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Metallophilicity in Annular Ru_2M_2 Derivatives of $(HMB)Ru^{II}(tpdt)$ versus (Bis)-η^2-dithiolate Bonding in Ru_2M Derivatives of $Cp^*Ru^{III}(tpdt)$ (HMB = η^6-C_6Me_6; Cp* = η^5-C_5Me_5; M = Cu^I, $Ag^{I,II}$, Au^I; tpdt = 3-thiapentane-1,5-dithiolate)

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The reaction of $[(HMB)Ru^{II}(\eta^3\text{-tpdt})]$ (**1**: HMB = η^6-C_6Me_6; tpdt = $S(CH_2CH_2S^-)_2$) with $[Cu(MeCN)_4]PF_6$, $AgPF_6$, and $(PPh_3)AuCl$ gave the annular species $[\{(HMB)Ru^{II}(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^3\text{-tpdt})\}_2(M)_2]^{2+}$ [**3**: M = Cu^I; **3A**: $(M)_2$ = Cu^I, $Cu^I(MeCN)$; **4**: M = Ag^I ; **6**: M = Au^I], isolated as PF_6 salts in high yields. Complex **6** was formed in a reversible process with $[\{(HMB)Ru^{II}(\mu\text{-}\eta^1\text{:}\eta^3\text{-tpdt})\}(AuPPh_3)]^+$ (**5**) involving dissociation/association of PPh_3. Similar reactions of $[Cp^*Ru^{III}(\eta^3\text{-tpdt})]$ (**2**: Cp* = η^5-C_5Me_5) gave, respectively, the cationic metal−metal bonded Ru_2M complexes $[\{Cp^*Ru(\mu\text{-}\eta^2\text{:}\eta^3\text{-tpdt})\}_2M]^{n+}$ (**7**: M = Cu^I, $n = 1$; **8**: M = Ag^{II}, $n = 2$) and $[\{Cp^*Ru(\mu\text{-}\eta^1\text{:}\eta^3\text{-tpdt})\}(AuPPh_3)]^+$ (**9**), isolated as PF_6 salts in 71, 73, and 72% yields, respectively. In MeCN or THF for an extended period, **9** underwent transformation to a mixture of complexes, from which $[\{Cp^*Ru\}_2\{\mu\text{-}\eta^6\text{-}(S(CH_2)_2S(CH_2)_2SAuPPh_3)_2\}]^{2+}$ (**10**), containing a μ-S_2 bridge, and $[\{Cp^*Ru(\mu_3\text{-}\eta^1\text{:}\ \eta^1\text{:}\eta^3\text{-tpdt})\}(AuPPh_3)_2]^+$ (**11**) could be identified. The new complexes, **3**−**9** and **11**, were all spectroscopically characterized, and the X-ray crystal structures of **3**−**10** have been determined. Cyclic voltammetry experiments were performed on compounds **3A**, **4**, and **6**−**8** at 233 K in CH_2Cl_2. **7** and **8** could be oxidized and reduced in several one-electron steps to form moderately stable species with extensive electron delocalization between the Ru_2M atoms. An EPR spectrum of **8**, a Ag(II) (d^9) species, was obtained at liquid He temperatures.

Introduction

Studies on heteronuclear aggregates and clusters of the coinage metals, first reported by Nyholm and Lewis in 1964,[1] have accelerated significantly in the last two decades,[2] with extensive work from the groups of Lewis and Raithby,[3a] Salter,[2a,f,h] Pignolet,[2e] Stone,[3b] Bruce,[3c] and Housecroft.[3d−f] The two main reasons for this interest relate to their implications in biochemical and technological applications[4] and in cooperative bimetallic reactivity to facilitate synthesis design and catalysis.[5] In particular, the importance of thiolate metal complexes in biology, catalysis, and materials has led to an upsurge of interest in the thiolate chemistry of Cu,[6,7a,b] Ag,[7,8a] and Au.[8] Although the occurrence of bridging

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(1) (a) Coffey, C. E.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1964**, 1741. (b) Kasenally, A. S.; Nyholm, R. S.; O'Brien, R. J.; Stiddard, M. H. B. *Nature* **1964**, *204*, 871. (c) Kasenally, A. S.; Nyholm, R. S.; Stiddard, M. H. B. *J. Am. Chem. Soc.* **1964**, *86*, 1884.

(2) See the following and references therein: (a) Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds. *Comprehensive Organometallic Chemistry II,* Vol. 10; Adams, R. D., Ed.; with special reference to Chetcuti, M. J., in Chapter 2, p 23, and Salter, I. D., in Chapter 5, p 255. (b) Gimeno, M. C.; Laguna, A. In McCleverty, J. A., Meyer, T. J., Eds. *Comprehensive Coordination Chemistry II*, Vol. 6; Fenton, D. E., Ed.; Elsevier: Amsterdam, 2004; Chapter 6.7, pp 911−1145. (c) Mukherjee, R. In *Comprehensive Coordination Chemistry II*, Vol. 6; Elsevier: Amsterdam, 2004; Chapter 6.6, pp 747−910. (d) *Coord. Chem Rev.* **1995**, *143*, 1−681 (entire volume). (e) Pignolet, L. H.; Krogstad, D. A. In *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; Wiley: New York, 1999; Chapter 13, pp 429−493. (f) Salter, I. D. *Adv. Organomet Chem.* **1989**, *29*, 249. (g) Mingos, D. M. P.; Watson, M. J. *Adv. Inorg. Chem.* **1992**, *39*, 327. (h) Salter, I. D. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: New York, 1999; Vol. 1, Chapter 1.27, pp 509−534. (i) Bardají, M.; Laguna, A. *Eur. J. Inorg. Chem.* **2003**, 3069 (microreview).

(3) See for instance the following and references therein: (a) Amoroso, A. J.; Beswick, M. A.; Li, C.-K.; Lewis, J.; Raithby, P. R.; Ramirez de Arellano, M. C. *J. Organomet. Chem.* **1999**, *573*, 247. (b) Stone, F. G. A. *Adv. Organomet. Chem.* **1990**, *31*, 53−89. (c) Bruce, M.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 2777. (d) Housecroft, C. E. *Chem. Soc. Rev.* **1995**, *24*, 515. (e) Housecroft, C. E. *Coord. Chem. Rev.* **1995**, *143*, 297. (f) Housecroft, C. E.; Draper, S. M.; Hattersley, A. D.; Rheingold, A. L. *J. Organomet. Chem.* **2000**, *614−615,* 202.

(4) See for instance the following and references therein: (a) Schmidbaur, H., Ed. *Gold: Progress in Chemistry, Biochemistry and Technology*; Wiley: New York, 1999. (b) Patai, S., Rappoport, Z., Eds. *The Chemistry of Organic Derivatives of Gold and Silver*; Wiley: New York, 1999. (c) Karlin, K. D., Tyeklar, Z., Eds. *Bioinorganic Chemistry of Copper*; Chapman & Hall: New York, 1993. (d) Yam, V. W.-W.; Chan, C.-L.; Li, C.-K.; Wong, K. M.-C. *Coord. Chem. Rev.* **2001**, *216−217*, 173. (e) Ford, P. C.; Cariati, E.; Bourassa, J. *Chem Rev.* **1999**, *99*, 3625. (f) Janssen, M. D.; Grove, D. M.; Van Koten, G. *Prog. Inorg. Chem.* **1997**, *46*, 97. (g) Mandal, S.; Das, G.; Singh, R.; Shukla, R.; Bharadwaj, P. K. *Coord. Chem. Rev.* **1997**, *160*, 191.

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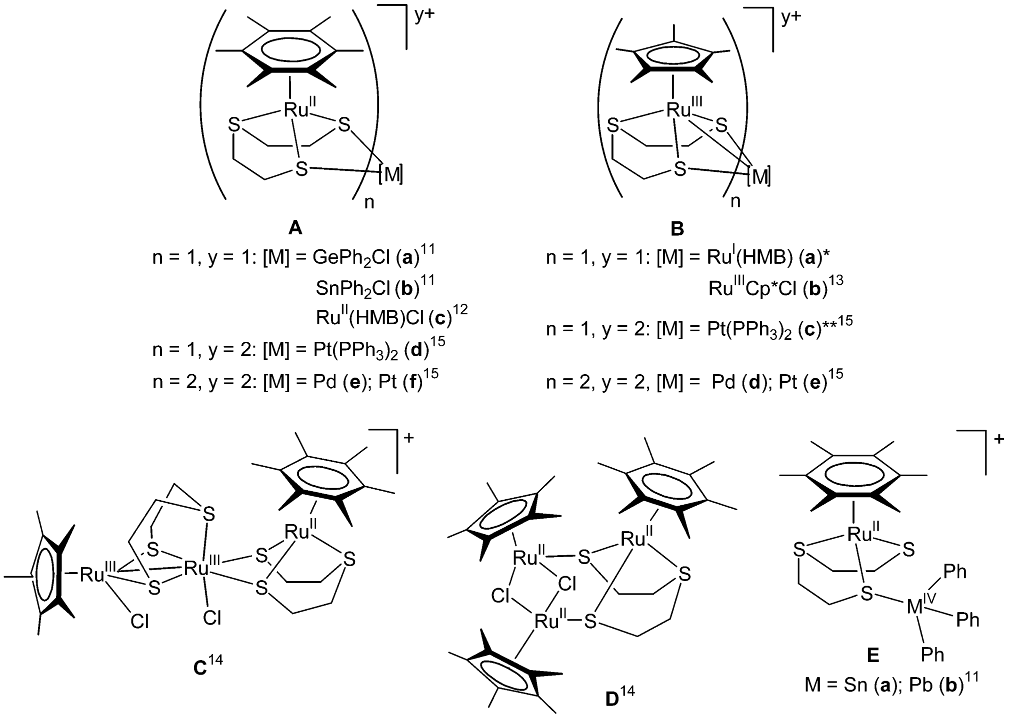
Chart 1. Tpdt-Bridged Organoruthenium Complexes



A

n = 1, y = 1: [M] = $\mathrm{GePh_2Cl}$ (**a**)[11]
$\mathrm{SnPh_2Cl}$ (**b**)[11]
$\mathrm{Ru^{II}}$(HMB)Cl (**c**)[12]
n = 1, y = 2: [M] = $\mathrm{Pt(PPh_3)_2}$ (**d**)[15]
n = 2, y = 2: [M] = Pd (**e**); Pt (**f**)[15]

B

n = 1, y = 1: [M] = $\mathrm{Ru^{I}}$(HMB) (**a**)*
$\mathrm{Ru^{III}Cp^{*}Cl}$ (**b**)[13]
n = 1, y = 2: [M] = $\mathrm{Pt(PPh_3)_2}$ (**c**)**[15]
n = 2, y = 2, [M] = Pd (**d**); Pt (**e**)[15]

C[14]

D[14]

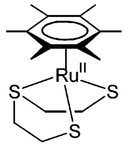
E

M = Sn (**a**); Pb (**b**)[11]

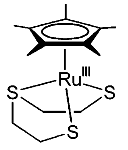
* Alternative oxidation states at Ru centers = (II,II)
** This compound does not possess a M-M bond

thiolates is prevalent,[6b,c,8c–g] bridging of these group 11 metal atoms to *cis*-dithiolate complexes is rare, except for complexes of formula type [$\mathrm{Cp_2M(\mu\text{-}SR)_2M'L_n}$)] (M = Ti, Zr, V; M′ = Cu, Ag; R = Me, Et; L = $\mathrm{PMe_3}$, $\mathrm{PCy_3}$; *n* = 0, 1), studied extensively by Stephan and coworkers,[9] and recently reported complexes of $\mathrm{Cu_2Ni_n}$ (*n* = 2, 3) bridged by the *cis*-dithiolate functions of an "N2S2" ligand.[10]

Our recent work has shown that the arene Ru(II) complex **1** and its Cp*Ru(III) analogue **2**, containing the tpdt≡$\mathrm{S(CH_2CH_2S^-)_2}$ ligand, behave as efficient metallodithiolate ligands, mainly in bidentate bonding mode, toward group 14 metal fragments[11] and fragments from complexes of Ru[12–14]and group 10 metals in +2 oxidation state,[15] forming di- or trinuclear species (**A**–**D**) shown in Chart 1. From these, it can be seen that conformity to the 18-electron rule requires that the 17-electron Cp*Ru(tpdt) moiety is metal–metal bonded to a second metal center in dinuclear compounds of both the homo- and heterometallic types (**B**).



