess of $CuSO_4$ gave brown solids of [Cp*Ru($\mu$-1$\kappa^3$*SSS*′:

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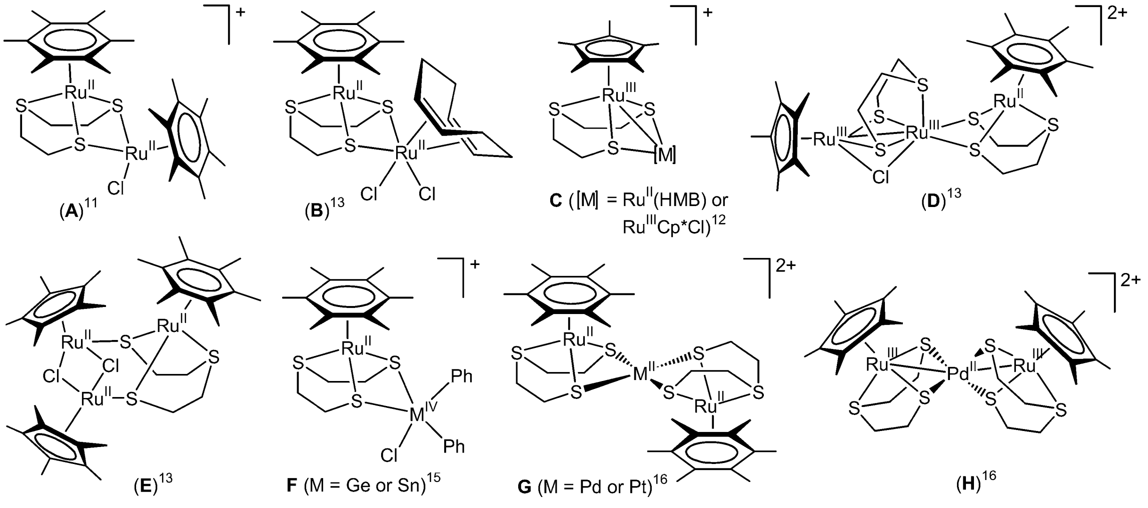
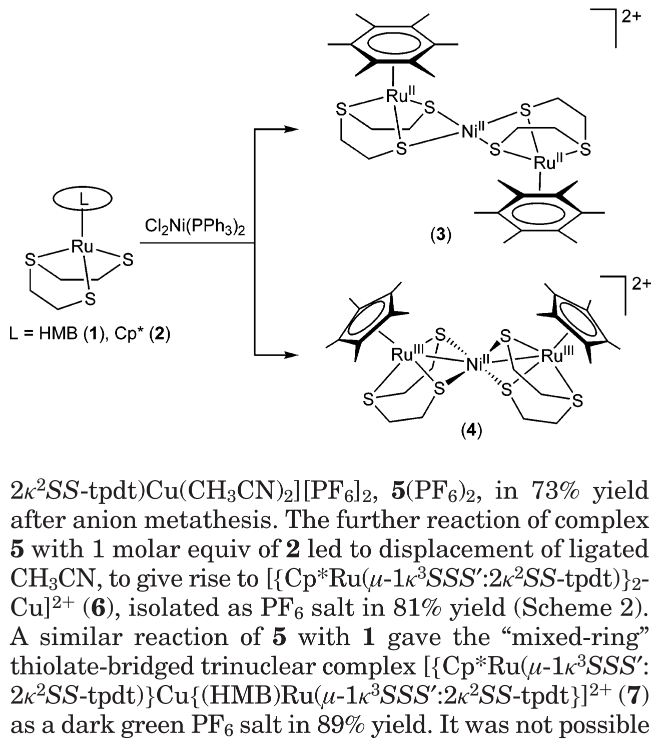
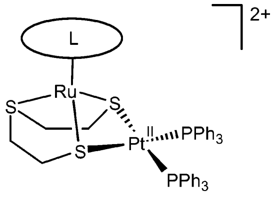
**Chart 2**



**Scheme 1**





(J) {L = HMB, Ru(II); Cp*, Ru(III)}

$2\kappa^2SS$-tpdt)Cu($CH_3CN$)$_2$][$PF_6$]$_2$, **5**($PF_6$)$_2$, in 73% yield after anion metathesis. The further reaction of complex **5** with 1 molar equiv of **2** led to displacement of ligated $CH_3CN$, to give rise to [{Cp*Ru($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)}$_2$-Cu]$^{2+}$ (**6**), isolated as $PF_6$ salt in 81% yield (Scheme 2). A similar reaction of **5** with **1** gave the "mixed-ring" thiolate-bridged trinuclear complex [{Cp*Ru($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)}Cu{(HMB)Ru($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt}]$^{2+}$ (**7**) as a dark green $PF_6$ salt in 89% yield. It was not possible to obtain **6** from a direct stoichiometric reaction of **2** with $CuSO_4$, which gave a brownish black oil, containing **6** in only negligible quantity.

We have obtained the Cu(I) analogue of **6** from the reaction of **2** with [Cu(MeCN)$_4$][$PF_6$].[17]

**Crystallographic Studies.** The molecular structures of complexes **3**−**7** have been determined by single-crystal diffraction analyses and are shown in Figures 1−5. Significant bond parameters are collectively given in Table 1. The dicationic nature of the complexes is in agreement with the oxidation states of the metal atoms in the precursor compounds, viz., as follows: **3** (Ru(II)-Ni(II)Ru(II)), **4** (Ru(III)Ni(II)Ru(III)), **5** (Ru(III)Cu(II)), **6** (Ru(III)Cu(II)Ru(III)), and **7** (Ru(III)Cu(II)Ru(II)).

The molecular structure of **3** possesses a center of inversion at Ni(II), with coordination to the thiolate S atoms of two [(HMB)Ru$^{II}$($\kappa^3$*SSS′*-tpdt)] moieties in a square planar arrangement. There is a close resemblance to complexes **G**, the *trans* isomers of the Pd and Pt analogues.[16] The Ru⋯Ni nonbond distance in **3** is 3.371 Å. The unit cell of the crystal structure of **4**, the Cp*Ru(III) analogue of **3**, contains two independent molecules, which possess slight variations in bond parameters, shown in Table 1. The geometry is very similar to that of the Pd(II) analogue, **H**. The central Ni atom is tetrahedrally coordinated to the thiolato sulfur atoms of two [Cp*Ru$^{III}$(($\kappa^3$*SSS′*-tpdt)] units, but it is rendered six-coordinate with the participation of M−M bonding to the terminal Ru atoms (Ru−Ni distances 2.5919(12)−2.6167(12) Å, and Ru−Ni−Ru 154.88-(5)° and 157.26(5)°, respectively, in the two molecules).

