Reviews

Dinuclear Ruthenium and Osmium Arene Trihydrido Complexes: Versatile Water-Soluble Synthons in Organometallic Chemistry†

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Recent developments in the chemistry of dinuclear ruthenium arene complexes are reviewed. Although cationic ruthenium and osmium arene trihydrido complexes have been known for more than 20 years, little synthetic use has been made of these unsaturated molecules prior to the discovery of their hydrophilicity. Most salts of the dinuclear cations $[(\eta^6\text{-arene})_2M_2(\mu_2\text{-H})_3]^+$ (M = Ru, Os) are soluble not only in polar organic solvents but also in water. The aqueous solutions can be handled without hydrolytic degradation. This property conditions these unsaturated complexes (with an electron count of only 30) to be versatile synthons in organometallic chemistry, especially in reactions carried out in water.

1. Introduction

While classical coordination chemistry is typically considered as chemistry in aqueous solution, organometallic coordination chemistry takes place almost exclusively in organic solution. Owing to the high sensitivity of many organometallics toward hydrolysis, the organic solvents employed in most organometallic reactions are thoroughly dried prior to use. The rigorous exclusion of water has become a general feature of laboratory techniques in this field, to such an extent that water is rarely considered to be a suitable reaction medium for organometallic complexes.

The obvious gap between organometallic and classical coordination chemistry is bridged by the steadily growing number of water-soluble organometallics. A breakthrough in this field was the discovery of organometallic aquo complexes containing both soft organic and hard aquo ligands. The first complex of this type is presumably the dinuclear cation $[(\eta^5\text{-}C_5H_5)_2Ti_2(\mu_2\text{-O})(H_2O)_2]^{2+}$, first synthesized by Wilkinson and Birmingham in 1954 and erroneously believed to be $[(\eta^5\text{-}C_5H_5)_2Ti_2(OH)Br]\cdot H_2O$.[1] The correct nature of this species was established later by IR and NMR measurements[2] and by single-crystal X-ray structure analysis of the dithionite salt.[3] The existence of (arene)aquoruthenium complexes was observed by NMR spectroscopy in 1972 by Zelonka and Baird in the reaction of $[(\eta^6\text{-}C_6H_6)_2Ru_2(\mu_2\text{-Cl})_2Cl_2]$ with D_2O.[4] The osmium complex $[(\eta^6\text{-}C_6H_6)Os(H_2O)_3]^{2+}$ was synthesized by analogy and spectroscopically characterized by Hung, Kung, and Taube.[5] Finally, Stebler-Röthlisberger et al. succeeded in isolating the cationic benzene triaquo complexes $[(\eta^6\text{-}C_6H_6)Os(H_2O)_3]^{2+}$ and $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ as the tosylate salts; the molecular structure of the (benzene)ruthenium triaquo dication was confirmed by single-crystal X-ray analysis of the sulfate.[6] Since these early pioneering reports, the chemistry of organometallic aquo complexes has been steadily developed in the 1980s and 1990s.[7,8] After the introduction of the Rhône-Poulenc-Ruhrchemie process for the catalytic olefin hydrogenation under biphasic conditions,[9,10] water-soluble hydrido complexes have received much attention,[11−18] and the availability of such complexes as organometallic synthons is of great interest.

The first dinuclear cation of the type $[(\eta^6\text{-arene})_2M_2(\mu_2\text{-H})_3]^+$ to be reported in the literature was the ruthenium complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-H})_3]^+$, which had been obtained by Bennett et al. by the reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-H})(\mu_2\text{-Cl})_2]^+$ with $NaBH_4$ in ethanol and isolated as the hexafluorophosphate salt. This salt was reported to be a dark green-gray material; it was only characterized by the ^1H NMR signal of the three equivalent hydrido ligands, and no yield was given.[19] Ten years later, a more reliable synthesis was reported, involving the reaction of a mononuclear complex of the empirical formula $[(\eta^6\text{-}C_6Me_6)Ru(OSO_2CF_3)_2]\cdot 2H_2O$ with isopropyl alcohol and anhydrous sodium carbonate (eq 1), followed by reaction with sodium hexafluorophosphate. The salt $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-H})_3]$-

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† This paper is dedicated to Jack Lewis (The Lord Lewis of Newnham), a great scientist and friend.

(1) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 4281−4284.

(2) Döppert, K. *J. Organomet. Chem.* **1979**, *178*, C3−C4.

(3) Thewalt, U.; Schleuβner, G. *Angew. Chem., Int. Ed.* **1978**, *17*, 531−532.

(4) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063−3072.

(5) Hung, Y.; Kung, W.-J.; Taube, H. *Inorg. Chem.* **1981**, *20*, 457−463.

(6) Stebler-Röthlisberger, M.; Hummel, W.; Pittet, A.-M.; Bürgi, H.-B.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1358−1363.

(7) Koelle, U. *Coord. Chem. Rev.* **1994**, *135/136*, 623−650.