(1)



(2)

This paper describes an extension of this study to the coinage metals in +1 oxidation states. It will be demonstrated that (i) the relative chemistries of **1** and **2** are distinctly different, (ii) each complex shows analogous chemistry with Cu and Ag, but very different reactivity

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(5) (a) Adams, R. D., Herrmann, W. A., Eds. The Chemistry of Heteronuclear Clusters and Multimetallic Catalysts. In *Polyhedron* **1988**, *7*, 2251. (b) Wheatley, N.; Kalck, P. *Chem Rev*. **1999**, *99*, 3379, and references therein. (c) McCollum, D. G.; Bosnich, B. *Inorg. Chim. Acta* **1998**, *270*, 13. (d) Xiao, J.; Puddephatt, R. J. *Coord. Chem. Rev*. **1995**, *143,* 457. (e) Guczi, L. In *Metal Clusters in Catalysis*; Gates, B. C., Guczi, L., Knozinger, H., Eds.; Elsevier: New York, 1986. (f) Sinfelt, J. H. In *Bimetallic Catalysts: Discoveries, Concepts and Applications*; Wiley: New York, 1983. (g) Adams, R. D., Cotton, F. A., Eds. *Catalysis by Di- and Polynuclear Metal Cluster Complexes*; Wiley-VCH: Weinheim, 1998. (h) Braunstein, P.; Rose, J. *Met. Cluster Chem*. **1999**, *2*, 616, and in Chapter 7, pp 351–387 of ref 2a above. (i) van den Beuken, E. K.; Feringa, B. L. *Tetrahedron* **1998**, *54*, 12985. (j) Pignolet, L. H.; Aubart, M. A.; Craighead, K. L.; Gould, R. A. T.; Krogstad, D. A.; Wiley, J. S. *Coord. Chem. Rev*. **1995**, *143*, 219.

(6) Some recent reports on Cu thiolates: (a) Liu, C. W.; Staples, R. J.; Fackler, J. P., Jr. *Coord. Chem. Rev*. **1998**, *174*, 147. (b) Kotera, T.; Mikuyira, M. *Chem. Lett*. **2002**, 654. (c) Stibrany, R. T.; Fikar, R.; Brader, M.; Potenza, M. N.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **2002**, *41*, 5203. (d) Ueno, Y.; Tachi, Y.; Itoh, S. *J. Am. Chem. Soc.* **2002**, *124*, 12428. (e) Holland, P. L.; Tolman, W. *J. Am. Chem. Soc.* **2000**, *122*, 6331, and references therein. (f) Casado, M. A.; Pérez-Torrente, J. J.; Ciriano, M. A.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem.* **2004**, *43*, 1558. (g) Bennett, S. M. W.; Brown, S. M.; Conole, G.; Dennis, M. R.; Fraser, P. K.; Radojevic, S.; McPartlin, M.; Topping, C. M.; Woodward, S. *J. Chem. Soc*., *Perkin Trans. 1* **1999**, 3127.

(7) For recent reports of Cu and Ag thiolates: (a) Casado, M. A.; Pérez-Torrente, J. J.; Ciriano, M. A.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem.* **2004**, *43*, 1558. (b) Fackler, J. P., Jr.; Staples, R. J.; Liu, C. W.; Stubbs, R. T.; Lopez, C.; Pitts, J. T. *Pure. Appl. Chem.* **1998**, *70*, 839. (c) Liu, C. W.; McNeal, C. J.; Fackler, J. P., Jr. *J. Cluster Sci.* **1996**, *7*, 385.

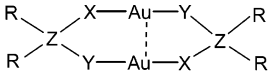
(8) Recent reports on Au thiolates: (a) Howard-Lock, H. E. *Metal-Based Drugs.* **1999**, *6*, 201 (a review on Ag and Au thiolates). (b) Gimeno, M. C.; Laguna, A. *Chem Rev*. **1997**, *97*, 511. (c) Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Terroba, R. *Inorg. Chem.* **1994**, *33*, 3932. (d) Hunks, W. J.; Jennings, M. C.; Puddephatt, R. J. *Chem. Commun.* **2002**, 1834. (e) Del Rio, I.; Terroba, R.; Cerrada, E.; Hursthouse, M. B.; Laguna, M.; Light, M. E.; Ruiz, A. *Eur. J. Inorg. Chem*. **2001**, 2013. (f) Tang, S. S.; Chang, C. P.; Lin, I. J. B.; Liou, L. S.; Wang, J. C. *Inorg. Chem.* **1997**, *36*, 2294. (g) Dávila, R. M.; Elduque, A.; Grant, T.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **1993**, *32*, 1749.

(9) Stephan, D. W. *Coord. Chem Rev.* **1989**, *95*, 41–107, and citations in ref 5b.

(10) Krishnan, R.; Voo, J. K.; Riordan, C. G.; Zahkarov, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 4422.

(11) Shin, R. Y. C.; Vittal, J. J.; Zhou, Z.-Y.; Koh, L. L.; Goh, L. Y. *Inorg. Chim. Acta* **2003**, *352*, 220; **2004**, *357*, 635.

with Au, (iii) derivatives of **2** with Cu(I) and Ag(II) resemble those of Pd and Pt in +2 oxidation state, and (iv) derivatives of **1** are of an annular Ru_2M_2 tetranuclear type (**F**, where $R_2Z(X)(Y)$ = (HMB)Ru(tpdt)), exhibiting close M⋯M contacts between the group 11 metal centers. Such annular/transannular compounds possessing metallophilic interactions are frequently encountered with various combinations of nonmetal elements and CH_2 groups for X, Y, Z, and alkyl/phenyl groups R, e.g., Z = P: (i) X = Y = S; (ii) X = S, Y = CH_2; (iii) X = Y = CH_2; or (iv) Z = N and X = Y = S; (v) ZR_2 = [C=C(CN)$_2$], X = Y = S; (vi) $ZR_2 = WS_2$, X = Y = S; (vii) $ZR_2 = Pt(PPh_3)_2$ and X = Y = S and $(X)(Y)ZR_2$ = dppm or dppf; (viii) $ZR_2 = Au(PPh_2)_2$.[2b,16–18] The annular complexes **3**, **4**, and **6** obtained here constitute a complete congeneric set of compounds with an identical ligand environment. Acquisition of solid state structural data on congeneric sets of complexes of all three coinage metals has not been feasible to date, owing to the generally encountered instability of the Cu(I) analogue.[18] Lately this obstacle was almost overcome by Laguna in the synthesis of $[M_2(PPh_2CH_2SPh)]^{2+}$ complexes of the three metals, thus enabling a theoretical and experimental comparison of their metallophilicity, although X-ray structural data for the Cu complex was unattainable.[19]



(**F**)

Experimental Section

General Procedures. All reactions were carried out using conventional Schlenk techniques under an atmosphere of nitrogen or argon in a M. Braun Labmaster 130 inert gas system. NMR spectra were measured on a Bruker 300 MHz FT NMR spectrometer (^1H at 300.14 MHz and ^{13}C at 75.43 MHz); ^1H and ^{13}C chemical shifts were referenced to residual solvent in the deuterosolvents CD_3OD and 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 a Finnigan Mat 95XL-T and a MATLCQ spectrometer, respectively. Voltammetric experiments were conducted with a computer-controlled Eco Chemie μAutolab III potentiostat. The electrochemical cell was jacketed in a glass sleeve and cooled to 233 K using a Lauda RL6 variable-temperature methanol-circulating bath. EPR spectra were recorded on a Bruker ESP 300e spectrometer in a TE_{102} cavity at 10 K using liquid He cooling. Elemental analyses were performed by the microanalytical laboratory in-house. The compounds [(HMB)Ru(η^3-tpdt)] (**1**),[12] [Cp*Ru(η^3-tpdt)] (**2**),[13] and $[Cu(CH_3CN)_4]PF_6$[20] were prepared as previously reported. 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.

Reactions of 1. (a) With $[Cu(MeCN)_4]PF_6$. To a stirred deep red solution of **1** (20 mg, 0.048 mmol) in MeOH (10 mL) was added solid $[Cu(MeCN)_4]PF_6$ (18 mg, 0.048 mmol). The solution instantaneously turned orange. After stirring for 10 min the slightly cloudy solution was filtered on a sintered glass filter (Por.4) and the orange filtrate concentrated. Addition of ether gave orange crystalline solids of [{(HMB)Ru(μ_3-η^1:η^1:η^3-$C_4H_8S_3$)}$_2$Cu(CuMeCN)}]$(PF_6)_2$, **3A**$(PF_6)_2$ (25 mg, 83.1% yield), after 12 h at −30 °C. ^1H NMR (δ, CD_3OD): SCH_2: 2.78−2.69 (7-line m, 4H), 2.61−2.49 (10-line m, 8H), 2.11−2.04 (6-line m, 4H); C_6Me_6: 2.19 (s, 36H); *Me*CN: 2.03 (s, 3H). ^{13}C NMR (δ, CD_3OD): C_6Me_6: 101.1; SCH_2: 41.8, 30.8; C_6Me_6: 15.8. FAB$^+$MS: *m/z* 1105 [M − PF_6 − MeCN + 2H]$^+$. FAB$^-$MS: *m/z* 145 $[PF_6]^-$. Anal. Found: C, 31.93; H, 4.79; N, 0.69; S, 14.52. Calcd for $C_{34}H_{55}NF_{12}P_2S_6Cu_2Ru_2$: C, 31.67; H, 4.30; N, 1.09; S, 14.92.

Drying a sample of crystals of **3A** under vacuum for several hours resulted in loss of coordinated MeCN, giving [{(HMB)-Ru(μ_3-η^1:η^1:η^3-$C_4H_8S_3$)}$_2$(Cu)$_2$}]$(PF_6)_2$, **3**$(PF_6)_2$. Anal. Found: C, 31.19; H, 4.40; S, 15.09. Calcd for $C_{32}H_{52}F_{12}P_2S_6Cu_2Ru_2$: C, 30.79; H, 4.20; S, 15.41. The NMR spectral data of **3** are similar to that of **3A** except for the presence of the peak of coordinated MeCN in **3A**.

A repeat of the above reaction in THF resulted in an immediate color change from red to yellow with simultaneous precipitation of yellow solids (32 mg). These were filtered after stirring for 5 min. Diffusion of ether into a CH_2Cl_2 solution of a sample of the yellow solids for 4 days at −30 °C gave a mixture of needle-shaped crystals of **3**$(PF_6)_2$ and rectangular crystals of **3A**$(PF_6)_2$, from which was selected a needle of the former for X-ray diffraction analysis.

(b) With $AgPF_6$. To a stirred deep red solution of **1** (17 mg, 0.041 mmol) in THF (8 mL) was added solid $AgPF_6$ (40 mg, 0.16 mmol). The solution instantaneously turned yellow, and brownish orange solids were precipitated. After stirring for 25 min the solids were filtered on a sintered glass filter (Por.4) and washed with ether (5 mL). The solids were then extracted using acetonitrile (3 × 2 mL), and addition of ether to the concentrated extract gave [{(HMB)Ru(μ_3-η^1:η^1:η^3-$C_4H_8S_3$)}$_2$-(Ag)$_2$}]$(PF_6)_2$, **4**$(PF_6)_2$, as orange crystals (23 mg, 84.0% yield). ^1H NMR (δ, CD_3CN): SCH_2: 2.59−2.47 (m, 10H), unresolved multiplet centered at δ 2.15 (m, 6H); C_6Me_6: 2.09 (s, 36H). ^{13}C NMR (δ, CD_3CN): C_6Me_6: 100.7; SCH_2: 41.6, 29.2; C_6Me_6: 15.8. FAB$^+$MS: *m/z* 1193 [M − PF_6 + H]$^+$. FAB$^-$MS: *m/z* 145 $[PF_6]^-$. Anal. Found: C, 28.30; H, 3.92; F, 16.72; S, 14.08. Calcd for $C_{32}H_{52}F_{12}P_2S_6Ag_2Ru_2$: C, 28.75; H, 3.92; F, 17.05; S, 14.39.