The Ni−S distances are found as follows: **3**, 2.2043-(9)−2.2111(10) Å; **4**, 2.184(2)−2.270(2) Å; these lie in the observed range (2.26−2.33 Å for flattened tetrahedral geometries, and 2.18−2.20 Å for square planar geometries).[18] The S−Ni−S angles (87.68(3)−92.32(3)° in **3**, and 103.52(9)−116.43(9)° in **4**) also lie in the reported range of 88−125°.[18] Like **4**, the Cu(II) analogue **6** crystallizes with two independent molecules in the unit cell and possesses a molecular structure similar to that of **4**, except that the pair of Ru−Cu distances in each independent molecule are very dissimilar ($\Delta$ =

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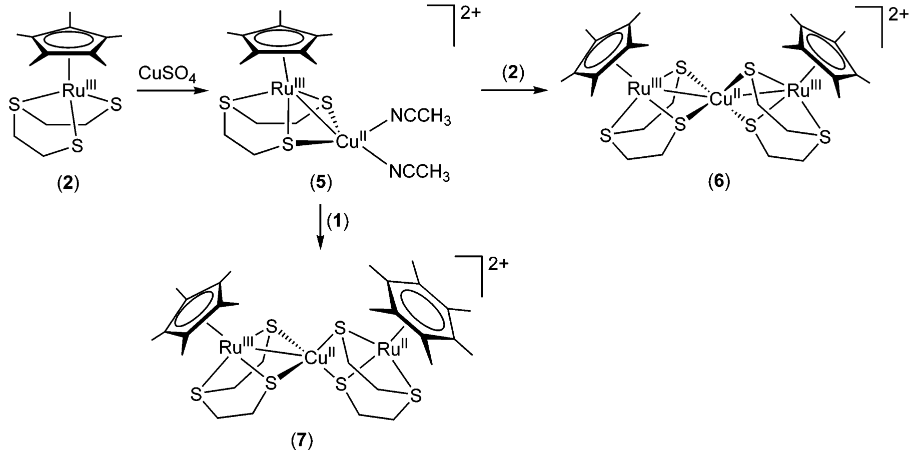
**Scheme 2**



0.0684 and 0.1875 Å, respectively); in the absence of any apparent cause, this difference can be merely a crystal packing effect associated with different lattice solvent molecules. However, the observed distances (2.6053(12)−2.7928(12) Å) fall in the range reported for such bonds in RuCu clusters (2.509(6)−2.909(2) Å).[19] The Ru−Cu−Ru angles in the two molecules are very close (154.52(5)° and 154.78(5)°, versus 154.88(5)° and 157.26(5)° in **4**). The Cu−S distances are observed in the range as follows: **5**, 2.273(2)−2.287(2) Å; **6**, 2.271(2)−2.380(2) Å; **7**, 2.2426(10)−2.3999(10) Å. These are longer than those found in adamantine-like cluster complexes of Cu−Cu and Cu−Ni thiolates (range 2.23(1)−2.24(1) Å).[20] An examination of the Ru−S distances in these complexes shows that (i) Ru(II)−S bonds (as in **3** and **7**) are significantly longer than Ru(III)−S bonds (as in **4**−**7**) and (ii) Ru(II) is more strongly bonded to the thioether S atom (i.e., S(3) in **3** and S(6) in **7**), whereas for Ru(III) centers, as in complexes **4**−**7**, the M−S (thioether) bonds are weaker than the M−S (thiolate) bonds.

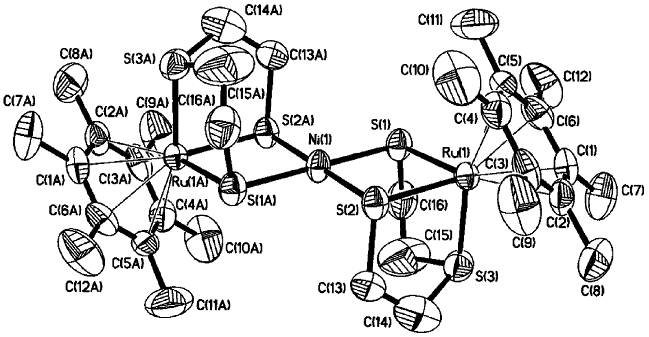


**Figure 1.** ORTEP plot for the molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level.

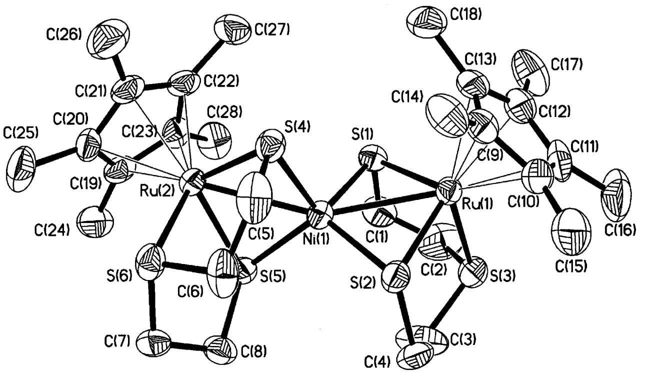


**Figure 2.** ORTEP plot for the molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level.

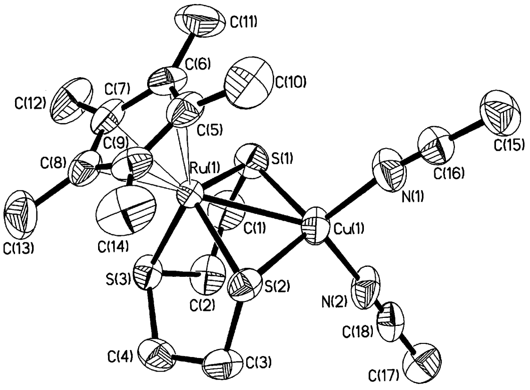


**Figure 3.** ORTEP plot for the molecular structure of **5**. Thermal ellipsoids are drawn at the 50% probability level.

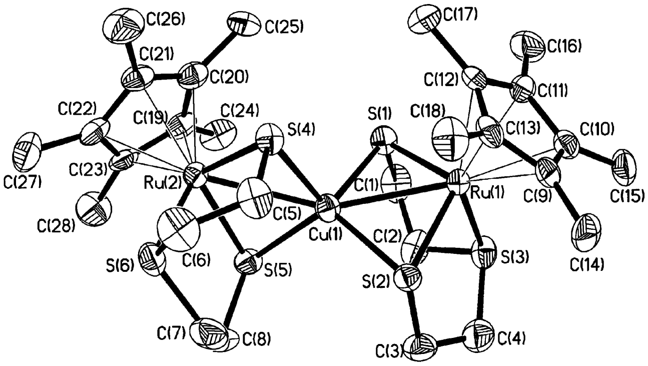


**Figure 4.** ORTEP plot for the molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level.

It is interesting to note that the Cu(II) central atom in the Cp*Ru(III)/(HMB)Ru(II) complex **7** is five-coordinate, with a bond to Ru of the Cp*Ru(III) moiety (bond length of 2.5717(5) Å, compared to 3.283 Å for the

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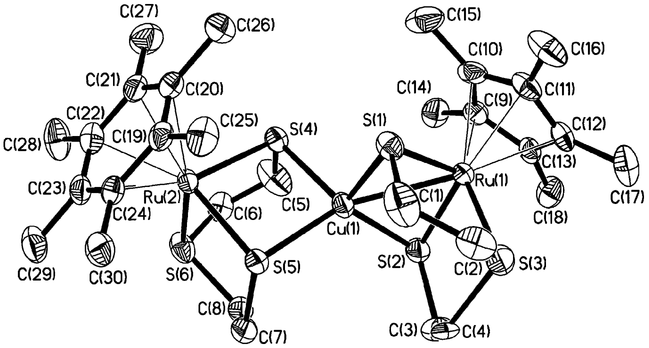

**Figure 5.** ORTEP plot for the molecular structure of **7**. Thermal ellipsoids are drawn at the 50% probability level.

nonbond distance Ru(2)···Cu(1)) and coordination to four thiolate sulfur atoms with a very distorted tetrahedral geometry, indicated by large deviations of some of the S–Cu–S angles from the tetrahedral angle, and one of the bonds to S, viz., Cu(1)–S(4), being much longer than the other three (see Table 1).