(8) Süss-Fink, G.; Meister, A.; Meister, G. *Coord. Chem. Rev.* **1995**, *143*, 97−111.

(9) Kuntz, E. G. Fr. Patent 2,314,910, 1975.

(10) Kuntz, E. G. *CHEMTECH* **1983**, *17*, 570−575.

(11) Darensbourg, D. J.; Bischoff, C. J.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 1144−1147.

(12) Samuelson, A. G. *Curr. Sci.* **1992**, *63*, 547−550.

(13) Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed.* **1993**, *32*, 1542−1544.

(14) Meister, G.; Rheinwald, G.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1995**, *496*, 197−205.

(15) Süss-Fink, G.; Meister, G.; Haak, S.; Rheinwald, G.; Stoeckli-Evans, H. *New J. Chem.* **1997**, *21*, 785−790.

(16) Chérioux, F.; Maisse-François, A.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *Dalton Trans.* **2001**, 2184−2187.

(17) Allardyce, C. S.; Dyson, P. J.; Ellis, D. J.; Salter, P. A.; Scopelliti, R. *J. Organomet. Chem.* **2003**, *668*, 35−42.

(18) Ogo, S.; Uehara, K.; Abura, T.; Watanabe, Y.; Fukuzumi, S. *Organometallics* **2004**, *23*, 3047−3052.

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$$2[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{OSO}_2\text{CF}_3)_2] + 3\text{Me}_2\text{CHOH} \rightarrow [(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+ + [\text{SO}_3\text{CF}_3]^- + 3\text{HSO}_3\text{CF}_3 + 3\text{Me}_2\text{CO} \quad (1)$$

$[\text{PF}_6]$—now reported to be a light brown solid—as well as the corresponding chloride and triflate salts and the durene analogues $[(\eta^6\text{-1,2,4,5-C}_6\text{H}_2\text{Me}_4)_2\text{Ru}_2(\mu_2\text{-H})_3][\text{PF}_6]$ and $[(\eta^6\text{-1,2,4,5-C}_6\text{H}_2\text{Me}_4)_2\text{Ru}_2(\mu_2\text{-H})_3][\text{SO}_3\text{CF}_3]$ were fully characterized by IR and NMR spectroscopy and elemental analysis; the molecular structure of these complexes, however, remained unknown.[20] In the meantime, the osmium complex $[(\eta^6\text{-1,4-}^i\text{PrC}_6\text{H}_2\text{Me})_2\text{Os}_2(\mu_2\text{-H})_3]^+$ had been obtained from the hydroxo derivative $[(\eta^6\text{-1,4-}^i\text{PrC}_6\text{H}_2\text{Me})_2\text{Os}_2(\mu_2\text{-OH})_3]^+$ with either isopropyl alcohol or formaldehyde as the hydrogen source (eq 2).[21] The molecular structure was proposed as written on the basis of the FAB-MS and the ^{1}H and the ^{187}Os NMR data by analogy with the isoelectronic cation $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}_2(\mu_2\text{-H})_3]^+$.[22,23]

$$[(\eta^6\text{-1,4-}^i\text{PrC}_6\text{H}_4\text{Me})_2\text{Os}_2(\mu_2\text{-OH})_3]^+ + 3\text{HCHO} \rightarrow [(\eta^6\text{-1,4-}^i\text{PrC}_6\text{H}_4\text{Me})_2\text{Os}_2(\mu_2\text{-H})_3]^+ + 3\text{H}_2\text{O} + 3\text{CO} \quad (2)$$

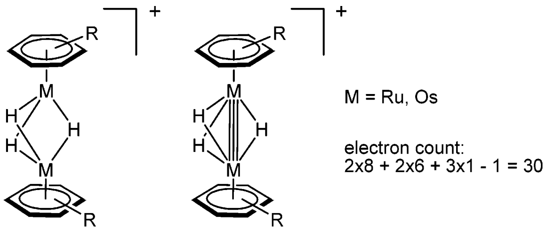
The direct hydrogenation of (hexamethylbenzene)ruthenium dichloride dimer in aqueous solutions was found to yield the dinuclear cation $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ (eq 4),[24] while the same reaction of the benzene derivative gave the tetranuclear dication $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4(\mu_2\text{-H})_6]^{2+}$ (eq 3), at first erroneously considered to be $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4(\mu_3\text{-H})_4]^{2+}$ [25] but later correctly established when the tetranuclear dications $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4(\mu_2\text{-H})_6]^{2+}$ and $[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4(\mu_3\text{-H})_4]^{2+}$ were both isolated and structurally characterized.[26,27] From the aqueous solution, the dinuclear cation $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ was crystallized as the hexafluorophosphate and for the first time characterized by single-crystal X-ray analysis.[28]

$$2[(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2(\mu_2\text{-Cl})_2\text{Cl}_2] + 6\text{H}_2 \rightarrow [(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4(\mu_2\text{-H})_6]^{2+} + 8\text{Cl}^- + 6\text{H}^+ \quad (3)$$

$$[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-Cl})_2\text{Cl}_2] + 3\text{H}_2 \rightarrow [(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+ + 4\text{Cl}^- + 3\text{H}^+ \quad (4)$$