(c) With $(PPh_3)AuCl$. (i) To a deep red solution of **1** (49 mg, 0.12 mmol) in MeOH (8 mL) was added triphenylphosphine gold chloride (56 mg, 0.11 mmol). There was no apparent change in color; hence the mixture stirred for 10 h. NH_4PF_6 (100 mg, 0.61 mmol) was then added to the resultant solution, whereupon red solids precipitated. These were collected on a sintered glass filter (Por.4) and washed with methanol (5 mL), followed by ether (5 mL). Acetonitrile (15 mL) was allowed to seep through the filter so as to extract the product, leaving behind the precipitated NH_4Cl and excess NH_4PF_6. The red filtrate was concentrated to half-volume and ether added, giving red crystals of [{(HMB)Ru(μ-η^1:η^3-$C_4H_8S_3$)}($AuPPh_3$)]-(PF_6), **5**(PF_6) (54 mg, 44.9% yield), after 1 day at −30 °C. Concentration of the orange mother liquor, followed by addition of ether, gave a second smaller crop of solids, consisting mainly of yellow solids of [{(HMB)Ru(μ_3-η^1:η^1:η^3-$C_4H_8S_3$)}$_2$-(Au)$_2$]$(PF_6)_2$, **6**$(PF_6)_2$, and more of **5**(PF_6). For **5**(PF_6): ^1H NMR

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[12] Shin, R. Y. C.; Bennett, M. A.; Goh, L. Y.; Chen, W.; Hockless, D. C. R.; Leong, W. K.; Mashima, K.; Willis, A. C. *Inorg. Chem.* **2003**, *42*, 96.

[13] Goh, L. Y.; Teo, M. E.; Khoo, S. B.; Leong, W. K.; Vittal, J. J. *J. Organomet. Chem.* **2002**, *664*, 161.

[14] Shin, R. Y. C.; Ng, S. Y.; Tan, G. K.; Koh, L. L.; Khoo, S. B.; Goh, L. Y. *Organometallics* **2004**, *23*, 547.

[15] Shin, R. Y. C.; Tan, G. K.; Koh, L. L.; Goh, L. Y.; Webster, R. D. *Organometallics* **2004**, *23*, 6108.

[16] Jiang, Y.; Alvarez, S.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 749, and references therein.

[17] Schmidbaur, H.; Graf, W.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417. Schmidbaur. H. *Gold Bull.* **1990**, *23*, 11.

[18] Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597, and references therein.

[19] Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Rodríguez, M. A.; Crespo, O.; Gimeno, M. C.; Laguna, A.; Jones, P. G. *Inorg. Chem.* **1998**, *37*, 6002.

[20] Kubas, G. J. *Inorg. Synth.* **1990**, *28*, 68.

(δ, CD_3CN): $\mathrm{P}\mathit{Ph}_3$: 7.61−7.51 (m, 15H); $\mathrm{S}\mathit{CH}_2$: 2.84−2.76 (6-line m, 2H), unresolved multiplets centered at δ 2.62 (2H) and 2.45 (2H), 2.26−2.18 (6-line m, 2H); $\mathrm{C_6}\mathit{Me}_6$: 2.05 (s, 18H). ^{13}C NMR (δ, CD_3CN): $\mathrm{P}\mathit{Ph}_3$: 134.7 (d, *ortho*, $^2J_{PC} = 14.5$ Hz), 132.5 (s, *para*), 130.8 (d, *ipso*, $^1J_{PC} = 49.8$ Hz), 130.1 (d, *meta*, $^3J_{PC} = 11.2$ Hz); $\mathit{C}_6\mathrm{Me}_6$: 100.0; $\mathrm{S}\mathit{C}\mathrm{H}_2$: 43.1, 32.1, 29.5, 23.1; $\mathrm{C_6}\mathit{Me}_6$: 15.6. ^{31}P NMR (δ, CD_3CN): $\mathit{P}\mathrm{Ph}_3$: 31.6; $\mathit{P}\mathrm{F}_6$: −142.9 (septet, J_{P-F} 706 Hz). ESI$^+$MS: *m/z* 875 $[M - PF_6]^+$. ESI$^-$MS: *m/z* 145 $[PF_6]^-$. Anal. Found: C, 39.66; H, 4.28; S, 9.43. Calcd for $C_{34}H_{41}F_6P_2S_3AuRu$: C, 40.04; H, 4.05; S, 9.43.

A repeat of the reaction in the presence of excess PPh_3 (40 mg, 0.15 mmol) led to the isolation of **5**(PF_6) in 64% yield, followed by a second smaller crop, consisting mainly of **5**(PF_6) contaminated with PPh_3.

(ii) To a solid mixture of **1** (23 mg, 0.055 mmol), (PPh_3)AuCl (32 mg, 0.065 mmol), and NH_4PF_6 (20 mg, 0.12 mmol) was injected MeOH (12 mL) with stirring. Orange solids were formed almost immediately, and after stirring for 5 min these were collected on a sintered glass filter (Por.4) and washed with ether (5 mL). A similar workup as described above, but using 6 mL of acetonitrile and addition of excess ether with vigorous stirring, precipitated out yellow solids of **6**$(PF_6)_2$, in admixture with some **5**$(PF_6)_2$. Two recrystallizations of this mixture in CH_2Cl_2 and ether gave pure **6**$(PF_6)_2$ as golden yellow crystals (20 mg, 47.6%). For **6**$(PF_6)_2$: ^{1}H NMR (δ, CD_3CN): $\mathrm{S}\mathit{CH}_2$: unresolved multiplets centered at δ 2.82 (8H), 2.65 (4H), 2.37 (4H); $\mathrm{C_6}\mathit{Me}_6$: 2.11 (s, 36H). ^{13}C NMR (δ, CD_3CN): $\mathit{C}_6\mathrm{Me}_6$: 102.1; $\mathrm{S}\mathit{C}\mathrm{H}_2$: 41.1, 32.0; $\mathrm{C_6}\mathit{Me}_6$: 15.8. ESI$^+$MS: *m/z* 1370 $[M - PF_6]^+$. FAB$^-$MS: *m/z* 145 $[PF_6]^-$. Anal. Found: C, 24.30; H, 3.15; S, 12.41. Calcd for $C_{32}H_{52}F_{12}P_2S_6Au_2Ru_2.CH_2Cl_2$: C, 24.77; H, 3.40; S, 12.02.

An NMR experiment showed that the treatment of **6**$(PF_6)_2$ with 10 molar equiv of PPh_3 resulted in total conversion to the mononuclear species **5**(PF_6).

Reactions of 2. (a) With $[Cu(MeCN)_4]PF_6$. To a stirred deep purple solution of **2** (30 mg, 0.077 mmol) in MeOH (8 mL) was added solid $[Cu(MeCN)_4]PF_6$ (14 mg, 0.038 mmol). The solution underwent instantaneous color change to dark brown; after stirring for 15 min the solution was filtered on a sintered glass filter (Por.4), and the dark brown filtrate was concentrated. Addition of ether gave black rectangular crystals of $[\{Cp^*Ru(\mu\text{-}\eta^2{:}\eta^3\text{-}C_4H_8S_3)\}_2Cu](PF_6)$, **7**($PF_6$) (27 mg, 71.0% yield), after 12 h at −30 °C, with more of **7**(PF_6) remaining in the mother liquor. ^{1}H NMR (δ, CD_3CN): $\mathrm{C_5}\mathit{Me}_5$: 14.58 (br s, $\nu_{1/2}$ ca. 38 Hz); $\mathrm{S}\mathit{CH}_2$: four broad peaks ($\nu_{1/2}$ ca. 120 Hz each) centered at δ −0.42, −1.27, −4.46, and −18.24, respectively. FAB$^+$MS: *m/z* 841 $[M - PF_6]^+$. FAB$^-$MS: *m/z* 145 $[PF_6]^-$. Anal. Found: C, 34.30; H, 4.85; S, 19.08. Calcd for $C_{28}H_{46}CuF_6PRu_2S_6$: C, 34.12; H, 4.70; S, 19.52.

(b) With $AgPF_6$. To a stirred deep purple solution of **2** (20 mg, 0.077 mmol) in MeOH (10 mL) was added solid $AgPF_6$ (40 mg, 0.16 mmol). The solution underwent an instantaneous color change to dark brown, and after stirring for 1.5 h, the solution was filtered on a sintered glass filter (Por.4) to remove some blackish particles, presumably of metallic silver. The dark brown filtrate was concentrated to half-volume, and addition of ether gave black crystalline solids of $[\{Cp^*Ru(\mu\text{-}\eta^2{:}\eta^3\text{-}C_4H_8S_3)\}_2Ag](PF_6)_2$, **8**$(PF_6)_2$ (22 mg, 72.8% yield), after 2 days at −30 °C. ^{1}H NMR (δ, CD_3CN): $2(\mathrm{C_5}\mathit{Me}_5) + \mathrm{S}\mathit{CH}_2$'s: 9.01 (br s, $\nu_{1/2}$ ca. 720 Hz). FAB$^+$MS: *m/z* 885 $[M - 2PF_6]^+$. FAB$^-$MS: *m/z* 145 $[PF_6]^-$. Anal. Found: C, 28.56; H, 3.99; S, 16.34. Calcd for $C_{28}H_{46}AgF_{12}P_2Ru_2S_6$: C, 28.62; H, 3.95; S, 16.37.

(c) With (PPh_3)AuCl. To a stirred deep purple solution of **2** (20 mg, 0.051 mmol) in MeOH (8 mL) was added solid (PPh_3)AuCl (32 mg, 0.065 mmol). A color change to blackish blue was observed within a few minutes, and after stirring for 4 h, the solution was filtered on a sintered glass filter (Por.4). NH_4PF_6 (40 mg, 0.24 mmol) was then added to the resultant solution, whereupon blackish blue solids precipitated. These were collected on a sintered glass filter (Por.4) and washed with methanol (4 mL), followed by ether (5 mL). Acetonitrile (6 mL) was allowed to slowly "seep through" the filter so as to extract the product, leaving behind the precipitated NH_4Cl and excess NH_4PF_6. The blackish blue filtrate was concentrated to half-volume, and layering with ether gave black diffraction-quality needles of $[\{Cp^*Ru(\mu\text{-}\eta^1{:}\eta^3\text{-}C_4H_8S_3)\}(AuPPh_3)](PF_6)$, **9**($PF_6$) (15 mg, 26.8% yield), after 24 h at −30 °C, followed by a second crop of black microcrystalline solids (25 mg, 44.7% yield) of **9**(PF_6). For **9**(PF_6): ^{1}H NMR (δ, CD_3CN): $\mathrm{P}\mathit{Ph}_3$: 7.98, 7.72, and 7.41 (overlapping br s, $\nu_{1/2}$ ca. 36, 105 and 30 Hz, respectively, 15H); $\mathrm{C_5}\mathit{Me}_5 + \mathrm{S}\mathit{CH}_2$'s: 1.88 (br s, ca. 23H, partially obscured by solvent peak). FAB$^+$MS: *m/z* 848 $[M - PF_6]^+$. FAB$^-$MS: *m/z* 145 $[PF_6]^-$. Anal. Found: C, 38.68; H, 3.50; S, 9.59. Calcd for $C_{32}H_{38}AuF_6P_2RuS_3$: C, 38.71; H, 3.86; S, 9.69.

A THF solution of **9**(PF_6) kept under ether diffusion for 1 week gave a few dark orange rectangular diffraction-quality plates of $[\{Cp^*Ru\}_2\{\mu\text{-}\eta^6\text{-}(S(CH_2)_2S(CH_2)_2SAuPPh_3)_2\}](PF_6)_2$, **10**$(PF_6)_2$, mixed with black needles of **9**(PF_6), the predominant component. The pale orange mother liquor was evacuated to dryness for a proton NMR spectrum; this showed a species (see data below) consistent with a formulation of $[\{Cp^*Ru(\mu_3\text{-}\eta^1{:}\,\eta^1{:}\eta^3\text{-tpdt})\}(AuPPh_3)_2](PF_6)$, **11**($PF_6$), which is also supported by its mass spectrum. A blackish blue solution of **9**(PF_6) in CH_3CN under ether diffusion gradually transformed to an orange homogeneous solution over 10 weeks at −30 °C. Removal of solvent in vacuo gave an orange oil, the NMR and mass spectra of which indicated the presence of **11**(PF_6), which unfortunately could not be obtained in solid or crystalline form. Data supporting **11**(PF_6): ^{1}H NMR (δ, CD_3CN): $\mathrm{P}\mathit{Ph}_3$: 7.52−7.23 (unres m, 30H); $\mathrm{S}\mathit{CH}_2$: unresolved multiplets centered at δ 2.86 (2H), 2.33 (6H); $\mathrm{C_5}\mathit{Me}_5$: 1.55 (s, 15H). ^{31}P NMR (δ, CD_3CN): $\mathit{P}\mathrm{Ph}_3$: 35.3; $\mathit{P}\mathrm{F}_6$: −142.9 (septet, J_{P-F} 706 Hz). FAB$^+$MS: *m/z* 1307 $[M - PF_6]^+$, and 389 $[M - PF_6 - 2AuPPh_3]^+$ (the latter fragment being also the mother ion of complex **2**). FAB$^-$MS: *m/z* 145 $[PF_6]^-$.