In the dinuclear Ru(III)–Cu(II) complex **5**, Cu(II) is five-coordinate with tetrahedral connection to two $CH_3CN$ ligands and two thiolate S atoms and a Ru(III)–Cu(II) bond (2.5700(11) Å), very close to that in **7**; these are very much shorter than similar bonds in **6**, where Cu(II) is simultaneously bonded to two Ru(III) centers. In all these tpdt-bridged tri- or diheteronuclear complexes, the occurrence of M–M bonds between central Ni(II) or Cu(II) and the terminal Ru atoms is dictated by the 18e requirement at Ru; thus M–M bonds are formed with 17e Cp*Ru(III) moieties (as in **4**–**7**) but not with 18e (HMB)Ru(II) moieties (as in **3** and **7**), as we have also observed previously for the di- and trinuclear complexes in Chart 2. M–M bond formation thus confers on Ni in complex **4** and Cu in complex **6** valence electron counts of 18 and 19, respectively, which is consistent with their observed diamagnetic and paramagnetic character.

Notably the dithiolate-bridged tpdt trinuclear complexes, **4**, **6**, and **7**, possess a tetrahedral arrangement of thiolato sulfur donor atoms at Ni or Cu, with supporting M–M bonds. In complex **3**, the $NiS_4$ core is square planar, the most stable geometrical state for Ni(II) $d^8$ systems.[21] It has been observed that this is the predominant geometry for $NiS_4$ or $NiN_2S_2$ moieties in thiolate Ni complexes, whether mono-, di-, or polynuclear, e.g., in mononuclear $[Ni(SS)_2]^{n-}$ ($n = 0, 2$) complexes of chelating thiolates and Ni(II) centers in polynuclear complexes linked by two thiolate bridges.[18] However, in mononuclear arylthiolate $[Ni(SR)_4]^{2-}$ complexes, there exists a general tendency for Ni(II) to adopt a flattened tetrahedral geometry for bulky R groups, and there have been recent reports of tetrahedral Ni in $[Ni_2(SC_4H_9)_6]^{2-}$ [22] and in $\{Ni\{Fe(\mathit{NS}_3)(CO)\text{-}S,S'\}_2$,[23] of square pyramidal Ni in the complex $\{Fe(\mathit{NS}_3)(CO)_2\text{-}S,S'\}NiCl(dppe)$, where $\mathit{NS}_3 = N(CH_2CH_2S)_3^{3-}$ and Ni('$S_5$') where '$S_5$'$^{2-}$ is a pentasulfur-donor ligand,[24] and of trigonal bipyramidal Ni in complexes containing tetradentate tripodal $NS_3$ ligands with a coligand.[25]

Organo-Ru–Ni or -Ru–Cu bimetallic complexes are scarce in the literature. The rare examples include the catalyst precursor $CpNiRu_3H_3(CO)_9$,[26] (*ansa*-$\eta^5$-$Cp_2$)-$RuNi(CO)_3$,[27] $[Cp^*Ru(NiS_2N_2)]_2^{2+}$ and its derivatives $[Cp^*Ru(NiS_2N_2)L]^+$ (L = CO, MeNC, $PPh_3$), and related (arene)Ru complexes, in which slightly distorted square planar $NiS_2N_2$ units serve as metallodithiolate ligands to Ru.[28]

Very few trimetallic complexes of M–Ni–M type are known. A structure analogous to that of **4** was reported for $[Cp_2Ti(\mu\text{-}SC{\equiv}CPh)_2]_2Ni$, in which two $Cp^*{}_2Ti$ moieties each acts as a dithiolate ligand to a central Ni, with a dative bond between $d^{10}$ Ni and $d^0$ Ti.[29] Similarly, two moieties of bis(dithiolate)$Mn(CO)_4$[30] or $[Fe(\mathit{NS}_3)(CO)]$[23] each function as a metallodithiolate ligand to a central Ni, without any M–M bond interaction. The dicationic trinickel compound $[(BME\text{-}DACO)Ni]_2Ni$ (BME-DACO = *N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctane) is another close analogue.[31]

To our knowledge, there is only one known example of a non metal–metal bonded Cu(II) thiolate-bridged $M_2Cu$ complex, viz., triply thiolate-bridged $[LCo(III)Cu(II)Co(III)L]^{2+}$ where L is a macrocyclic tris(sulfidobenzyl)triazacyclononane trianion.[32] Another $M_2Cu$ complex is $\{[Cp_2Mo(SPh)_2]_2Cu\}^+$, which contains Cu(I), but is however not structurally characterized.[33] Four complexes of formula $[\{Ru(bipy)_2\}(m\text{-}AA)\{Cu(phen)(H_2O)\}][PF_6]_3$ (where m-AA = bridging groups consisting of bipy with a side-chain of $\alpha,\omega$-diamino acids) appear to be the only compounds known of Ru(II)–Cu(II).[34]

**Spectral Characteristics.** The NMR spectra of **3** in $CD_3CN$ are consistent with the presence of a center of inversion at Ni, as shown in the X-ray structure. Thus, in the $^1H$ NMR spectrum, a singlet is observed at $\delta$ 2.16 for the two equivalent $C_6Me_6$ rings, while the methylene protons of the sulfur ligand are seen as two sets of 5-line multiplets at $\delta$ 3.05–4.13 and two broad singlets at $\delta$ 3.34 and 1.96. The $^{13}C$ NMR spectrum shows $SCH_2$ carbon resonances at $\delta$ 30.2 and 45.2 and Me substituents and ring carbons of $C_6Me_6$ at $\delta$ 15.7 and 102.0, respectively. The highest fragment in the $FAB^+$ MS at *m/z* 889 corresponds to the mother dication associated with a proton.