The fact that the benzene derivative gives a dicationic tetranuclear hexahydrido complex, while the hexamethylbenzene derivative leads to a cationic dinuclear trihydrido complex, can be explained on the basis of steric reasons, because the bulky hexamethylbenzene ligands cannot form a tetrahedral ligand envelope around a Ru_4 cluster core due to steric hindrance of the methyl groups. Accordingly, in the case of the less bulky (*p*-cymene)osmium system, in the reaction of $[(\eta^6\text{-1,4-}^i\text{PrC}_6\text{H}_2\text{Me})_2\text{Os}_2(\mu_2\text{-OH})_3]^+$ with isopropyl alcohol both the tetranuclear complex $[(\eta^6\text{-1,4-}^i\text{PrC}_6\text{H}_2\text{Me})_4\text{Os}_4(\mu_3\text{-H})_4]^{2+}$ and the dinuclear complex $[(\eta^6\text{-1,4-}^i\text{PrC}_6\text{H}_2\text{Me})_2\text{Os}_2(\mu_2\text{-H})_3]^+$ were obtained.[21]

Chart 1. Alternative Representations of the Electron-Deficient Complexes $[(\eta^6\text{-arene})_2\text{M}_2(\mu_2\text{-H})_3]^+$ with Three Three-Center Bonds or with a Metal−Metal Triple Bond



The dinuclear cations $[(\eta^6\text{-arene})_2\text{M}_2(\mu_2\text{-H})_3]^+$ represent a species which is exactly half of the corresponding tetranuclear dications $[(\eta^6\text{-arene})_4\text{M}_4(\mu_2\text{-H})_6]^{2+}$, which are, with an electron count of 60, an electron-precise system in accordance with the 18e rule for closed tetrahedral clusters. Thus, the dinuclear cations $[(\eta^6\text{-arene})_2\text{M}_2(\mu_2\text{-H})_3]^+$, with an electron count of 30, represent an electron-deficient system.

The electron deficiency of the dinuclear cations $[(\eta^6\text{-arene})_2\text{M}_2(\mu_2\text{-H})_3]^+$ can be expressed either by formulating three three-center−two-electron (3c−2e) M−H−M bonds or, more conventionally, by formulating a M≡M triple bond that is bridged by three hydrido ligands (Chart 1). From a theoretical point of view, the multicenter bond representation is presumably a more realistic description, since in the case of the isoelectronic complex $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ru}_2(\mu_2\text{-H})_4]$, originally formulated with a Ru≡Ru triple bond and four hydrido bridges by Suzuki et al. on the basis of the 18e (EAN) rule,[29] ab initio molecular orbital calculations showed no direct metal−metal interaction, the short ruthenium−ruthenium distance of 2.463(1) Å being accounted for by assuming four Ru−H−Ru 3c−2e bonds.[30,31] However, for the sake of systematics and of predictability on the basis of the 18e rule, the triple-bond formalism for the cationic complexes $[(\eta^6\text{-arene})_2\text{M}_2(\mu_2\text{-H})_3]^+$ is preferable, even though a DFT analysis we carried out recently (see section 7) shows no noticeable overlap population between the two ruthenium atoms in $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$.[65]

The high reactivity of these electron-deficient molecules, their cationic nature, and their solubility in both polar organic solvents and in water, combined with a high resistance to hydrolysis, makes the dinuclear complexes $[(\eta^6\text{-arene})_2\text{M}_2(\mu_2\text{-H})_3]^+$ (M = Ru, Os) versatile building blocks for organometallic synthesis.

2. Synthesis

Given the problems of reproducibility or of ill-characterized starting materials in the early syntheses,[19,20] we developed an improved synthesis with higher yields and easier workup: the reaction of triaquo(hexamethylbenzene)ruthenium $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{OH}_2)_3]^{2+}$, employed as the sulfate or tosylate salt, with sodium borohydride (1.5 equiv) in degassed aqueous solution afforded $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\mu_2\text{-H})_3]^+$ in 85% yield (see Scheme

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[19] Bennett, M. A.; Ennett, J. A.; Gell, K. I. *J. Organomet. Chem.* **1982**, *233*, C17−C20.

[20] Bennett, M. A.; Ennett, J. A. *Inorg. Chim. Acta* **1992**, *198−200*, 583−592.

[21] Cabeza, J. A.; Mann, B. A.; Maitlis, P. M.; Brevard, C. *J. Chem. Soc., Dalton Trans.* **1988**, 629−634.

[22] White, A.; Oliver, A. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1901−1907.

[23] Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872−3874.

[24] Jahncke, M.; Süss-Fink, G. Unpublished results. See: Jahncke, M.; Ph.D. Thesis, University of Neuchâtel (Switzerland), 1998; p 28.