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 Kα radiation (λ = 0.71073 Å) at 223 K, except for **6** at 298 K, and **7** and **9** at 295 K. The program SMART[21] was used for collecting the intensity data, indexing ,and determination of lattice parameters, SAINT[21] was used for integration of the intensity of reflections and scaling, SADABS[22] was used for absorption correction, and SHELXTL[23] 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. The data for **3** are very poor. The asymmetric unit of its crystal contains one and a half cations. The full cation is disordered with the two Cu atoms twisted into two positions at 55:45 occupancy ratio. The S atoms are not disordered. The half cation is not disordered and is generated into the whole cation through a 2-fold symmetry operation. The PF_6^- anions are in six different positions (two general positions and four special positions, of which two are disordered with 0.5 occupancy). There are two PF_6^- anions for each cation. One of the PF_6^- anions of **3A** is disordered at 50:50 occupancy ratio (the other anion is at a special position). Fluorine atoms of the PF_6^- anion of **5** and **8** are disordered into two sets of positions at 60:40 and 50:50 occupancy ratio, respectively. The asymmetric unit of the crystal of **6** contains one cation which shows quite large thermal parameters in the methylene carbons (C1 and C2) of the tpdt ligands. Similarly, half of the

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[21] *SMART & SAINT* Software Reference manuals, version 5.1; Bruker Analytical X-ray Systems: Madison, WI, 2000.

[22] Sheldrick, G. M. *SADABS*, A Program for Empirical Absorption Correction; Göttingen, Germany, 2000.

[23] *SHELXTL* Reference Manual, version 5.1; Bruker AXS Inc.: Madison, WI, 1998.

Table 1. Crystallographic Data and Data Collection Parameters for the (HMB)Ru Complexes 3–6

	3$(PF_6)_2$	**3A**$(PF_6)_2$	**4**$(PF_6)_2$	**5**(PF_6)	**6**$(PF_6)_2$
empirical formula	$C_{34.50}H_{57}Cu_2F_{12}NO_{0.50}P_2Ru_2S_6$	$C_{32}H_{52}Cu_2F_{12}O_{0.67}P_2Ru_2S_6$	$C_{35}H_{59}Ag_2F_{12}NOP_2Ru_2S_6$	$C_{34.50}H_{41.75}AuF_6N_{0.25}P_2RuS_3$	$C_{34}H_{56}Au_2F_{12}O_{0.50}P_2Ru_2S_6$
temperature, K	223(2)	223(2)	223(2)	223(2)	298(2)
cryst syst	triclinic	tetragonal	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	*P*4/*ncc*	*Cc*	$P\bar{1}$	*P*2(1)/*c*
a, Å	12.8818(13)	23.7164(9)	21.4107(16)	8.9270(5)	12.8833(9)
b, Å	13.2769(14)	23.7164(9)	13.9823(11)	14.3503(7)	23.5699(17)
c, Å	16.2719(16)	49.973(4)	17.6141(14)	15.0100(8)	16.5363(12)
α, deg	97.257(2)	90	90	88.792(1)	90
β, deg	100.978(2)	90	108.202(2)	82.193(1)	99.254(2)
γ, deg	111.208(2)	90	90	86.655(1)	90
V, Å^3	2488.4(4)	28108(3)	5009.3(7)	1901.6(2)	4956.0(6)
Z	2	24	4	2	4
density, g cm^{-3}	1.742	1.785	1.870	1.799	2.079
abs coeff, mm^{-1}	1.828	1.938	1.750	4.553	6.889
no. of reflns collected	32 854	149 596	15 747	28 972	28 287
no of indep reflns	11 424	12 384	7812	11 024	8722
no. of data/restraints/params	11 424/21/587	12 384/95/828	7812/215/501	11 024/432/496	8722/6/532
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0466, wR2 = 0.1211	R1 = 0.0864, wR2 = 0.2372	R1 = 0.0395, wR2 = 0.0790	R1 = 0.0407, wR2 = 0.0551	R1 = 0.0882, wR2 = 0.1845
R indices (all data)	R1 = 0.0586, wR2 = 0.1271	R1 = 0.1548, wR2 = 0.2798	R1 = 0.0523, wR2 = 0.0807	R1 = 0.0592, wR2 = 0.0576	R1 = 0.0972, wR2 = 0.1883
goodness-of-fit on F^2	1.080	1.009	1.002	0.993	1.266

Table 2. Crystallographic Data and Data Collection Parameters for the Cp*Ru Complexes 7–10

	7(PF_6)	**8**$(PF_6)_2$	**9**(PF_6)	**10**$(PF_6)_2$
empirical formula	$C_{28}H_{48}CuF_6OPRu_2S_6$	$C_{28.25}H_{48}AgF_{12}O_{0.50}P_2Ru_2S_6$	$C_{32}H_{38}AuF_6P_2RuS_3$	$C_{40}H_{54}AuF_6O_2P_2RuS_3$
temperature, K	295(2)	223(2)	295(2)	223(2)
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	*P*2(1)/*n*	$P\bar{1}$
a, Å	8.935(2)	12.2374(5)	8.653(5)	11.3788(7)
b, Å	14.707(4)	17.5939(7)	26.368(17)	13.5233(8)
c, Å	17.053(4)	22.0809(9)	15.926(9)	15.4576(9)
α, deg	66.723(4)	71.7830(10)	90	76.6090(10)
β, deg	76.713(5)	74.9610(10)	91.236(18)	89.6120(10)
γ, deg	81.282(5)	72.2410(10)	90	79.8020(10)
V, Å^3	1998.7(9)	4229.3(3)	3633(4)	2275.9(2)
Z	2	4	4	2
density, g cm^{-3}	1.668	1.866	1.815	1.659
abs coeff, mm^{-1}	1.677	1.612	4.763	3.816
no. of reflns collected	20 997	29 994	20 158	13 092
no. of indep reflns	7052	19 260	6373	7967
no. of data/restraints/params	7052/50/473	19 260/202/1075	6373/217/436	7967/70/501
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0726, wR2 = 0.1631	R1 = 0.0754, wR2 = 0.1486	R1 = 0.0984, wR2 = 0.2694	R1 = 0.0856, wR2 = 0.1756
R indices (all data)	R1 = 0.1010, wR2 = 0.1744	R1 = 0.1187, wR2 = 0.1650	R1 = 0.1157, wR2 = 0.2817	R1 = 0.0930, wR2 = 0.1789
goodness-of-fit on F^2	1.112	1.066	1.062	1.328

cation of **7** is disordered into two positions, involving the flipping of the Cp* ring, with 65:35 occupancy ratio. The data for complex **9** are poor, resulting in large residual peaks around Au and Ru, probably due to the poor quality of the crystal. In addition the Cp* ring is disordered (splitting into two sets staggered at 36°), and one of the phenyl rings is disordered with 50:50 occupancy ratio. There are also solvent molecules present as space-filling solvent in complexes, viz., **3**·2/3H_2O, **3A**·MeOH, **4**·MeCN·MeOH, **5**·1/4MeCN, **6**·Et_2O, **7** (two partially occupied H_2O, each at occupancy ratio of 50:50), **8**·1/2MeCN·1/2MeOH, and **10**·2THF. Crystallographic data collection and refinement parameters are briefly listed in Tables 1 and 2 and given in full in Table S1 in the Supporting Information.

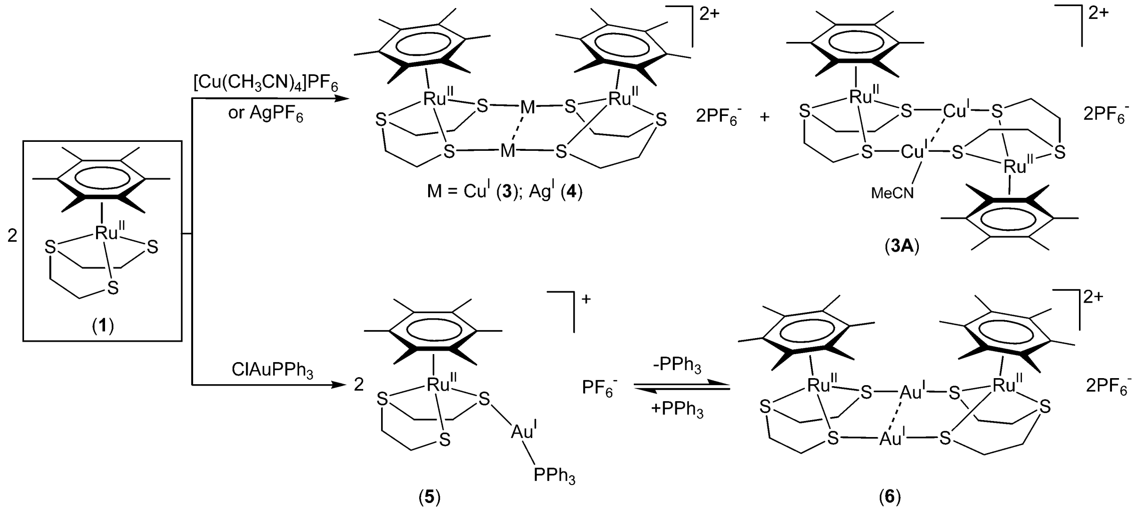
Diffraction-quality crystals of the PF_6 salts of **3**–**10** were obtained at −30 °C as follows: **3** from a solution of a mixture of **3** and **3A** in CH_2Cl_2 with ether diffusion for 4 days, **3A**, **7**, and **8** from solutions in MeOH with ether diffusion for 1 week, **4** and **5** from solutions in MeCN with ether diffusion for 2 weeks, **6** from a solution in CH_2Cl_2 with hexane diffusion for 3 days. Suitable crystals of the salts of **9** and **10** were selected in the course of their isolation procedures described above.

Results and Discussion

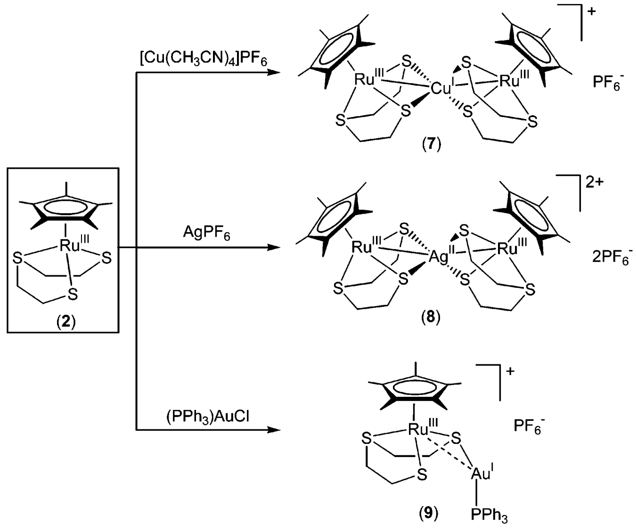
Syntheses. The arene Ru(II) complex **1** undergoes an instantaneous reaction with $[Cu(MeCN)_4]PF_6$ (1 molar equiv) or $AgPF_6$ (4 molar equiv) to give annular dithiolate-bridged diruthenium complexes of Cu(I) (**3** and **3A**, in admixture) and of Ag(I) (**4**) as orange crystals, respectively, in 83–84% yields. An apparently instantaneous reaction with 1 molar equiv of $(PPh_3)AuCl$ in MeOH gave red S-"aurated" derivative **5** (45% yield) and the yellow complex **6**, the Au analogue of **3** or **4**, as PF_6 salts, upon treatment of the product solution with NH_4PF_6 at the end of 10 h.