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**Table 1. Selected Bond Lengths (Å) and Angles (deg)**

| **3**[a] | | **4**[b] | | | **5** | | **6**[b] | | | **7** | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | A | B | | | | A | B | | |
| Ru(1)−S(1) | 2.3472(11) | Ru(1)−S(1) | 2.279(2) | 2.282(2) | Ru(1)−S(1) | 2.2549(18) | Ru(1)−S(1) | 2.283(2) | 2.315(2) | Ru(1)−S(1) | 2.2616(9) |
| Ru(1)−S(2) | 2.3532(9) | Ru(1)−S(2) | 2.289(2) | 2.280(2) | Ru(1)−S(2) | 2.2672(17) | Ru(1)−S(2) | 2.304(2) | 2.347(2) | Ru(1)−S(2) | 2.2804(9) |
| Ru(1)−S(3) | 2.3030(10) | Ru(1)−S(3) | 2.322(2) | 2.313(3) | Ru(1)−S(3) | 2.3200(18) | Ru(1)−S(3) | 2.334(2) | 2.319(2) | Ru(1)−S(3) | 2.3169(10) |
| S(1)−Ni(1) | 2.2043(9) | Ru(2)−S(4) | 2.261(2) | 2.265(2) | Cu(1)−S(1) | 2.273(2) | Ru(2)−S(4) | 2.307(2) | 2.254(2) | Ru(2)−S(4) | 2.3927(9) |
| S(2)−Ni(1) | 2.2111(10) | Ru(2)−S(5) | 2.310(2) | 2.303(2) | Cu(1)−S(2) | 2.287(2) | Ru(2)−S(5) | 2.322(2) | 2.276(2) | Ru(2)−S(5) | 2.3700(9) |
| Ru...Ni | 3.371 | Ru(2)−S(6) | 2.314(2) | 2.310(2) | Cu(1)−N(1) | 2.029(6) | Ru(2)−S(6) | 2.326(2) | 2.321(2) | Ru(2)−S(6) | 2.3232(10) |
| | | S(1)−Ni(1) | 2.270(2) | 2.184(2) | Cu(1)−N(2) | 1.944(6) | S(1)−Cu(1) | 2.316(2) | 2.380(2) | S(1)−Cu(1) | 2.2473(10) |
| | | S(2)−Ni(1) | 2.191(2) | 2.263(2) | Ru(1)−Cu(1) | 2.5700(11) | S(2)−Cu(1) | 2.284(2) | 2.273(2) | S(2)−Cu(1) | 2.2426(10) |
| | | S(4)−Ni(1) | 2.224(2) | 2.239(2) | | | S(4)−Cu(1) | 2.364(2) | 2.302(2) | S(4)−Cu(1) | 2.3999(10) |
| | | S(5)−Ni(1) | 2.210(2) | 2.190(2) | | | S(5)−Cu(1) | 2.272(2) | 2.271(2) | S(5)−Cu(1) | 2.2479(9) |
| | | Ru(1)−Ni(1) | 2.6001(12) | 2.5919(12) | | | Ru(1)−Cu(1) | 2.6422(12) | 2.7928(12) | Ru(1)−Cu(1) | 2.5717(5) |
| | | Ru(2)−Ni(1) | 2.6167(12) | 2.5991(12) | | | Ru(2)−Cu(1) | 2.7106(12) | 2.6053(12) | Ru(2)···Cu(1) | 3.283 |
| S(1)−Ru(1)−S(2) | 81.18(3) | S(1)−Ru(1)−S(2) | 105.37(8) | 105.26(8) | S(1)−Ru(1)−S(2) | 110.03(7) | S(1)−Ru(1)−S(2) | 107.34(8) | 103.48(8) | S(1)−Ru(1)−S(2) | 107.80(3) |
| S(1)−Ru(1)−S(3) | 86.32(4) | S(1)−Ru(1)−S(3) | 86.73(8) | 86.09(9) | S(1)−Ru(1)−S(3) | 86.29(7) | S(1)−Ru(1)−S(3) | 85.78(8) | 86.13(8) | S(1)−Ru(1)−S(3) | 86.75(4) |
| S(2)−Ru(1)−S(3) | 85.44(4) | S(2)−Ru(1)−S(3) | 86.18(8) | 87.22(9) | S(2)−Ru(1)−S(3) | 87.02(6) | S(2)−Ru(1)−S(3) | 85.99(8) | 86.00(9) | S(2)−Ru(1)−S(3) | 86.52(4) |
| Ni(1)−S(1)−Ru(1) | 95.70(4) | S(1)−Ni(1)−S(2) | 109.06(8) | 109.24(9) | S(1)−Ru(1)−Cu(1) | 55.75(5) | S(1)−Cu(1)−S(2) | 106.91(8) | 103.73(8) | S(1)−Ru(1)−Cu(1) | 54.96(3) |
| Ni(1)−S(2)−Ru(1) | 95.34(4) | S(1)−Ni(1)−S(4) | 112.38(9) | 103.86(9) | S(2)−Ru(1)−Cu(1) | 56.01(5) | S(1)−Cu(1)−S(4) | 109.11(9) | 112.97(8) | S(2)−Ru(1)−Cu(1) | 54.66(3) |
| S(1)−Ni(1)−S(2) | 87.68(3) | S(1)−Ni(1)−S(5) | 106.67(8) | 115.27(9) | S(1)−Cu(1)−Ru(1) | 55.09(5) | S(1)−Cu(1)−S(5) | 110.78(9) | 106.85(8) | S(1)−Cu(1)−Ru(1) | 55.49(2) |
| S(1)−Ni(1)−S(2A) | 92.32(3) | S(2)−Ni(1)−S(4) | 103.52(9) | 112.86(9) | S(2)−Cu(1)−Ru(1) | 55.28(5) | S(2)−Cu(1)−S(4) | 108.62(8) | 107.52(9) | S(2)−Cu(1)−Ru(1) | 56.04(3) |
| | | S(2)−Ni(1)−S(5) | 116.43(9) | 105.73 | S(1)−Cu(1)−S(2) | 108.69(7) | S(2)−Cu(1)−S(5) | 115.58(9) | 118.77(9) | S(1)−Cu(1)−S(2) | 109.64(4) |
| | | S(4)−Ni(1)−S(5) | 108.91(8) | 110.09(9) | S(1)−Cu(1)−N(1) | 111.9(2) | S(4)−Cu(1)−S(5) | 105.71(8) | 107.17(9) | S(1)−Cu(1)−S(4) | 109.82(4) |
| | | S(4)−Ru(2)−S(5) | 104.23(8) | 105.24(8) | S(1)−Cu(1)−N(2) | 112.1(2) | S(4)−Ru(2)−S(5) | 105.96(8) | 108.66(8) | S(1)−Cu(1)−S(5) | 107.60(4) |
| | | S(4)−Ru(2)−S(6) | 86.62(8) | 87.57(9) | S(2)−Cu(1)−N(1) | 108.3(2) | S(4)−Ru(2)−S(6) | 86.18(8) | 87.16(8) | S(2)−Cu(1)−S(4) | 113.72(4) |
| | | S(5)−Ru(2)−S(6) | 86.35(8) | 86.55(9) | S(2)−Cu(1)−N(2) | 111.1(2) | S(5)−Ru(2)−S(6) | 85.86(8) | 86.06(8) | S(2)−Cu(1)−S(5) | 122.86(4) |
| | | Ru(1)−Ni(1)−Ru(2) | 154.88(5) | 157.26(5) | | | Ru(1)−Cu(1)−Ru(2) | 154.52(5) | 154.78(5) | S(4)−Cu(1)−S(5) | 91.73(3) |
| | | | | | | | | | | S(4)−Ru(2)−S(5) | 88.97(3) |
| | | | | | | | | | | S(4)−Ru(2)−S(6) | 85.39(3) |
| | | | | | | | | | | S(5)−Ru(2)−S(6) | 86.13(4) |
| | | | | | | | | | | Ru(1)−Cu(1)···Ru(2) | 156.6 |

[a] Molecule possesses center of inversion at Ni. [b] A and B refer to two independent molecules in the asymmetric unit.