[25] Bodensieck, U.; Meister, A.; Meister, G.; Rheinwald, G.; Stoeckli-Evans, H.; Süss-Fink, G. *Chimia* **1993**, *47*, 189−191.

[26] Meister, G.; Rheinwald, G.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Chem. Soc., Dalton Trans.* **1994**, 3215−3223.

[27] Süss-Fink, G.; Plasseraud, L.; Maisse-François, A.; Stoeckli-Evans, H.; Berke, H.; Fox, T.; Gautier, R.; Saillard, J.-Y. *J. Organomet. Chem.* **2000**, *609*, 196−203.

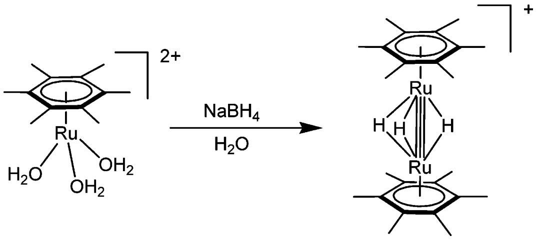
[28] Jahncke, M.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1998**, *561*, 227−235.

[29] Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Moro-oka, Y. *Organometallics* **1988**, *7*, 2243−2245.

[30] Koga, N.; Morokuma, K. *J. Mol. Struct.* **1993**, *300*, 181−189.

[31] Suzuki, H.; Omori, H.; Lee, D. H.; Yoshida, Y.; Fukushima, M.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1994**, *13*, 1129−1146.

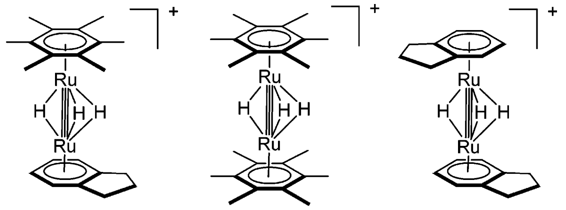
Scheme 1. High-Yield Synthesis of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ from the Aquo Complex $[(\eta^6\text{-}C_6Me_6)Ru(OH_2)_3]^{2+}$and Sodium Borohydride in O_2-Free Aqueous Solution



1).[32] The method was successfully used to synthesize other diruthenium trihydrido complexes.[33]

It is noteworthy that by using a mixture of two different (arene)ruthenium triaquo complexes for the formation of mixed $[(\eta^6\text{-arene})_2Ru_2(\mu_2\text{-}H)_3]^+$ complexes, three different diruthenium trihydrido cations can be expected. For instance, with hexamethylbenzene and indane as η^6-arene ligands, the reaction afforded two symmetrical and one asymmetrical diruthenium complex (see Chart 2).[34] Surprisingly, the major component of the reaction solution was the asymmetrical complex $[(\eta^6\text{-}C_9H_{10})(\eta^6\text{-}C_6Me_6)Ru_2(\mu_2\text{-}H)_3]^+$ (52% yield). This cation is stable for days under an inert atmosphere but decomposes slowly in air or in solution to form the corresponding hydroxo-bridged complex $[(\eta^6\text{-}C_9H_{10})(\eta^6\text{-}C_6Me_6)Ru_2(\mu_2\text{-}OH)_3]^+$.[34] Analogously, the asymmetrical cation $[(\eta^6\text{-}1,4\text{-}^iPrC_6H_4Me)(\eta^6\text{-}C_6Me_6)Ru_2(\mu_2\text{-}H)_3]^+$ was synthesized from a 1:1 mixture of $[(\eta^6\text{-}C_6Me_6)Ru(OH_2)_3]^{2+}$ and $[(\eta^6\text{-}1,4\text{-}^iPrC_6H_4Me)Ru(OH_2)_3]^{2+}$ and sodium borohydride in aqueous solution and isolated as the tetrafluoroborate salt in 32% yield.[35]

Chart 2. The Three Mixed (One Asymmetrical and the Two Symmetrical) Diruthenium Trihydrido Cations Formed by Reaction of $NaBH_4$ with a Mixture of $[(\eta^6\text{-}C_6Me_6)Ru(OH_2)_3]^{2+}$ and $[(\eta^6\text{-}C_9H_{10})Ru(OH_2)_3]^{2+}$ in Aqueous Solution



The first osmium analogue, the *p*-cymene derivative $[(\eta^6\text{-}1,4\text{-}^iPrC_6H_4Me)_2Os_2(\mu_2\text{-}H)_3]^+$, was obtained as the hexafluorophosphate salt by the reaction of $[(\eta^6\text{-}1,4\text{-}^iPrC_6H_4Me)_2Os_2(\mu_2\text{-}OH)_3][PF_6]$ with isopropyl alcohol,[36,37] while the mesitylene derivative $[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Os_2(\mu_2\text{-}H)_3]^+$ was prepared from $[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Os_2Cl_2]_2$ and a 2:1 mixture of $NaBH_4$ and $ZnCl_2$ in benzene solution.[38]

The stability of the trihydrido arene metal complexes depends mainly on the number and the nature of the substituents on the arene ligand: the C_6Me_6 derivatives are the most stable, whereas the benzene derivatives cannot be prepared.[39] The nature of the counteranion plays only a minor role in the stability but governs the solubility of these compounds. In general, the triflate, tetrafluoroborate, and hexafluorophosphate salts are readily soluble in dichloromethane, chloroform, acetone, and methanol but sparingly soluble in water and diethyl ether. In contrast, the chloride salts are soluble in ether and water.