A repeat reaction in the presence of NH_4PF_6 in MeOH led to precipitation of the insoluble PF_6 salt of **6** as orange solids in admixture with a small amount of **5**, as the reaction progressed. Recrystallization of this mixture gave pure **6**$(PF_6)_2$ as golden yellow crystals in 48% yield. In the presence of excess PPh_3, the predominant product was **5** (64% isolated yield). An independent NMR-scale reaction showed that the treatment of **6** with

Scheme 1



Scheme 2



10 molar equiv of PPh_3 resulted in total conversion to **5** (Scheme 1). Such facile reversible dissociation of PPh_3 from $AuPPh_3$ observed here had been demonstrated to be involved in reductive elimination and *cis−trans* isomerization processes in trialkyl(phosphine)gold complexes,[24] although such dissociations have not been found to occur in $AuPPh_3$ ligated to clusters.[25]

A heterogeneous mixture of **2** and $[Cu(MeCN)_4]PF_6$ (0.5 mol equiv) in MeOH reacted instantaneously, giving dark brown solutions, from which were isolated the thiolate-bridged Cu(I) complex **7** (71% yield). A similar reaction with $AgPF_6$ (2 molar equiv) led to the Ag(II) complex **8** as black crystalline solids in 73% yield, after removal of some black insoluble precipitate, which was presumably metallic silver. It is surprising that the Ag(I) compound was not isolated. In the context of this observation, we note here that the reaction of a Ag(I) salt with tetraphenylporphine ("PH_2") in pyridine gave a Ag(I) complex (PAg^I_2), which underwent slow disproportionation to PAg^{II} and Ag^0 upon reflux. In acetic acid, PAg^{II} was formed directly, presumably via the oxidation of the primary Ag(I) compound by H^+, which was reduced to H_2 in the process.[26] In this reaction, it is clear that $AgPF_6$, used in 2 molar excess, has served concurrently as a Lewis acid for the formation of a Ag(I) complex and as an oxidant. The ease of oxidation of complexed Ag(I) had also been demonstrated in the instantaneous transformation of Ag(I) *N*,*N*-dialkyldithiocarbamates (RSAg) to Ag(II) derivatives $(RS)_2Ag$ upon treatment with thiuram disulfides, RSSR.[27]

The Pd(II) analogue of **8** was previously obtained from the reaction of **2** with $Pd(MeCN)_2Cl_2$ or $PdCl_2$.[15]

The reaction of **2** with ca. 1 molar equiv of $(PPh_3)AuCl$ gave a dark blue solution, from which was isolated black microcrystalline solids of the S-"aurated" derivative **9** in 72% yield (Scheme 2). In the process of obtaining diffraction-quality crystals with ether diffusion at −30 °C, a few orange crystals of a μ-S_2 diruthenium(II) complex, $\mathbf{10}(PF_6)_2$ (characterized only by single X-ray crystallography), were obtained in admixture with needle-shaped crystals of species **9** after a week in THF (with mother liquor containing species **11**), while a dark blue solution of **9** in MeCN, after prolonged standing at −30 °C, was transformed to a homogeneous orange solution, which yielded a noncrystallizable oil. The proton NMR and FAB mass spectra of this oil were supportive of a species formulated as $\mathbf{11}(PF_6)$, possibly contaminated with complexes **2** and **10**. These preliminary observations indicate a transformation of species **9** to **10** and **11** (Scheme 3). We point out here that $\mathbf{10}(PF_6)_2$ and $\mathbf{11}(PF_6)$ are analogues of the μ-S_2 complex **G** and di-S-methylated derivative **H**, which we have previously isolated from the alkylation of **2** (Scheme 4).[28]

Spectral Features. The mass spectra of all the complexes show their respective mother cations (lower mass fragments are given in the Supporting Information). The (HMB)Ru complexes, **3**−**6**, are diamagnetic, consistent with the 18e count at the Ru centers and the overall *even* total valence electron count (TEC) of

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(24) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7255.

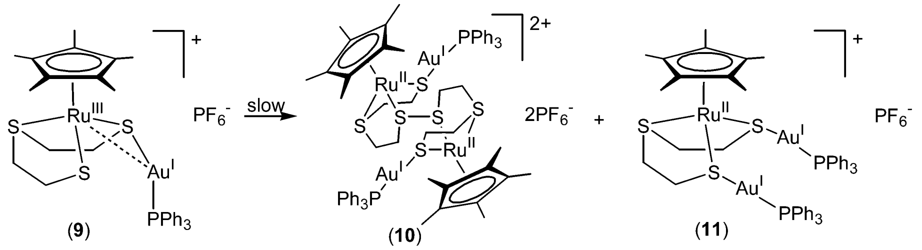
(25) See for instance: (a) Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Puga, J.; Whitmire, K. H. *J. Chem. Soc., Dalton Trans.* **1983**, 787. (b) Bruce, M. I.; Liddell, M. J.; Williams, M. L.; Nicholson, B. K. *Organometallics* **1990**, *9*, 2903.

(26) Dorough, G. D.; Miller, J. R.; Huennekens, F. M. *J. Am. Chem. Soc.* **1951**, *73*, 4315.

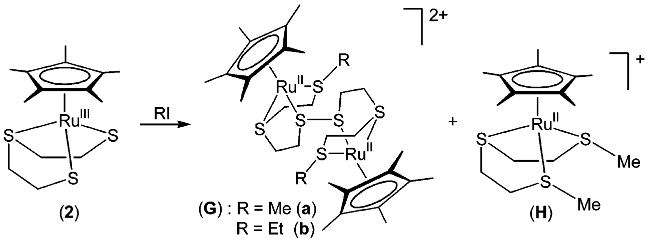
(27) Vänngard, T.; Åkerström, S. *Nature (London)* **1959**, *184*, 183.

(28) Shin, R. Y. C.; Teo, M. E.; Leong, W. K.; Vittal, J. J.; Yip, J. H. K.; Goh, L. Y.; Webster, R. D. Submitted.

Scheme 3



Scheme 4



dicationic **3A** (66e), **3**, **4**, and **6** (each 64e), and monocationic **5** (32e). The ^1H NMR spectra of these compounds show Me singlets of the arene ring at δ 2.05−2.19 and SCH_2's as *n* sets of multiplets, namely for **3** and **3A**, $n = 3$, range δ 2.04−2.78; for **4**, $n = 2$, range δ 2.15−2.59; for **5**, $n = 4$, range δ 2.18−2.84; and for **6**, $n = 3$, range δ 2.37−2.82. Their ^{13}C NMR spectra show Me and ring carbon resonances in the ranges δ 15.6−15.8 and 100.0−102.1, respectively. Complexes **3**, **3A**, **4**, and **6** each shows two ^{13}C signals for the SCH_2 groups at δ 29.2−41.8, while **5** possesses four such signals at δ 23.1−43.1. Complexes **7** and **8** can be visualized as composed of two 17e neutral Cp^*Ru^{III}(tpdt) moieties, linked by chelation of the dithiolate S atoms of their tpdt ligand to a central metal atom, viz., Cu(I) and Ag(II), resulting in TECs of 52 and 51, respectively, for the trimetallic species. This is reflected in the relative resolution of resonances observed in their ^1H NMR spectra; thus while broad peaks are observed in the spectrum of **7**, assignable to Cp* and SCH_2's, albeit in abnormally lower and higher fields, respectively, the spectrum of **8** possesses only *one* unresolved (extremely broad) resonance centered at δ 9.01. The very broad resonances in the proton NMR spectrum of **9** are in agreement with the 17e count on Ru and the *odd* TEC (31).

The μ_2-S_2 diruthenium complex **10** is an S-aurated analogue of the bis(SMe) complex, **G**(**a**), that we have previously obtained from alkylation of **2** (Scheme 4). These two structures are consistent with the isolobal nature of the $AuPPh_3$ and Me moieties.[29]

Solid State Structures. The molecular structures of **3**−**10** have been determined by X-ray diffraction analyses. The ORTEP diagrams for the structures of **3**, **4**, and **6** are shown in Figure 1, and that of **3A** is shown in Figure 2. The asymmetric unit in the crystal structure of **3** contains a half nondisordered and one disordered cation. The ORTEP diagram and metric data discussed are based on the former (see Experimental Section). These three (arene)Ru complexes possess similar Ru_2M_2 annular structures, with M···M distances of 2.637(3) Å (Cu), 2.9098(9) Å (Ag), and 2.9161(10) Å (Au), the magnitudes of which are indicative of bonding interactions between the group 11 metal centers (cf. the single-bond radii of Cu(I) (1.352 Å), Ag(I) 1.528 Å, and Au(I) (1.520 Å),[30a] interatomic distance in crystals of the elements being 2.556(12), 2.889(12), and 2.884(12) Å, respectively).[30b] Unlike the double bridges in the commonly reported annular/transannular structures of type **F**,[16] the bridging arene-ruthenium-thioether dithiolate in **3**, **4**, and **6** is in a class of its own in terms of steric bulkiness. The steric demand of this bridge is the probable cause of the "puckering" of the two M_2SRuS moieties conjoined at the M···M junction in each case and their twist about that junction (see Figures 1 and 2). The magnitude of the "twist" is reflected in the dihedral angles between the triangular planes (i) M(1)M(2)S(1) and M(1)M(2)S(2) and (ii) M(1)M(2)S(4) and M(1)M(2)S(5). In compounds **3**, **4**, and **6**, which possess a similar geometrical arrangement of metal centers and ligands, these angles are 41.5 and 41.5° in **3**, 18.7 and 26.0° in **4**, and 35.0° and 40.2° in **6**. In complex **3A**, the Cu−Cu distance 2.6131(8) Å is slightly shorter than in **3**. Its structure shows that an additional MeCN ligand at one of the Cu atoms has changed the orientation of the metallodithiolate ligands from "*cis*" with respect to each other relative to the M_2S_4 moiety in **3** to "*trans*" in **3A** and increased by a large amount the dihedral angles between the triangular planes at Cu···Cu (66.1° and 71.9°). The M···M contact distance in **6** is very close to values recently reported for the doubly bridged transannular compounds, $Au_2(PPh_2CH_2SPh)_2$ (2.9020(5) Å),[19] Au_2(diphosphine)(dithiolate) complexes (2.850(1)−3.219(6) Å),[8f] and $Au_2(S_2COBu^n)_2$ (2.8494(15) Å)[31] and is in the range of very short M···M contacts (2.582−2.977 Å) found in many coordination compounds.[18,32] It has been observed from experimental and theoretical data that Au···Au distances in compounds showing aurophilic interactions range from 2.8 Å for strong interactions connected with soft ligands to 3.5 Å for weak interactions.[33]

While Au−Au bond interactions are now well-established in the solid state structures of numerous compounds,[18] examples of similar interactions in Ag compounds are far less common and the phenomenon is still under some controversy, though much less so than for Cu. Ag···Ag contact distances, indicative of metallophilicity, have been found to range from 2.725 to 2.989 Å in di- to polyelemental aggregates and coordination

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[29] (a) Lauher, J.; Wald, K. *J. Am. Chem. Soc.* **1981**, *103*, 7648. (b) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

[30] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; (a) p 420, (b) p 410, and (c) p 256.

[31] Mohamed, A. A.; Kani, I.; Ramirez, A. O.; Fackler, J. P. Jr. *Inorg. Chem.* **2004**, *43*, 3833.

[32] Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098.

[33] Schwerdtfeger, P.; Bruce, A. E.; Bruce, M. R. M. *J. Am. Chem. Soc.* **1998**, *120*, 6587.

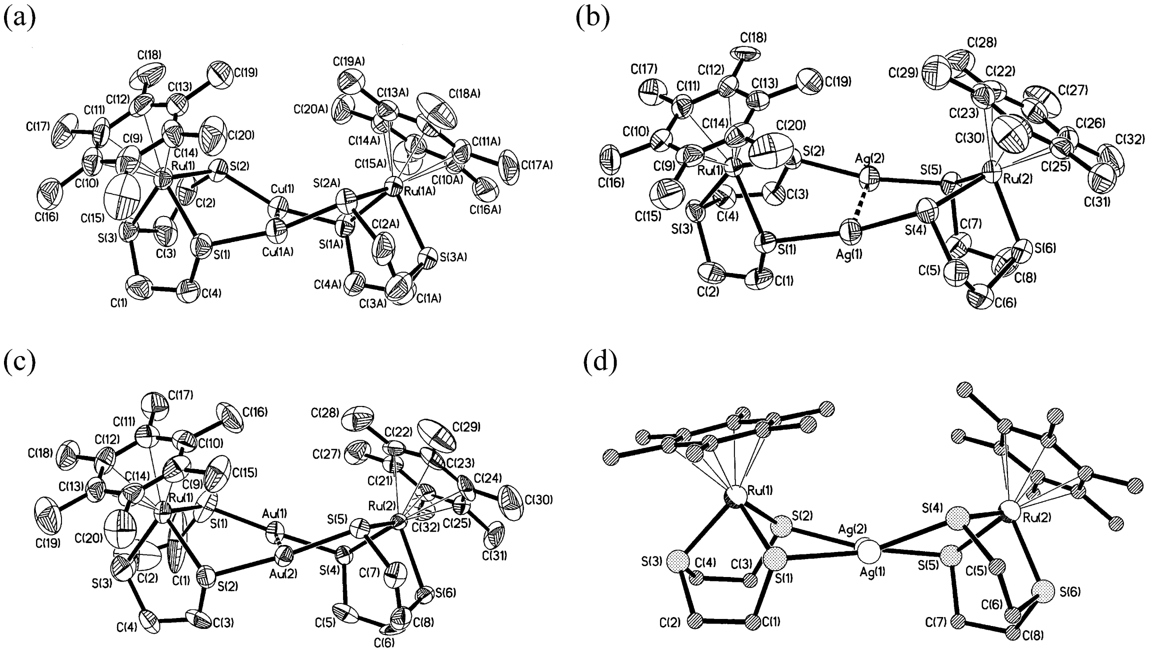

Figure 1. ORTEP plots for the molecular structures of the dication of (a) **3**, (b) **4**, and (c) **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. (d) Perspective view of the molecular structure of **4** along the Ag(1)−Ag(2) bond.

