SPh)$_3$]Cl (**1**). Complex **1** could also be prepared in slightly higher yield (36%) by the addition of excess benzenethiol and base to a THF solution of [(HMB)RuCl$_2$]$_2$. The ^{1}H and ^{13}C NMR spectra of **1** confirmed the presence of hexamethylbenzene and phenyl rings in **1** in a ratio of 2:3. The FAB mass spectrum also provided support for the formation of the product. An envelope centered at *m/e* 855, which was the base signal in the spectrum, corresponded to the mass of the cation ((HMB)Ru)$_2$(SPh)$_3^+$. Elemental analyses were also consistent with the proposed composition.

An X-ray diffraction study was carried out on a single crystal of **1** in order to confirm the bonding mode(s) of the benzenethiolate ligands. An Ortep plot of the cation with its numbering scheme is shown in Figure 1, selected bond distances and angles are given in Table II, and selected atomic coordinates are given in Table III. The compound contains discrete dinuclear units in which the Ru(II) ions are unsymmetrically bridged by three thiolate sulfurs. The Ru(1A)–S bonds are 0.02–0.04 Å shorter than the Ru(1)–S distances. The disordered thiolate ligands showed 50% occupancy at each of two positions related by a mirror plane that passes through the metal–metal vector. The gross structure is similar to that reported for the pentamethylcyclopentadienyl analogue of Ru(III), [(Cp*Ru)$_2$(μ-SPh)$_3$]Cl (**2**).[3] In both structures, the arrangement of the thiolate substituents is symmetrical so that the metal–metal vector lies on a pseudo-3-fold rotation axis. The major structural differences between **1** and **2** arise from the differences in formal oxidation states of the ruthenium ions. While the Ru(III) ions in **2** undergo a significant metal–metal interaction (Ru–Ru = 2.630 (1) Å), the Ru(II) ions in **1** are not expected to participate in metal–metal bonding. The Ru–Ru distance of 3.354 Å in **1** is similar to those of other triply bridged Ru(II) dimers.[5,6] The Ru–S–Ru angles in **1** average 88.5°, which is also similar to those observed for other ruthenium(II) dimers and significantly larger than the same angles in **2** (68°).

Because of the relatively large separation between (HMB)Ru centers in **1**, the three phenyl rings of the thiolate ligands are not constrained to a coplanar arrangement as they were in **2**. With respect to the plane defined by S(1)–C(11), S(2)–C(21), and S(3)–C(31), the plane of the phenyl ring of C(11) is rotated by an angle of 18.8° and that of C(21) by an angle of 7.9°. The third phenyl ring is nearly coplanar, with a dihedral angle of 1.1°. The two parallel hexamethylbenzene rings are in an eclipsed conformation, while the more sterically hindered structure of **2** led to staggered pentamethylcyclopentadienyl ligands. The mixed-valence dimer (Cp*Ru)$_2$(μ-S-*i*-Pr)$_3$ has also been structurally characterized.[4] In this complex the metal–metal distance was 2.968 (2) Å and the Cp* ligands were found to be oriented between an eclipsed and a staggered arrangement.

The reaction of [(HMB)RuCl$_2$]$_2$ with about a 3-fold excess of benzenethiol in dichloromethane led to the formation of a second dinuclear complex which was tentatively formulated as [((HMB)Ru)$_2$(μ-SPh)$_2$(μ-Cl)]Cl on the basis of spectroscopic data. Under these reaction conditions, which were only slightly different from those of the reaction described for the preparation of **1**, the bis(thiolate) dimer was isolated in 60% yield and **1** was not detected. The result suggests that these synthetic reactions are highly dependent on solvent and on reactant stoichiometry. Similar effects have been observed in the reactions of the Cp*Ru systems.[3,4]

Conclusion. The factors which determine the geometry and metal–metal separation of triply bridged dinuclear complexes have been found in both theoretical and experimental work to be a complex function of ligand–ligand interactions as well as of metal–metal interactions.[17] In many cases, electron-counting conventions have not been a reliable indicator of structural variations in the dimers. Nevertheless, the series of Ru(II/II–II/III–III/III) dimers discussed here provide a good example of systematic compression of the dimer structure as the expected metal–metal interaction increases.

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Supplementary Material Available: A figure showing the disordered thiolate ligands in the structure of **1** and complete tables of data collection parameters, bond distances and angles, atomic coordinates, and displacement parameters for **1** (14 pages); a listing of observed and calculated structure factors for **1** (14 pages). Ordering information is given on any current masthead page.

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[17] Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3821 and references therein.

Additions and Corrections

1992, Volume 31

Johann W. Buchler,* Jürgen Löffler, and Mark Wicholas*: Metal Complexes with Tetrapyrrole Ligands. 62. ^{13}C NMR Spectra of Dicerium(III) and Dipraseodymium(III) Tris(octaethylporphyrinate).

Page 524. The assignments for the methylene and methyl resonances in Figure 2 have been mislabeled and should read from left to right as CH$_2$(o), CH$_3$(o), CH$_3$(i), CH$_2$(i), thus corresponding to the correct assignments listed in Table I.—Mark Wicholas