Sometimes, reactions with chlorinated solvents are observed: the trihydrido derivative $[(\eta^6\text{-}1,4\text{-}^iPrC_6H_4Me)_2Os_2(\mu_2\text{-}H)_3]^+$ reacted in the presence of acetic acid with CCl_4 to give quantitatively the trichloro complex $[(\eta^6\text{-}1,4\text{-}^iPrC_6H_4Me)_2Os_2(\mu_2\text{-}Cl)_3]^+$.[37] Similarly, the ruthenium complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ was found to react with dichloromethane in the presence of diphenylsilane to give a mixture of the chloro complexes $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}Cl)_3]^+$ and $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}Cl)_2Cl_2]$.[40]

3. Spectroscopic Features

The cationic trihydrido complexes $[(\eta^6\text{-arene})_2M_2(\mu_2\text{-}H)_3]^+$ give rise to characteristic nuclear magnetic resonance and infrared spectroscopic features. In the ^1H NMR spectra of all $[(\eta^6\text{-arene})_2M_2(\mu_2\text{-}H)_3]^+$ salts a singlet appears around δ −16.0 ppm, which is due to the three hydrido bridge protons. The chemical shift is essentially independent of the counteranion (see Table 1). The IR spectra of these complexes show a weak to medium band around 1150 cm^{-1}, assigned to the ν(Ru−H−Ru) vibration.

As expected, the isoelectronic complexes $[(\eta^5\text{-}C_5Me_5)_2Ir_2(\mu_2\text{-}H)_3]^+$ and $[(\eta^5\text{-}C_5Me_5)_2Ru_2(\mu_2\text{-}H)_4]$ show similar IR and ^1H NMR features (ν_{IrHIr} 936 cm^{-1}, δ_{IrHIr} −15.33 ppm[22] and δ_{RuHRu} −13.99 ppm,[29] respectively). In the case of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$, H/D exchange processes of the hydrido ligands have been studied: At elevated temperature (80 °C), the three hydrido bridges undergo intermolecular H/D exchange with D_2O (slow) or with D_2 (rapid).[40] A dihydride/dihydrogen equilibrium mechanism has been proposed for the H/D exchange of the analogous $[(\eta^5\text{-}C_5Me_5)_2Ru_2(\mu_2\text{-}H)_4]$ complex.[42]

Ultraviolet spectrum and electrochemical characteristics are known for the (hexamethylbenzene)ruthenium derivative $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$: the UV spectrum of a dichloromethane solution of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3][BF_4]$ shows two maxima at 363 nm ($\epsilon = 9175\ M^{-1}\ cm^{-1}$) and 573 nm ($\epsilon = 624\ M^{-1}\ cm^{-1}$),[40] while the cyclic voltammogram of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3][BF_4]$ in CH_2Cl_2 solution (0.0005 M with 0.005 M $[NBu_4][PF_6]$ supporting electrolyte, stationary platinum disk electrode, scan rate 200 mV/s) reveals the cation $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ to be oxidized in a single, irreversible diffusion-controlled two-electron process at $E_{p,a} = 0.76$ V (relative to SCE reference ferrocene/ferrocenium at 0.47 V), which can be assigned to the Ru(II) → Ru(III) oxidation involving both metal centers, followed by decomposition of the complex.[62]

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(32) Jahncke, M.; Meister, G.; Rheinwald, G.; Stoeckli-Evans, H.; Süss-Fink, G. *Organometallics* **1997**, *16*, 1137−1143.

(33) Vieille-Petit, L.; Therrien, B.; Süss-Fink, G. *Inorg. Chim. Acta* **2003**, *355*, 394−398.

(34) Vieille-Petit, L.; Therrien, B.; Süss-Fink, G. *Inorg. Chem. Commun.* **2004**, *7*, 232−234.

(35) Vieille-Petit, L.; Süss-Fink, G.; Therrien, B.; Ward, T. R.; Stoeckli-Evans, H.; Labat, G.; Karmazin-Brelot, L.; Neels, A.; Bürgi., T.; Finke, R. G.; Hagen, C. M. *Organometallics* **2005**, *24*, 6104−6119.

(36) Cabeza, J. A.; Mann, B. E.; Brevard, C.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1985**, 65−67.

(37) Cabeza, J. A.; Mann, B. E.; Maitlis, P. M.; Brevard, C. *J. Chem. Soc., Dalton Trans.* **1988**, 629−634.