The $^1$H NMR spectrum of **4** in $CD_3CN$ shows a singlet at $\delta$ 1.79 for the methyl protons of a Cp* ligand and six sets of multiplets at $\delta$ 2.55−3.41 for the methylene protons of tpdt. In the $^{13}$C NMR spectrum are seen singlets for the Cp* ring and methyl carbon atoms at $\delta$ 105.9 and 10.2, respectively. The methylene carbons are observed as eight singlets at $\delta$ 14.2−42.1, indicating the presence of eight different methylene groups in a low-symmetry environment. The formulation of the complex is supported by its positive ESI mass spectrum, which shows the parent ion at *m/z* 837. The negative ESI mass spectrum shows *m/z* 145, assigned to the $PF_6$ anion. The presence of this anion is also manifested in the IR spectrum as intense P−F stretching frequencies at 840 and 557 $cm^{-1}$.

The proton NMR spectrum of **5** in $CD_3CN$ shows resonances at $\delta$ 1.76 for Cp* and three sets of multiplets at $\delta$ 2.76−3.63 for the $SCH_2$ groups, with corresponding $^{13}$C resonances at $\delta$ 10.1, $\delta$ 41.0 and 41.5, respectively, and at $\delta$ 108.7 for the Cp* ring carbons. A singlet at $\delta$ 1.97 was also observed in the $^1$H NMR spectrum for the coordinated $CH_3CN$. Both Ru(1) and Cu(1) possess an odd valence electron count (17e each). The observed diamagnetism indicates effective coupling of the odd electrons, facilitated by the presence of a M−M bond. The highest peak in the FAB$^+$ MS shows the mother cation with loss of one $CH_3CN$ molecule and association with two protons.

The coordination of another unit of **2** to **5** resulted in the overall paramagnetic complex **6**. The proton NMR spectrum of this paramagnetic compound shows only a broad singlet at $\delta$ 10.26 ($\nu_{1/2} \approx 150$ Hz), which probably belongs to all the protons of the two Cp* rings and the $SCH_2$ groups. The highest peak in the FAB$^+$ MS clearly shows the mother cation at *m/z* 841.

The $^1$H NMR spectrum of **7** in $CD_3CN$ displays two sharp singlets at $\delta$ 1.74 and 2.08, assignable to the methyl protons of Cp* and $C_6Me_6$ rings, respectively. The $SCH_2$ protons were observed as very broad peaks spanning $\delta$ 2.0−3.8. The $^{13}$C NMR resonances of $C_6Me_6$ are observed as intense singlets at $\delta$ 15.5 (Me) and 101.0 (ring carbons), while those of Cp* are very much weaker ($\delta$ 10.0 (Me) and 106.4 (ring carbons) and those of the $SCH_2$ groups appear as extremely weak broad peaks hardly above the noise level. The FAB$^+$ MS shows the mother ion at *m/z* 868.

**Magnetic Susceptibilty Studies.** Variable-temperature magnetic susceptibilities (4.2−300 K; field = 1 T) were measured on powdered samples of compounds **2**, **3**, **4**, and **6**. The plots of $\mu_{eff}$ and $\chi^{-1}$ versus temperature for **2** are shown in Figure 6 and are indicative of Curie-like behavior ($C = 0.38$ cm$^3$ mol$^{-1}$ K, $\theta = -0.18$ K). The magnetic moment, per Ru(III), remains constant at 1.75 $\mu_B$, with a small decrease occurring below 10 K, reaching 1.67 $\mu_B$ at 4.2 K. This is the behavior expected for a distorted octahedral, paramagnetic $t_{2g}{}^5$ ($S = {}^1/_2$) species. Compound **3** shows a very weak paramagnetism with the magnetic moment at 300 K of 0.26 $\mu_B$, per trinuclear molecule, decreasing gradually to reach 0.07 $\mu_B$ at 4.2 K. Such small values are not big enough to cause any paramagnetic shifts in the NMR resonances (vide infra). They probably arise from second-order Zeeman effects (temperature-independent paramagnetism, TIP) and/or traces of paramagnetic impurity. As indicated in the crystallographic section, the data are compatible with the electron count of 18e at each Ru(II) and 16e at Ni(II) (planar) and no Ru−Ni bond, as well as with the spin states {Ru(II)($S = 0$)Ni(II)($S = 0$)Ru(II)($S = 0$)}.

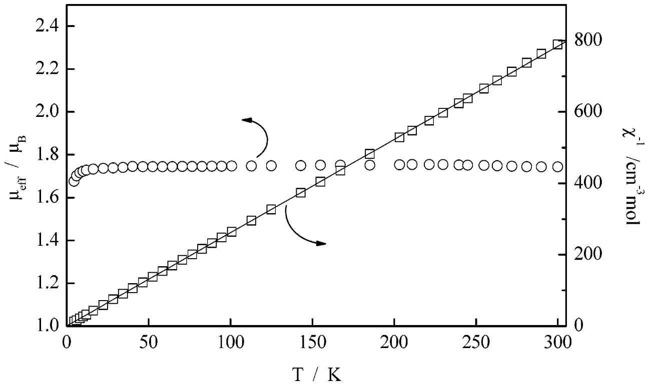

**Figure 6.** Plots of $\mu_{eff}$ (○) and $\chi^{-1}$ (□) versus temperature for complex **2**.

Compound **4** also displays weak paramagnetism, with the $\mu_{eff}$ value per molecule being 0.6 $\mu_B$ at 250 K and decreasing to 0.22 $\mu_B$ at 4.2 K. Again, these values are not big enough to cause any broadening or shifts in the (solution) NMR lines. The corresponding electron count is 18e at each Ru(III) and 18e at Ni. From a ligand field/spin state perspective,[35] the situation is rather harder to analyze. The spin states are {Ru(III)($S = {}^1/_2$)Ni(II)($S = 1$ (tetrahedral)Ru(III)($S = {}^1/_2$)}. Heisenberg−Van Vleck spin coupling of type $-2JS_1{\cdot}S_2$ commonly used to analyze the magnetism of first-row[35] and (occasionally) second-row[36] d-block non metal−metal bonded trinuclear complexes can yield a spin-zero ground state when strong antiferromagnetic coupling (large negative $J$) is present across the Ru−S(R)−Ni bridges. The small observed paramagnetism could then arise from thermal population of low-lying, coupled spin levels having $S$ greater than zero. Such populations would yield larger moments at higher temperatures, as observed. Measurements of magnetization, $M$, per trimer of **4** (where $M = \chi H$), over the field range 0−5 T, yielded identical values at 2 and 3 K, which followed a linear type dependence on $H$, with a very low value of 0.03 N $\mu_B$ at $H = 5$ T. Such behavior is that expected for a strongly antiferromagnetically coupled system.