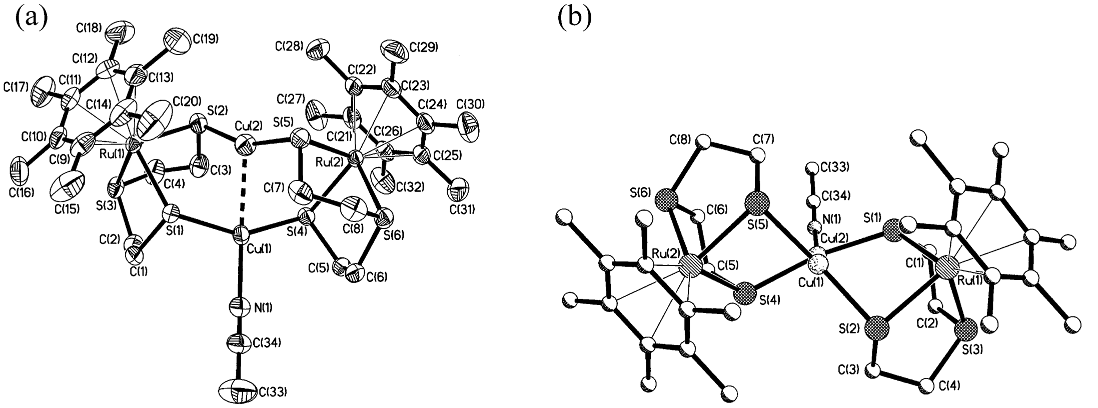

Figure 2. (a) ORTEP plot for the molecular structure of dication **3A**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. (b) Perspective view of the molecular structure along the Cu(1)−Cu(2) bond.

compounds[18,32] and 2.9501(8)−2.9732(9) Å in transannular $Ag_2(PPh_2CH_2SPh)_2$[19] and 2.705(1) Å for transannular $Ag_2((p\text{-tolyl})NCHN(p\text{-tolyl}))_2$.[18]

Controversy over the occurrence of cuprophilicity has been a long-standing matter,[18,34] the resolution of which was largely hampered by the inability to obtain solid state structural data on a complete congeneric set of complexes of all three coinage metals in an identical ligand environment.[18,19] Lately Laguna reported theoretical and experimental evidence for a Cu(I)−Cu(I) bond in the $[M_2(PPh_2CH_2SPh)]^{2+}$ complexes of the coinage metals.[19] More recent support for cuprophilicity came from theoretical studies by Schwerdtfeger,[35] X-ray structural data of a dimer between two $[CuCl_2]^-$ anions in a complex by Köhn,[36] structural and spectroscopic investigations by Che on luminescent Cu(I) dinuclear and cluster species containing bridging diphosphanes,[37] and direct observation of Cu−Cu bonding from a recent investigation on Cu_2O based on electron and X-ray diffraction experiments.[38] The Cu···Cu contact distances in **3** and **3A** (2.637(3) and 2.6131(8) Å, respectively) lie in the observed range 2.403−2.790 Å,[32] which encompasses values of 2.497(2) Å in the transannular complex $Cu_2((p\text{-tolyl})NCHN(p\text{-tolyl}))_2$[18] and 2.475(1)−3.005(1) Å in other diphosphine complexes $Cu_2(dcpm)_2X_2$ and related Cu_3 analogues.[37] Other selected bond parameters of **3**, **3A**, **4**, and **6** are given in Table 3, wherein

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[34] (a) Cotton, F. A.; Feng, X.; Matusz, M.; Poli, R. *J. Am. Chem. Soc.* **1988**, *110*, 7077. (b) Lee, S. W.; Trogler, W. C. *Inorg. Chem.* **1990**, *29*, 1659. (c) Abraham, S. P.; Samuelson, A. G.; Chandrasekhar, J. *Inorg. Chem.* **1993**, *32*, 6107. (d) Pyykkö, P.; Li, J.; Runeberg, N. *Chem. Phys. Lett.* **1994**, *218*, 133. (e) Siemeling, U.; Vorfeld, U.; Neumann, B.; Stammler, H.-G. *Chem. Commun.* **1997**, 1723. (f) Poblet, J.-M.; Bénard, M. *Chem. Commun.* **1998**, 1179. (g) Carvajal, M. A.; Alvarez, S.; Novoa, J. J. *Chem. Eur. J.* **2004**, *10*, 2117.

[35] Hermann, H. L.; Boche, G.; Schwerdtfeger, P. *Chem. Eur. J.* **2001**, *7*, 5333.

[36] Köhn, R. D.; Seifert, G.; Pan, Z.; Mahon, M. F.; Kociok- Köhn, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 793.

[37] (a) Che, C.-M.; Phillips, D. L.; Mao, Z.; Miskowski, V. M.; Tse, M.-C.; Chan, C.-K.; Cheung, K.-K.; Leung, K.-H. *Angew. Chem., Int. Ed.* **2000**, *39*, 4084. (b) Fu, W.-F.; Gan, X.; Che, C.-M.; Cao, Q.-Y.; Zhou, Z.-Y.; Zhu, N. N.-Y. *Chem. Eur. J.* **2004**, *10*, 2228.

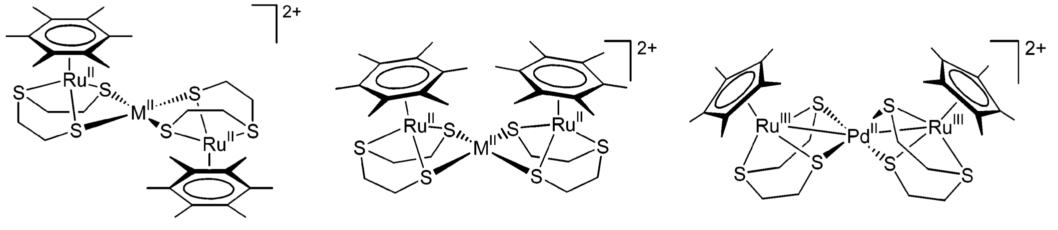
[38] Zuo, J. M.; Kim, M.; O'Keeffe, M.; Spence, J. C. H. *Nature* **1999**, *401*, 49.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of 1 and Dicationic $[\{(HMB)Ru(tpdt)\}_2M_2]^a$ Complexes

	1[12]	**3**[b]	**3A**	**4**	**6**
M		Cu	Cu	Ag	Au
Ru(1)−S(1)	2.3807(10)	2.368(3)	2.3917(11)	2.373(2)	2.370(5)
Ru(1)−S(2)	2.3851(10)	2.368(3)	2.3820(12)	2.379(2)	2.372(5)
Ru(1)−S(3)	2.3396(10)	2.317(3)	2.3412(11)	2.325(2)	2.339(6)
Ru(2)−S(4)			2.4065(11)	2.365(2)	2.342(4)
Ru(2)−S(5)			2.3859(11)	2.373(2)	2.372(4)
Ru(2)−S(6)			2.3407(11)	2.334(2)	2.329(4)
M(1)−S(1)		2.152(4)	2.2259(11)	2.383(2)	2.289(5)
M(1)−S(4)			2.2173(11)	2.387(2)	2.293(4)
M(2)−S(2)		2.155(4)	2.1728(14)	2.381(2)	2.287(5)
M(2)−S(5)			2.1685(13)	2.393(2)	2.290(4)
M(1)−M(2)		2.637(3)	2.6131(8)	2.9098(9)	2.9161(10)
M(1)−N(1)			2.089(5)		
S(1)−Ru(1)−S(2)	92.18(4)	93.69(12)	92.26(4)	93.08(8)	95.07(18)
S(1)−Ru(1)−S(3)	85.41(4)	85.20(12)	85.55(4)	85.56(7)	84.9(3)
S(2)−Ru(1)−S(3)	85.18(4)	86.39(12)	85.59(4)	85.59(8)	84.6(2)
S(4)−Ru(2)−S(5)			92.37(4)	92.44(8)	95.45(15)
S(4)−Ru(2)−S(6)			85.32(4)	85.70(8)	85.39(16)
S(5)−Ru(2)−S(6)			85.96(4)	85.95(8)	85.85(15)
S(1)-M(1)−S(4)		160.55(16)	149.49(5)	157.70(8)	173.14(17)
S(2)-M(2)−S(5)			158.22(5)	169.10(8)	171.03(17)
Cu(2)−Cu(1)−N(1)			162.56(15)		
N(1)−C(34)−C(33)			178.6(7)		
S(1)−M(1)−M(2)		96.91(12)	74.41(3)	97.62(6)	95.55(13)
S(4)−M(1)−M(2)			75.91(3)	96.68(5)	91.10(11)
S(2)−M(2)−M(1)		95.54(12)	104.04(4)	93.29(6)	91.98(12)
S(5)−M(2)−M(1)			97.70(4)	91.45(6)	93.84(11)

[a] Complex **3A** has MeCN coordinated to one of the Cu atoms. [b] Complex has center of inversion. Data of the nondisordered cation in the asymmetric unit.

Chart 2



A(e,f)(*trans*) (M = Pd, Pt) **A(e,f)**(*cis*) (M = Pd, Pt) **B(d)**

they are compared with equivalent parameters in complex **1**. There are only slight differences in the Ru−S distances of these complexes. Likewise the corresponding ranges for the S−Ru−S angles in each of these three complexes are also very close and are similar to the range found in **1**. We note that the "open" S−Ru−S angle in **1** (92.18(4)°) is increased in the formation of the annular complexes, viz., +1.51° in **3**, +0.08 and +0.19° in **3A**, +0.90 and +0.26° in **4**, and +2.89 and +3.27° in **6**. The linearity of the S−M−S linkage decreases in the order M = Au ≫ Ag > Cu.

In comparison, our earlier studies have shown that derivatives from Pd(II) and Pt(II) compounds were of the Ru_2M type (**A**(**e**, **f**)), wherein M is coordinated to the four thiolate S atoms of the Ru moiety in planar geometry, with HMB rings in both *trans* and *cis* orientation with respect to the MS_4 plane (Charts 1 and 2).[15]

The Cp*Ru(III) complexes **7**(Cu^I) and **8**(Ag^{II}) possess molecular structures illustrated in Figure 3, and selected metric data are listed in Table 4, where they are compared with those of the original complex **2**. Resembling the tetrathiolate-bridged complex of Pd(II) (**B**(**d**), Charts 1 and 2), the MS_4 moiety of both **7** and **8** also possesses a distorted tetrahedral environment at M, with similar distorted tetrahedral angles in the range

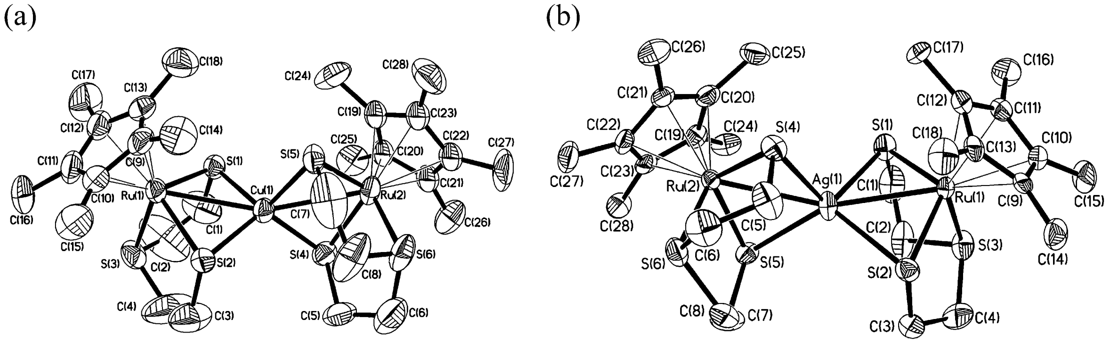


Figure 3. ORTEP plots for the molecular structures of (a) monocation **7** and (b) dication **8**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of 2 and Cationic [{Cp*Ru(tpdt)}$_2$M] Complexes