(38) Schulz, M.; Stahl, S.; Werner, H. *J. Organomet. Chem.* **1990**, *394*, 469−479.

(39) In an effort to synthesize the dinuclear cation $[(\eta^6\text{-}C_6H_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with benzene ligands, the tetranuclear dication $[(\eta^6\text{-}C_6H_6)_4Ru_4(\mu_2\text{-}H)_6]^{2+}$ was obtained instead; cf. refs 26 and 27.

(40) Therrien, B.; Süss-Fink, G. Unpublished results.

(41) Bennett, M. A.; Huang, T.-N.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1979**, 312−312.

(42) Suzuki, H. *Eur. J. Inorg. Chem.* **2002**, 1009−1023.

Table 1. Selected ^1H NMR and IR Data for Dinuclear Arene Ruthenium and Osmium Trihydrido Complexes

	^1H NMR (ppm)		IR (cm^{-1})	
compd	δ(hydride)	δ(arene)	ν(M−H−M)^{d}	ref
$[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]CF_3SO_3$	-16.09^{a}	2.30^{a}	1160	20
$[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]Cl$	-16.30^{a}			19
$[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]PF_6$	-16.09^{a}	2.31^{a}	1160	20
$[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]Cl\cdot 4H_2O$	-15.92^{a}	2.30^{a}		20
$[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Ru_2(\mu_2\text{-}H)_3]Cl$	-19.05^{a}	$2.30, 5.12^{a}$	1180	41
$[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]_2SO_4$	-16.41^{b}	2.27^{b}		28
$[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]PF_6$	-15.91^{c}	2.38^{c}		28
$[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]BF_4$	-16.38^{b}	2.29^{b}		40
$[(\eta^6\text{-}C_6H_2Me_4)_2Ru_2(\mu_2\text{-}H)_3]CF_3SO_3$	-15.57^{a}	$2.24, 5.60^{a}$	1140	20
$[(\eta^6\text{-}C_6H_2Me_4)_2Ru_2(\mu_2\text{-}H)_3]PF_6$	-15.57^{a}	$2.24, 5.59^{a}$	1160	20
$[(\eta^6\text{-}C_6H_2Me_4)_2Ru_2(\mu_2\text{-}H)_3]BF_4$	-15.47^{c}	$2.31, 5.96^{c}$		33
$[(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_2Me)(\eta^6\text{-}C_6Me_6)Ru_2(\mu_2\text{-}H)_3]BF_4$	-15.52^{c}	$5.83, 5.75, 2.59^{c}$ $2.41, 2.27, 1.28^{c}$		35
$[(\eta^6\text{-}C_9H_{10})(\eta^6\text{-}C_6Me_6)Ru_2(\mu_2\text{-}H)_3]BF_4$	-15.46^{c}	$2.07, 2.44, 2.67^{c}$ $2.69, 5.69, 6.00^{c}$		28
$[(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)_2Os_2(\mu_2\text{-}H)_3]PF_6$	-14.87^{a}	$1.29, 2.50, 2.51^{a}$ $5.80, 5.84^{a}$		21
$[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Os_2(\mu_2\text{-}H)_3]Cl$	-15.11^{a}	$2.60, 5.66^{a}$		38
$[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Os_2(\mu_2\text{-}H)_3]PF_6$	-15.10^{a}	$2.60, 5.66^{a}$		38
$[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Os_2(\mu_2\text{-}H)_3]BF_4$	-15.08^{c}	$2.62, 5.95^{c}$		38

[a] In CD_2Cl_2. [b] In D_2O. [c] In $(CD_3)_2CO$. [d] In KBr.

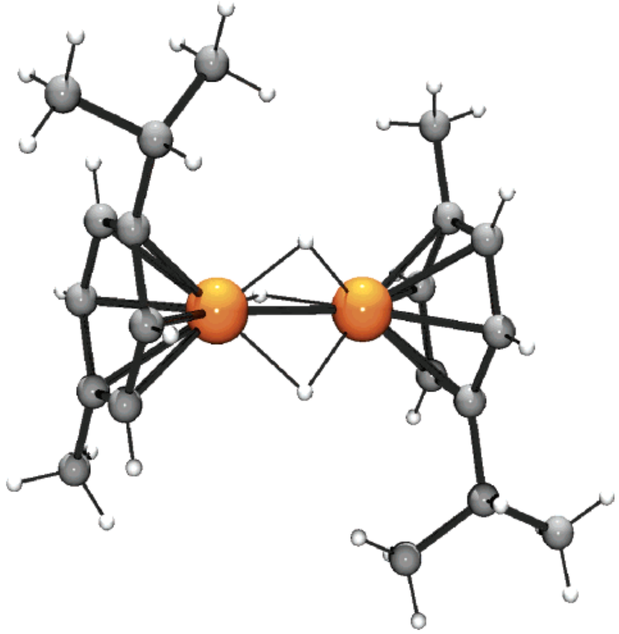

Figure 1. Molecular structure of $[(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)_2Os_2(\mu_2\text{-}H)_3]^+$.