Compound **6** displays Curie-like $S = {}^1/_2$ magnetic behavior in the $\mu_{eff}$ and $\chi^{-1}$, per molecule (Figure 7). The moments, of value 1.76 $\mu_B$, remain independent of temperature. The Curie−Weiss constants are $C = 0.38$ cm$^3$ mol$^{-1}$ K and $\theta = 0.44$ K. This behavior is indicative of an energetically isolated $S = {}^1/_2$ ground level. As indicated earlier, the {electron count/M−M bond} approach yields a 19e count on Cu, hence paramagnetic $S = {}^1/_2$. EPR spectroscopy would be useful to probe the electron spin localization on Cu or delocalization to the S-donor groups. The spin-coupling model involves {Ru(III)($S = {}^1/_2$)Cu(II)($S = {}^1/_2$)Ru(III)($S = {}^1/_2$)}, which yields a $S = {}^1/_2$ ($^2$E) ground state when very strong antiferromagnetic coupling is present. There is precedence for such a situation in a (non M−M bonded)

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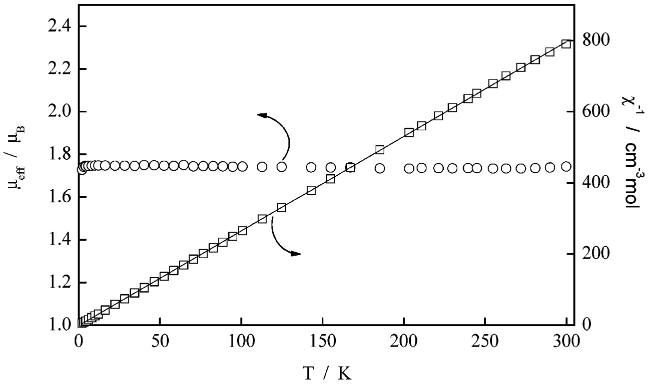

**Figure 7.** Plots of $\mu_{eff}$ (○) and $\chi^{-1}$ (□) versus temperature for the RuCuRu complex **6**.

Cu(II) S-bridged $\{S = {}^1/_2,{}^1/_2,{}^1/_2\}$ trimer, with a $J$ value of $-483$ cm$^{-1}$.[37] Complex **6** will have a $J$ value a little larger than this since, in contrast to the Cu(II) trimer, there is no evidence of thermal population of higher levels at temperatures near room temperature.

## Conclusion

The thiolate sulfur atoms of [(HMB)Ru$^{II}$($\kappa^3$*SSS′*-tpdt)] (**1**) and [Cp*Ru$^{III}$($\kappa^3$*SSS′*-tpdt)] (**2**) effect an efficient nucleophilic displacement of all the ligands of $Cl_2Ni(PPh_3)_2$ to give high yields of diamagnetic trinuclear complexes [{(HMB)Ru$^{II}$($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)}$_2$Ni$^{II}$]$^{2+}$ (**3**) and [{Cp*Ru$^{III}$($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)}$_2$Ni$^{II}$]$^{2+}$ (**4**), respectively. The Cu(II) analogue of **4**, [{Cp*Ru$^{III}$-($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)}$_2$Cu$^{II}$]$^{2+}$ (**6**), was obtained from a similar reaction with $CuSO_4$. A general structural feature in the trimetallic Ru−M−Ru arrays in these complexes is the presence of metal−metal bonding between M and terminal Ru(III) centers. Thus in these cases, while the central Ni or Cu atom is coordinated to four thiolate sulfurs in a distorted tetrahedral geometry, its coordination number is six and can be five as in a Ru$^{III}$−M−Ru$^{II}$ complex such as [{Cp*Ru-($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)}Cu{(HMB)Ru($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)}]$^{2+}$ (**7**). Magnetic studies of the neat solids yield information generally compatible with the spectral, crystallographic, and electron count/M−M bonded data, as well as with spin-coupling trinuclear models (for **3**, **4**, **6**). More detailed molecular orbital calculations, for instance of the density functional theoretical (DFT) kind,[38] would be very useful on such novel trinuclear Ru−M bonded thiometalate compounds.

## Experimental Section

**General Procedures.** All reactions were carried out using conventional Schlenk techniques under an atmosphere of nitrogen or under argon in a M. Braun Labmaster 130 inert gas system. NMR spectra were measured on a Bruker 300 MHz FT NMR spectrometer ($^1$H at 300.14 MHz and $^{13}$C at 75.43 MHz); $^1$H and $^{13}$C chemical shifts were referenced to residual solvent in the deutero-solvent $CD_3CN$. Coupling constants ($J$) are in Hz. IR spectra were measured in KBr pellets in the range 4000−400 cm$^{-1}$ on a BioRad FTS-165 FTIR instrument. FAB and ESI mass spectra were obtained on Finnigan Mat 95XL-T and MATLCQ spectrometers, respectively. Magnetic susceptibility measurements were made on ~20 mg samples of powders contained in a gel capsule which was held in the center of a soda straw, the latter fixed firmly to the end of the sample rod of a Quantum Design MPMS5 Squid magnetometer. The instrument was calibrated against the accurately known susceptibilities of a standard (Quantum Design) palladium pellet and against chemical calibrants such as $CuSO_4 \cdot 5H_2O$ and Hg[Co(NCS)$_4$]. Diamagnetic corrections for ligands were calculated using Pascal's constants (magnetic moments can be converted to the often used $\chi$T values by the relation $\mu^2 = 7.999\ \chi T$). Elemental analyses were performed by the microanalytical laboratory in-house. The compounds [(HMB)Ru(tpdt)] (**1**)[11] and [Cp*Ru(tpdt)] (**2**)[12] were prepared as reported in the literature. $CH_3CN$ was distilled from calcium hydride and MeOH from freshly generated magnesium methoxide before use. All other solvents were distilled from sodium benzophenone ketyl.