	2[13]	**7**	**8**	
M		Cu(I)	Ag(II)	
			(A)[a]	(B)[a]
Ru(1)−S(1)	2.3808(12)	2.292(9)	2.302(2)	2.253(2)
Ru(1)−S(2)	2.3850(12)	2.399(11)	2.299(2)	2.237(2)
Ru(1)−S(3)	2.3409(12)	2.312(3)	2.295(2)	2.314(2)
Ru(2)−S(4)		2.263(5)	2.314(2)	2.338(2)
Ru(2)−S(5)		2.378(4)	2.296(2)	2.353(2)
Ru(2)−S(6)		2.298(4)	2.312(2)	2.290(2)
M(1)−S(1)		2.330(6)	2.499(2)	2.507(2)
M(1)−S(2)		2.306(7)	2.528(2)	2.512(2)
M(1)−S(4)		2.314(5)	2.522(2)	2.546(2)
M(1)−S(5)		2.327(4)	2.499(2)	2.495(2)
M(1)−Ru(1)		2.786(3)	2.7679(8)	2.7137(9)
M(1)−Ru(2)		2.776(3)	2.7999(8)	2.8920(9)
S(1)−Ru(1)−S(2)	92.23(5)	103.0(3)	113.91(8)	116.49(8)
S(1)−Ru(1)−S(3)	85.40(4)	87.4(2)	84.98(9)	86.48(9)
S(2)−Ru(1)−S(3)	85.22(5)	84.2(3)	85.07(9)	85.01(9)
S(4)−Ru(2)−S(5)		104.38(14)	112.35(8)	108.96(8)
S(4)−Ru(2)−S(6)		87.33(18)	85.70(8)	84.62(8)
S(5)−Ru(2)−S(6)		85.46(15)	84.41(9)	85.33(9)
S(1)−M(1)−S(2)		104.8(4)	100.22(7)	99.04(7)
S(1)−M(1)−S(4)		108.1(3)	113.33(8)	118.79(7)
S(1)−M(1)−S(5)		116.4(3)	116.81(8)	108.78(7)
S(2)−M(1)−S(4)		117.8(3)	110.03(7)	111.85(8)
S(2)−M(1)−S(5)		106.0(3)	117.54(7)	121.22(8)
S(4)−M(1)−S(5)		104.39(17)	99.42(7)	98.46(7)
Ru(1)−M(1)−Ru(2)		158.61(11)	157.78(4)	157.66(3)

[a] A and B refer to two independent molecules in the asymmetric unit.

98.46(7)−118.79(7)°. The dihedral angle between the CuS_2 triangular planes in **7** is 82.5°, while those between the AgS_2 triangular planes in **8** are 88.3° and 82.4° for the two independent molecules. As in complex **B**(**d**), the Ru(III) centers in **7** and **8** are metal−metal bonded to the central atom M. The Ru−Cu distances in **7** (av 2.781(3) ± 0.06 Å) lie in the range observed in RuCu clusters for such bonds (2.509(6)−2.909(2) Å).[39] The Ru−Ag distances in **8** (2.7137(9)−2.8920(9) Å) fall close to values previously reported for a Ag-bridged ["Ru_4BH"]$_2$ cluster (2.746(1) Å),[3f] a complex wherein a $AgPPh_3$ fragment is η^2-bonded to a Ru−Ru edge of a Ru_3 cluster (2.785(3), 2.788(3) Å),[40a] and a $Ag_2Ru_4(\mu_3\text{-}H)_2$ complex (2.820(6)−3.151(6) Å).[40b] The large variation in the bond lengths of these bonds has been ascribed to the "softness" of this type of metal−metal bonding involving group 11 metal atoms.[39a] It is observed that with the exception of the Cu(I) complex **7**, the Ru−S distances in all these complexes are slightly diminished from those in the original complex **2**, e.g., by 0.066−0.079 Å for Ru(1)−S(1), 0.038−0.148 Å for Ru(1)−S(2), and 0.007−0.046 Å for Ru(1)−S(3)(thioether). In **7**, the Ru(1)−S(2) bond is anomalously 0.014 Å longer than in **2**. In all cases the S(thiolate)−Ru−S(thiolate) angles (104.23(8)−116.49(8)°) are substantially enlarged from the equivalent angle in **2** (92.23(5)°) and also appreciably higher than the S(thiolate)−Ru−S(thioether) angles in each case, with a range 84.2(3)−87.4(2)°, comparable to values 85.40(4)° and 85.22(5)° in **2**. The ranges of Ru−S distances in **7** (2.263(5)−2.399(10) Å) and **8** (2.237(2)−2.353(2) Å) are agreeable with the range in the Pd(II) complex **B**(**d**) (2.272(3)−2.319(3) Å). It is seen that in both complexes their respective S(1)−Ru(1)−S(2) and S(4)−Ru(2)−S(5) angles, which are "bisected" by Ru−M bonds, are significantly larger that the other S−Ru−S angles (range 84.2(3)−87.4(2)° for **7** and 84.41(9)−86.48(9)° for **8**). A similar observation was made in the S−Ru−S angles in **B**(**d**).

The ORTEP plots of **5**, **9**, and **10** are illustrated in Figure 4 and their bond parameters given in Table 5. Complex **5** is the geometrical analogue of molecules of type **E** (Chart 1) with $AuPPh_3$ substituted by $SnPh_3$ (**E**(**a**)) and $PbPh_3$ (**E**(**b**)). While the Ru−S(Au) distance in **5** is decreased from the corresponding Ru−S distances in **1** by ca. 0.016−0.020 Å, the differences are ca. 0.04 Å in the Sn and Pb complexes. The significantly longer M−S bond for Sn and Pb compared to that for Au (Δ ≈ 0.20 and 0.28 Å), despite the longest single-bond radii (1.520 Å) for Au(I) versus 1.399 Å (Sn(IV) and 1.430 Å (Pb(IV),[30a] is in agreement with the expected order of bond strength of M−S: Au ≫ Sn > Pb. The corresponding S−Ru−S angles in these three complexes are comparable with the "open" S(1)−Ru−S(2) angle and are larger than the other two "closed" angles (Δ ≈ 4° (Au), 1.6° (Sn), and 3° (Pb)). There are some differences in their Ru−S−M angles, being largest (112.27(13)°) for M = Au, 107.32(3)° for M = Sn, and 109.31(8)° for M = Pb. Although the molecular structures of **5** and its Cp* analogue **9** are very similar, the much shorter Ru···Au distance in **9** (3.211(2) versus 3.903 Å in **5**) could be indicative of weak bonding interaction, noting that nonvalence-dependent single-bond radii of Ru and Au are 1.246 and 1.336 Å, respectively,[30c] and that Ru−Au(PPh_3) distances fall in the range 2.758(2)−2.855(2) Å in Ru clusters.[41] This interaction is reflected in a much reduced Ru−S−Au angle (84.94(19)°) and an enlarged S(1)−Ru−S(2) angle (Δ = 19.69°) in **9**. The S(1)−Au−P(1) linkage is closer to linearity (angle 174.46(16)°). The Ru−S distances in **5** and **9** are only marginally different.

The molecular structure of **10**, into which **9** slowly converts on standing, is of an entirely different type. The S−S bonded diruthenium complex is an analogue of the di-S alkylated complexes **G**(**a**,**b**) that we have obtained from the alkylation of **2**[28] (discussed above). As shown in Table 3, the S(2)−S(2A) distance (2.209(6) Å) and Ru−S distances are very close to those in the SMe analogue **G**(**a**). The Au−P distances in **5**, **9**, and **10** fall in the range reported for such complexes, 2.252(4)−2.273(4) Å.[8b,f,g] The Ru···Au distance in **10** (3.96 Å) is much longer than that in **9**.

In summary, these crystallographic studies show that the tpdt ligand is capable of coordinating in diverse bonding modes in different environments in these (HMB/Cp*)Ru complexes. Thus, while the η^3 or κ^3SSS' mode is adopted in the mononuclear complexes **1** and **2**, the ligand also bonds in a variety of bridging modes,

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[39] See for instance: (a) Salter, I. D.; Šik, V.; Williams, S. A.; Adatia, T. *J. Chem. Soc., Dalton Trans.* **1996**, 643. (b) Brown, S. S. D.; McCarthy, P. J.; Salter, I. D.; Bates, P. A.; Hursthouse, M. B.; Colquhoun, I. J.; McFarlane, W.; Murray, M. *J. Chem. Soc., Dalton Trans.* **1988**, 2787. (c) Beswick, M. A.; Lewis, J.; Raithby, P. R.; Ramirez de Arellano, M. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2227.

[40] (a) Adatia, T.; McPartlin, M.; Salter, I. D. *J. Chem. Soc., Dalton Trans.* **1988**, 2889. (b) Brown, S. S. D.; Salter, I. D.; Šik, V.; Colquhoun, I. J.; McFarlane, W.; Bates, P. A.; Hursthouse, M. B.; Murray, M. *J. Chem. Soc., Dalton Trans.* **1988**, 2177.

[41] (a) Johnson, B. F. G.; Lewis, J.; Nicholls, J. N.; Puga, J.; Whitmire, K. H. *J. Chem. Soc., Dalton Trans.* **1983**, 787. (b) Bruce, M. I.; Liddell, M. J.; Williams, M. L.; Nicholson, B. K. *Organometallics* **1990**, *9*, 2903.

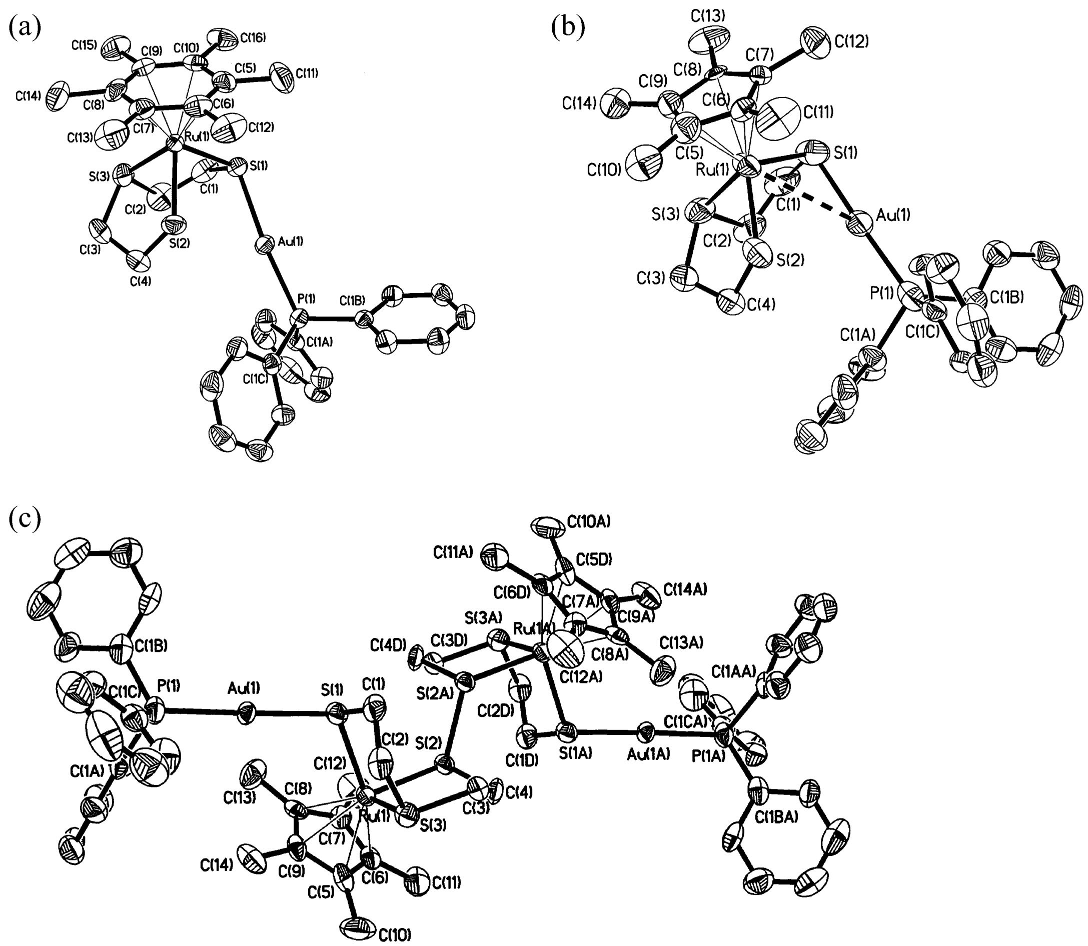

Figure 4. ORTEP plots for the molecular structures of (a) monocation **5**, (b) monocation **9**, and (b) dication **10**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) of Cationic [(HMB/Cp*)Ru(tpdt)Au(PPh_3)] Complexes and Complexes G(a) and G(b)