4. Structural Studies

The first structurally characterized dinuclear trihydrido cation was $[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Os_2(\mu_2\text{-}H)_3]^+$, reported by Schulz et al. in 1990: the X-ray structure analysis of the chloride salt reveals the molecule to consist of two $(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)Os$ units, linked by three bridging hydrido ligands. It possesses a crystallographic mirror plane bisecting both osmium atoms and the two 1,3,5-trimethylbenzene ligands.[38] The molecular structure of the *p*-cymene derivative $[(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)_2Os_2(\mu_2\text{-}H)_3]^+$ has only been solved recently (see Figure 1).[43] The metal−metal distances are 2.4741(2) Å in $[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Os_2(\mu_2\text{-}H)_3]^+$ and 2.4709(5) Å in $[(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)_2Os_2(\mu_2\text{-}H)_3]^+$. They are slightly longer than those found in other structures described in terms of an Os≡Os triple bond.[44−57]

The molecular structure of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$, solved by single-crystal X-ray structure analysis of the hexafluorophosphate salt,[28] is presented in Figure 2. The three hydrido ligands have been located from an electron-density difference map. The very short ruthenium−ruthenium distance of 2.4681(4) Å is in accordance with a formal metal−metal triple bond but can equally well be interpreted in terms of three three-center−two-electron Ru−H−Ru interactions. The metal−metal distance compares well with that of 2.463(1) Å in the isoelectronic tetrahydrido complex $[(\eta^5\text{-}C_5Me_5)_2Ru_2(\mu_2\text{-}H)_4]$[31] and is even in the range of those in the corresponding osmium complexes $[(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Os_2(\mu_2\text{-}H)_3]^+$ (2.4741(2) Å)[38] and $[(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)_2Os_2(\mu_2\text{-}H)_3]^+$ (mean 2.4709 Å).[43]

Replacing one of the hydrido bridges by a more bulky bridging ligand imposes a distortion on the dinuclear unit. In addition, the substitution of a μ_2-1e ligand (H) by a μ_2-3e ligand (X = OR, SR, PR_2, NR_2, Cl, Br, I) also modifies the nature of the metal−metal bond. Therefore, the two arene ligands in the

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(43) Therrien, B.; Vieille-Petit, L.; Süss-Fink, G. *J. Mol. Struct.* **2005**, *738*, 161−163.

(44) Cotton, F. A.; Thompson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 6437−6441.

(45) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1984**, *23*, 4693−4697.

(46) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1984**, *23*, 4697−4700.

(47) Fanwick, P. E.; King, M. K.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5009−5011.

(48) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1985**, *24*, 1334−1338.

(49) Cotton, F. A.; Dunbar, K. R.; Matusz, M. *Inorg. Chem.* **1986**, *25*, 1589−1594.

(50) Fanwick, P. E.; Tetrick, S. M.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 4546−4552.

(51) Agaskar, P. A.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 4850−4855.

(52) Cotton, F. A.; Dunbar, K. R. *J. Am. Chem. Soc.* **1987**, *109*, 2199−2200.

(53) Cotton, F. A.; Vidyasagar, K. *Inorg. Chem.* **1990**, *29*, 3197−3199.

(54) Cotton, F. A.; Ren, T.; Eglin, J. L. *Inorg. Chem.* **1991**, *30*, 2559−2563.

(55) Clérac, R.; Cotton, F. A.; Daniels, L. M.; Donahue, J. P.; Murillo, C. A.; Timmons, D. J. *Inorg. Chem.* **2000**, *39*, 2581−2584.

(56) Ren, T.; Parrish, D. A.; Deschamps, J. R.; Eglin, J. L.; Xu, G.-L.; Chen, W.-Z.; Moore, M. H.; Schull, T. L.; Pollack, S. K.; Shashidhar, R.; Sattelberger, A. P. *Inorg. Chim. Acta* **2004**, *357*, 1313−1316.

(57) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113−130.