**(a) Reaction of 1 with $Cl_2Ni(PPh_3)_2$.** To a stirred solution of **1** (70 mg, 0.17 mmol) in THF (25 mL) was added a solution of bis(triphenylphosphine)nickel(II) chloride (110 mg, 0.17 mmol) in acetonitrile (10 mL). The solution underwent instantaneous decolorization with precipitation of grayish black solids. After stirring for 15 min the solids were filtered and washed with acetonitrile (2 × 5 mL), followed by ether (2 × 5 mL). The solids were evacuated dry, and anion metathesis was carried out in MeOH (20 mL) by stirring with $NH_4PF_6$ (140 mg, 0.85 mmol). After 10 min, the solution turned colorless with precipitation of shiny black solids. The solids were collected on a sintered glass filter (Por. 4) and washed with ether (5 mL). The product was then extracted using acetonitrile (2 × 5 mL) and filtered through a disk of Celite (1.5 cm thick). Layering with ether gave [{(HMB)Ru($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt}$_2$-Ni][PF$_6$]$_2$, **3**(PF$_6$)$_2$ (95 mg, 96% yield). Diffusion of ether into a solution of **3** in acetone gave poor diffraction-quality crystals. Recrystallization of these in nitromethane with ether diffusion gave good diffraction-quality orthorhombic crystals (containing acetone in the crystal lattice) after 2 days at −15 °C. $^1$H NMR ($\delta$, $CD_3CN$): SC$H_2$: 4.13−4.05 (5-line m, 4H), 3.34 (br s, 4H), 3.14−3.05 (5-line m, 4H) and 1.96 (br s, ca. 4H, partly obscured by solvent peak); $C_6Me_6$: 2.16 (s, 36H). $^{13}$C NMR ($\delta$, $CD_3CN$): $C_6$Me$_6$: 102.0; SCH$_2$: 45.2, 30.2; C$_6$*Me*$_6$: 15.7. IR $\nu$ (cm$^{-1}$, KBr): 2971 msh, 2923 mbr, 1438 ssh, 1405 ssh, 1389 s, 1281 w, 1238 w, 1170 m, 1113 m, 1104 w, 932 wsh, 916 wsh, 844 vs (PF$_6$), 738 w, 668 w, 558 vs (PF$_6$), 464 w. FAB$^+$ MS: *m/z* 889 [M − 2 PF$_6$ + H]$^+$, 861 [M − 2 PF$_6$ − 2CH$_2$ + H]$^+$, 416 [M − 2 PF$_6$ − [(C$_6$Me$_6$)Ru{$\eta^3$-(SCH$_2$CH$_2$)$_2$S}] − Ni]$^+$, and other unassignable fragments: 909, 925. FAB$^-$ MS: *m/z* 145 (PF$_6$). Found: C, 32.9; H, 4.3; Ni, 4.5; S, 16.1. $C_{32}H_{52}F_{12}NiP_2Ru_2S_6$ requires C, 32.6; H, 4.4; Ni, 5.0; S, 16.3.

**(b) Reaction of 2. With (i) $Cl_2Ni(PPh_3)_2$.** To a stirred dark purple solution of **2** (20 mg, 0.05 mmol) in THF (15 mL) was added $Cl_2Ni(PPh_3)_2$ (34 mg, 0.05 mmol) as a solid. A black-brown precipitate was formed after ca. 5 min. After 1 h, the solids were collected on a sintered-glass filter and washed with hexane to remove PPh$_3$. After that, they were dissolved in methanol, giving a brown solution; $NH_4PF_6$ was added as a solid (34 mg, 0.2 mmol), whereupon immediate formation of a black-brown precipitate was observed. These were collected and extracted with $CH_3CN$, leaving behind colorless crystals of $NH_4Cl$ and excess $NH_4PF_6$. Concentration of the extract, followed by addition of ether, gave rhombic black-brown crystals of [{Cp*Ru($\mu$-1$\kappa^3$*SSS′*:2$\kappa^2$*SS*-tpdt)}$_2$Ni][PF$_6$]$_2$·(CH$_3$)$_2$-CO, **4**(PF$_6$)$_2$·(CH$_3$)$_2$CO (26 mg, 0.023 mmol, 61% yield). Diffraction-quality crystals were obtained from an acetone−ether solution of **4** after 2 days at −30 °C. $^1$H NMR ($\delta$, $CD_3CN$): SC$H_2$: 3.41−3.36 (8-line m, 4H), 3.31−3.26 (6-line m, 2H), 3.15−3.12 (5-line m, 2H), 2.83−2.77 (8-line m, 2H), 2.70−2.67 (5-line m, 2H), 2.63−2.55 (8-line m, 4H); (C$H_3$)$_2$CO: 2.08 (s, 6H); C$_5$*Me*$_5$: 1.78 (s, 30H). $^{13}$C NMR ($\delta$, $CD_3CN$): $C_5$Me$_5$: 105.9; SCH$_2$: 42.1, 40.5, 38.5, 36.7, 32.1, 30.7, 23.1, 14.2; C$_5$*Me*$_5$: 10.2.

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ESI$^+$ MS: $m/z$ 837 [M − 2PF$_6$]$^+$, 807 [M − 2PF$_6$ − 2CH$_2$ + 2H]$^+$, 777 [M − 2PF$_6$ − S(CH$_2$)$_2$]$^+$. ESI$^-$ MS: $m/z$ 145 (PF$_6^-$). IR $\nu$ (cm$^{-1}$, KBr): 2982 w, 2918 w, 1709 m (Me$_2$CO), 1454 m, 1422 m, 1380 m, 1281 vw, 1224 w, 1162 vw, 1077 w, 1025 m, 914 vw, 839 vvs (PF$_6$), 742 vw, 558 vs (PF$_6$). Found: C, 31.1; H, 4.1; S, 16.6. $C_{28}H_{46}F_{12}NiP_2Ru_2S_6{\cdot}(CH_3)_2CO$ requires C, 31.5; H, 4.4; S, 16.3.

**(ii) With CuSO$_4$.** To a stirred solution of **2** (55 mg, 0.14 mmol) in MeOH (15 mL) was added solid CuSO$_4$ (45 mg, 0.28 mmol). The color immediately changed from purple to dark brown. After stirring for 1.5 h, the solution was filtered and PF$_6$ metathesis was carried out by stirring the filtrate with NH$_4$PF$_6$ (100 mg, 0.61 mmol) for 30 min. The reaction mixture was evacuated dry and the product extracted with CH$_3$CN (3 × 4 mL). The extracts were filtered through a glass sinter (Por. 4), the dark brown filtrate was concentrated to ca. 8 mL, and ether was added. Brown solids (85 mg, 73% yield) of [Cp*Ru($\mu$-1$\kappa^3$*SSS*′:2$\kappa^2$*SS*-tpdt)Cu(CH$_3$CN)$_2$][PF$_6$]$_2$, **5**(PF$_6$)$_2$, were obtained after 1 day at −30 °C. $^1$H NMR ($\delta$, CD$_3$CN): SC*H*$_2$: 3.63−3.54 (7-line m, 2H), 3.27−3.08 (11-line m, 4H), 2.84−2.76 (7-line m, 2H); C*H*$_3$CN: 1.97 (s, ca. 3H, i.e., less than the expected 6H's, owing to nonprecise integration, caused by partial overlap with the signal of CD$_3$CN solvent (septet centered at $\delta$ 1.94) and likely exchange with CD$_3$CN); C$_5$*Me*$_5$: 1.76 (s, 15H). $^{13}$C NMR ($\delta$, CD$_3$CN): *C*$_5$Me$_5$: 108.7; SC*H*$_2$: 41.5, 41.0; C$_5$*Me*$_5$: 10.1. FAB$^+$ MS: $m/z$ 495 [M − 2PF$_6$ − MeCN + 2H]$^+$, 451 [M − 2PF$_6$ − 2MeCN + H]$^+$, 389 [M − 2PF$_6$ − 2MeCN − Cu]$^+$. FAB$^-$ MS: $m/z$ 145 (PF$_6$). IR $\nu$ (cm$^{-1}$, KBr): 2971 w, 2911 w, 2256 w (C≡N), 1471 m, 1453 m, 1420 m, 1401 m, 1381 m, 1274 w, 1229 w, 1156 w, 1084 w, 1028 m, 845 vs (PF$_6$), 562 s (PF$_6$). Found: C, 26.3; H, 3.6; N, 3.1; S, 11.4. $C_{18}H_{29}CuF_{12}N_2P_2RuS_3$ requires C, 26.2; H, 3.6; N, 3.4; S, 11.7.