	5	**9**	**10**[a]	**G(a)**[a]	**G(b)**[a]
M	Au	Au	Au(S−S bonded)		
Ru(1)−S(1)	2.365(3)	2.409(5)	2.400(3)	2.3702(19)	2.3474(17)
Ru(1)−S(2)	2.358(3)	2.326(5)	2.282(3)	2.2813(17)	2.2831(16)
Ru(1)−S(3)	2.328(4)	2.356(5)	2.322(4)	2.3261(18)	2.3276(16)
Au(1)−S(1)	2.336(3)	2.347(6)	2.309(3)		
Au(1)···S(2)	3.289	3.091	5.641		
Au(1)−P(1)	2.273(3)	2.300(6)	2.263(3)		
Au(1)···Ru(1)	3.903	3.211(2)	3.96		
S(2)−S(2A)			2.209(6)	2.194(3)	2.221(3)
S(1)−Ru(1)−S(2)	90.71(12)	110.40(18)	95.45(11)	95.9(6)	109.30(6)
S(1)−Ru(1)−S(3)	85.81(13)	84.9(2)	86.02(12)	86.1(6)	85.12(6)
S(2)−Ru(1)−S(3)	86.04(13)	86.18(17)	87.17(12)	86.96(6)	86.54(6)
S(1)−Au(1)−P(1)	172.37(12)	174.46(16)	176.44(14)		
Ru(1)−S(1)−Au(1)	112.27(13)	84.94(19)	114.51(13)		

[a] Molecule possesses center of inversion.

viz., μ-η^1:η^3 or μ-1κ^3*SSS*′:2κ*S* mode in the mono-RuAu complexes **5** and **9**, μ_3-η^1:η^1:η^3 or μ_3-1κ^3*SSS*′:2κ*S*:3κ*S* mode in the annular Ru_2M_2 complexes **3**, **3A**, **4**, and **6**, and in **11**, and μ-η^2:η^3 or μ-1κ^3*SSS*′:2κ^2*SS* mode in the metal−metal bonded Ru_2M complexes, **7** and **8**.

Electrochemical and EPR Studies. Cyclic voltammograms obtained at a GC electrode in solutions of **3A**, **4**, and **6** in CH_2Cl_2 at 233 K are shown in Figure 5. The voltammograms showed one oxidation (**3A** showed at least two) and one reduction process, although for most of the compounds the cyclic voltammograms indicated the reduced and oxidized states were very unstable (even at 233 K), since only a very small reverse peak was detected when the scan directions were reversed. The electrochemical behavior of **7** and **8** (Figure 6) is similar to that previously reported for the Ru^{III}−M^{II}−Ru^{III} group 10 analogues,[15] except that the oxidation and reduction processes for the present Cu- and Ag-containing complexes are shifted to substantially more negative potentials (up to ca. −1 V). The large change in oxidation (and reduction) potentials between the group 10[15] and 11 compounds indicates that both the oxidation and reduction occur within the region of the central Cu/Ag atoms, rather than isolated on the Ru(III) atoms or

Table 6. Cyclic Voltammetric Data Obtained at a Scan Rate of 100 mV s^{-1} at a 1 mm Diameter Glassy Carbon Electrode at 233 K in CH_2Cl_2 with 0.25 M Bu_4NPF_6 as the Supporting Electrolyte

	reduction processes[a]				oxidation processes[a]			
compound	E_p^{red}/V[b]	E_p^{ox}/V[c]	$E^r_{1/2}$/V[d]	ΔE/mV[e]	E_p^{ox}/V[c]	E_p^{red}/V[b]	$E^r_{1/2}$/V[d]	ΔE/mV[e]
3	−1.98							
					+0.32	+0.22	0.27	100
4	−1.94							
					+0.62			
6	−1.97							
					+0.94			
7	−1.322	−1.249	−1.29	73				
	−1.765	−1.692	−1.73	73				
					−0.247	−0.308	−0.28	61
					+0.284	+0.211	+0.25	73
8	−1.300	−1.200	−1.250	100				
					−0.167	−0.231	−0.20	64
					+0.170	+0.103	+0.14	67

[a] All potentials are relative to the ferrocene/ferrocenium redox couple. [b] E_p^{red} = reductive peak potential. [c] E_p^{ox} = oxidative peak potential. [d] $E^r_{1/2} = (E_p^{red} + E_p^{ox})/2$. [e] $\Delta E = |E_p^{ox} - E_p^{red}|$.

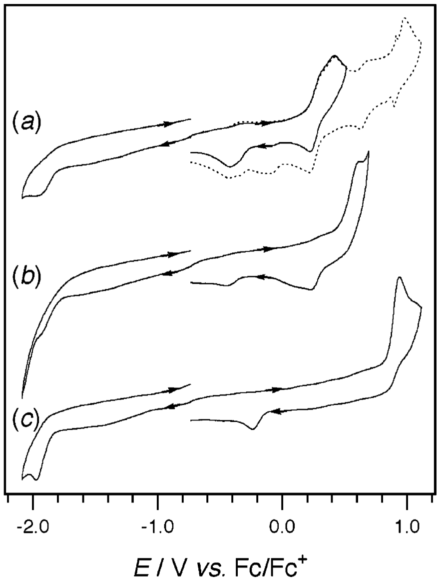

Figure 5. Cyclic voltammograms performed at a 1 mm diameter planar GC electrode in CH_2Cl_2 (0.25 M Bu_4NPF_6) at 233 K at a scan rate of 100 mV s^{-1} for (a) 0.70 mM **3**, (b) 0.75 mM **4**, and 0.80 mM **6**.

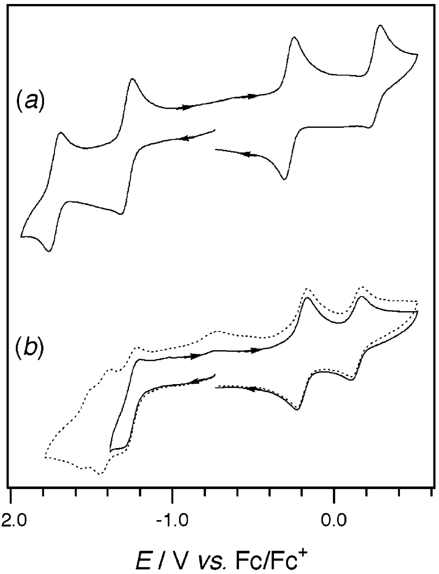

Figure 6. Cyclic voltammograms performed at a 1 mm diameter planar GC electrode in CH_2Cl_2 (0.25 M Bu_4NPF_6) at 233 K at a scan rate of 100 mV s^{-1} for (a) 0.75 mM **7** and (b) 0.60 mM **8**.

S ligands. Previous electrochemical and EPR experiments on the group 10 compounds indicated that there was considerable electron delocalization between the two Ru(III) atoms;[15] hence it is likely that the reduction/oxidation processes also occur within the Ru−Cu/Ru−Ag framework. Table 6 lists the reversible reduction potentials ($E^r_{1/2}$) that were calculated from CV data under conditions where the ratio of the oxidative (i_p^{ox}) to reductive (i_p^{red}) peak currents was equal to unity. In situations where no reverse peak was observed, only the peak potential is given.

For symmetrical compounds with more than one possible redox center, similar to Creutz−Taube type ions,[42] the separation in the electron transfer steps can be used to determine the comproportionation constant (K_c) that is a measure of the degree of interaction between the metal centers.

$$K_c = \exp[(E_1^{\circ} - E_2^{\circ})F/RT] \qquad (1)$$

For **7**, the difference in potential between the first and second reduction processes ($E_1^{\circ} - E_2^{\circ}$) is 0.44 V, which leads to a value of K_c of 10^9 for the equilibrium

$$[Ru-Cu-Ru]^+ + [Ru-Cu-Ru]^- \leftrightarrow 2[Ru-Cu-Ru]^0 \qquad (2)$$

Values of $K_c > 10^6$ are considered to be indicative of a Class III system (extensive delocalization) according to the Robin−Day scheme;[43] hence the redox properties must be considered in terms of a shared molecular orbital.

Although **7** and **8** contain two formally Ru(III) ions, previous EPR experiments on the group 10 analogues indicated that the diamagnetic ground states could be accounted for by pairing of one of the d^5 electrons from each Ru(III) in a shared molecular orbital.[15] Therefore, it was expected that **7**, which contains a Cu(I) (d^{10}) ion in addition to the two Ru(III) ions, would also be diamagnetic, and this was supported by EPR experi-

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(42) (a) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988. (b) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.

(43) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

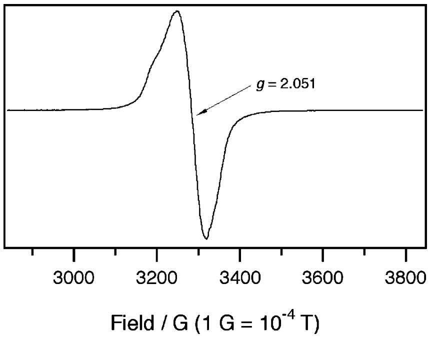

Figure 7. Continuous wave X-band EPR spectrum of **8** obtained at 5.5 K with microwave frequency = 9.437 GHz and microwave power = 0.2 mW.

ments that failed to detect a signal even at liquid He temperatures. In contrast, **8**, containing an Ag(II) (d^9) ion, was found to be paramagnetic, and an EPR spectrum was obtained at low temperatures (Figure 7). The EPR spectrum displayed broad lines indicating that the unpaired electron resides predominantly on the metal ions rather than on the organic ligands, which is a result similar to that obtained for frozen solutions of other paramagnetic heterobimetallic species.[15,44]

Conclusion

This study demonstrated that the electronic difference of $(HMB)Ru^{II}$ and Cp^*Ru^{III} influences markedly the manner in which their η^3-tpdt ligand functions as a dithiolate ligand toward the group 11 metals in +1 oxidation states, resulting in derivatives of very different geometries. Thus the dithiolate ligand at (HMB)Ru bridges in a μ-η^1:η^1 mode, resulting in annular tetranuclear Ru_2M_2 derivatives $[\{(HMB)Ru^{II}(\mu_3\text{-}\eta^1:\eta^1:\eta^3\text{-tpdt})]_2M_2\}]^{2+}$, the solid state structures of which show metallophilicity between the group 11 metals. In the case of M = Au, $[\{(HMB)Ru^{II}(\mu\text{-}\eta^1:\eta^3\text{-tpdt})\}(AuPPh_3)]^+$ (**5**) was the precursor to the annular compound. In comparison, $Cp^*Ru^{III}(\eta^3\text{-tpdt})$ behaves as a metallochelate toward bare Cu^I and Ag^{II} centers, yielding cationic (bis)-η^2-dithiolate metal−metal bonded Ru_2M derivatives, but coordinates as a monothiolate ligand to $AuPPh_3$, giving $[\{Cp^*Ru^{III}(\mu\text{-}\eta^1:\eta^3\text{-tpdt})\}\{AuPPh_3\}]^+$, which undergoes a slow conversion to Ru^{II} compounds $[\{Cp^*Ru(\mu_3\text{-}\eta^1:\ \eta^1:\eta^3\text{-tpdt})\}(AuPPh_3)_2]^+$ (**11**) and a μ-S_2 diruthenium species (**10**). Cyclic voltammetry experiments indicated that the Ru_2M_2 derivatives were unstable toward oxidation or reduction, while the Ru_2M complexes underwent two oxidation and at least one reduction process to form moderately stable species with extensive electron delocalization between the metal ions.

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Supporting Information Available: Table S1, giving crystal data collection and processing parameters. Table S2, giving IR and MS spectral data. Crystallographic data as CIF files for complexes **3**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[44] (a) Kraatz, H.-B.; Boorman, P. M.; Hinman, A. S.; Ziegler, T.; Collison, D.; Mabbs, F. E. *J. Chem. Soc., Dalton Trans.* **1993**, 1665. (b) Thomas, K. R. J.; Chandrasekhar, V.; Zanello, P.; Laschi, F. *Polyhedron* **1997**, *16*, 1003. (c) Donzello, M. P.; Ercolani, C.; Kadish, K. M.; Ou, Z.; Russo, U. *Inorg. Chem.* **1998**, *37*, 3682. (d) Hori, A.; Mitsuka, Y.; Ohba, M.; Okawa, H. *Inorg. Chim. Acta* **2002**, *337*, 113. (e) Ali, M.; Ray, A.; Sheldrick, W. S.; Mayer-Figge, H.; Gao, S.; Sahmes, A. I. *New J. Chem.* **2004**, *28*, 412.