**(c) Reaction of 5 with 2.** To a stirred solution of **5** (64 mg, 0.08 mmol) in MeOH (8 mL) was added solid **2** (32 mg, 0.08 mmol). After 2 h, the precipitated black solids (51 mg, 54%) of [{Cp*Ru($\mu$-1$\kappa^3$*SSS*′:2$\kappa^2$*SS*-tpdt)}$_2$Cu][PF$_6$]$_2$, **6**(PF$_6$)$_2$, were filtered. The supernatant was concentrated to ca. 4 mL, and addition of ether gave a second crop of **6** (25 mg, 27%) after 1 day at −30 °C. $^1$H NMR ($\delta$, CD$_3$CN): 2(C$_5$*Me*$_5$) + SC*H*$_2$'s: 10.26 (s, $\nu_{1/2} \approx 150$ Hz). FAB$^+$ MS: $m/z$ 986 [M − PF$_6$]$^+$, 841 [M − 2PF$_6$]$^+$, 451 [M − 2PF$_6$ − Cp*Ru(C$_4$H$_8$S$_3$) − H]$^+$. FAB$^-$ MS: $m/z$ 145 (PF$_6$). IR $\nu$ (cm$^{-1}$, KBr): 2978 w, 2918 w, 1479 m, 1452 m, 1413 m, 1378 m, 1281 w, 1237 w, 1161 w, 1077 w, 1025 m, 842 vs, (PF$_6$), 558 s (PF$_6$). Found: C, 29.9; H, 4.1; S, 16.7. $C_{28}H_{46}CuF_{12}P_2Ru_2S_6$ requires C, 29.7; H, 4.1; S, 17.0.

**(d) Reaction of 5 with 1.** To a stirred solution of **5** (20 mg, 0.02 mmol) in MeOH (10 mL) was added solid **1** (10 mg, 0.02 mmol). The color immediately changed from dark brown to dark green, and after 1 h, the solution was filtered and evacuated dry. The dark green residue was dissolved in CH$_3$CN, and addition of ether gave blackish green orthorhombic crystals (25 mg, 89%) of [{Cp*Ru($\mu$-1$\kappa^3$*SSS*′:2$\kappa^2$*SS*-tpdt)}-Cu{(HMB)Ru($\mu$-1$\kappa^3$*SSS*′:2$\kappa^2$*SS*-tpdt)}][PF$_6$]$_2$, **7**(PF$_6$)$_2$, after 1 day at −30 °C. $^1$H NMR ($\delta$, CD$_3$CN): SC*H*$_2$: very broad peaks centered at $\delta$ 3.54 ($\nu_{1/2}$ 66 Hz, 1H), $\delta$ 3.37 ($\nu_{1/2}$ 60 Hz, 2H), $\delta$ 3.07 ($\nu_{1/2}$ 45 Hz, 3H) overlapping with $\delta$ 2.96 ($\nu_{1/2}$ 72 Hz, 3H) and $\delta$ 2.40 ($\nu_{1/2}$ 60 Hz, 4H), all sitting on an extremely broad "base"; C$_6$*Me*$_6$: 2.08 (s, 18H), C$_5$*Me*$_5$: 1.74 (s, 15H). $^{13}$C NMR ($\delta$, CD$_3$CN): C$_6$Me$_6$: 101.0 and 15.5; C$_5$Me$_5$: 106.4 and 10.0 (both very low in intensity) and SCH$_2$: 44.4, 41.1, 40.0 and 25.9 (very weak and broad). FAB$^+$ MS: $m/z$ 1013 [M − PF$_6$]$^+$, 868 [M − 2PF$_6$]$^+$. FAB$^-$ MS: $m/z$ 145 (PF$_6$). IR $\nu$ (cm$^{-1}$, KBr): 2975 w, 2921 w, 2250 vvw (C≡N), 1452 m, 1409 m, 1385 m, 1283 w, 1238 w, 1164 w, 1105 w, 1072 w, 1025 m, 922 w, 842 vvs, 745 w, 558 s. Found: C, 32.0; H, 4.5; N, 0.7; S, 15.2. $C_{30}H_{49}CuF_{12}P_2Ru_2S_6$.MeCN requires C, 32.1; H, 4.4; N, 1.2; S, 16.1.

**Crystal Structure Determinations.** The crystals were mounted on glass fibers. X-ray data were collected on a Bruker AXS SMART APEX CCD diffractometer, using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) at 223 K. The program SMART[39] was used for collecting the intensity data, indexing, and determination of lattice parameters, SAINT[39] was used for integration of the intensity of reflections and scaling, SADABS[40] was used for absorption correction, and SHELXTL[41] was used for space group and structure determination and least-squares refinements against $F^2$. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The hydrogens were placed in calculated positions. Fluorine atoms of the four PF$_6^-$ anions of **4** are highly disordered into two sets of positions at 55:45 (P1), 70:30 (P2 and P3), and 50:50 (P4) occupancies. Both PF$_6^-$ anions in **5** are disordered into two sets of positions with occupancy of 75:25, while complexes **6** and **7** each has one PF$_6^-$ anion disordered into two sets of positions at 50:50 and 60:40 occupancy ratio, respectively. In complex **7**, the carbon atoms C2 and C4 are disordered with the occupancy of 55:45 and the carbon atoms C6 and C8 are disordered with the occupancy of 70:30. There are also solvent molecules present as space-filling solvent in complexes, viz., **3**·(CH$_3$)$_2$CO, **4**·2(CH$_3$)$_2$CO, **6**·$^1/_2$MeOH·$^1/_2$H$_2$O, and **7**·MeCN·Et$_2$O. Crystal data and refinement parameters are given in Table S1.

**Acknowledgment.** The authors thank the National University of Singapore for a Research Scholarship to R.Y.C.S. and Academic Research Fund Grant No. R143 000 209 112 to L.Y.G.

**Supporting Information Available:** Crystallographic data as CIF files for complexes **3**−**7**. Table S1 giving crystal data and refinement parameters of the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050200P

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