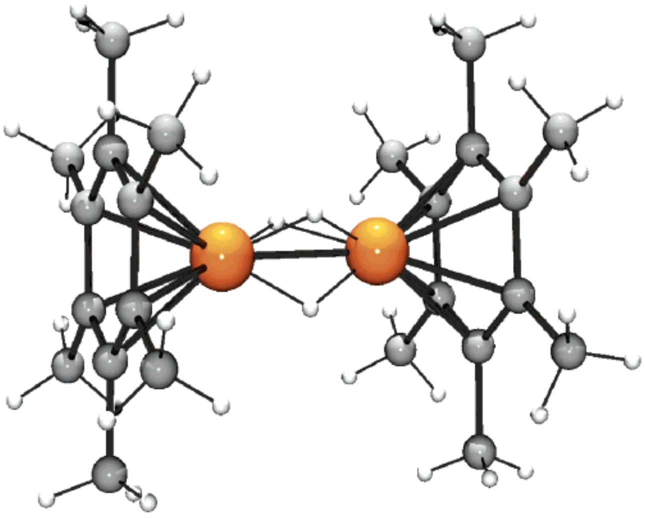
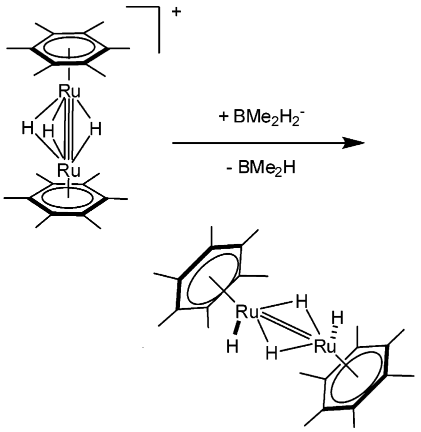


Figure 2. Molecular structure of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$.

Scheme 2. Reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with Lithium Dimethylborate in Hexane−Water To Give $[(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(\mu_2\text{-}H)_2]$



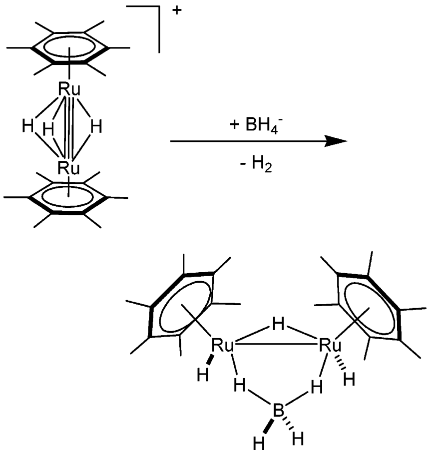
derivatives $[(\eta^6\text{-arene})_2M_2(\mu_2\text{-}H)_2(\mu_2\text{-}X)]^+$ are no longer parallel to each other, and the metal−metal distances are lengthened in such complexes. The steric hindrance imposed by the arene moiety and the newly introduced ligand can be judiciously exploited to control the formation of mono- or di-μ_2-bridged complexes.[58]

5. Reactions with Boron-Containing Molecules

Addition of $LiBMe_2H_2$ to a suspension of the hexafluorophosphate salt of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ in hexane, followed by addition of water, gave the neutral tetrahydrido complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(\mu_2\text{-}H)_2]$ (see Scheme 2).[32] The violet, air-sensitive compound can be isolated by filtration and extraction of the solid with benzene. Interestingly, other hydride reagents such as $LiAlH_4$, NaH, $K[B(OPr^i)_3H]$, $Na[B(O_2CMe)_3H]$, and $Na[BH_3CN]$, as well as alcohols in basic solution, failed to give this complex.

In the complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(\mu_2\text{-}H)_2]$, the four hydrido ligands are fluxional at room temperature: the ^1H NMR spectrum shows only one hydride resonance, a broad signal at δ −9.2 ppm at 20 °C, which splits into two signals at −80 °C in deuteriotoluene, a triplet at −1.52 ppm, assigned to the two terminal hydrido ligands, and a triplet at −17.18 ppm, which can be attributed to the two hydride bridges.

Scheme 3. Reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with Sodium Borohydride in Water To Give $[(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(\mu_2\text{-}H)(\mu_2\text{-}BH_4)]$



Under biphasic conditions (water/ether) the hexafluorophosphate salt of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ reacted with $NaBH_4$ to give the neutral borohydrido complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(\mu_2\text{-}H)(\mu_2\text{-}BH_4)]$ (see Scheme 3).[32] In a similar fashion the analogous complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(\mu_2\text{-}H)(\mu_2\text{-}BMe_2H_2)]$ was synthesized from $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ and $Na[BMe_2H_2]$.[32] The single-crystal X-ray structure analysis showed a Ru−Ru distance of 2.895(1) Å, for the terminal and bridging hydrido ligands. The bond distances $Ru-H_t$ and $Ru-H_b$ are 1.46(3) and 1.68(3) Å, respectively, and the $B-H_t$ and $B-H_b$ distances are 1.13(4) and 1.24(4) Å, respectively. In contrast to the case for the known iridium borohydride complex $[(\eta^5\text{-}C_5Me_5)_2Ir_2H(\mu_2\text{-}H)(\mu_2\text{-}BH_4)]$, the ^1H NMR spectrum of which stays unchanged over the temperature range from −80 to +25 °C,[59] variable-temperature ^1H NMR spectroscopy of $[(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(\mu_2\text{-}H)(\mu_2\text{-}BH_4)]$ revealed two independent fluxional processes taking place in solution, one being the exchange between the two terminal hydrido ligands and the hydrido bridge and the other being the exchange of the four hydrido ligands at the boron atom.[32]

6. Reactions with Nitrogen-Containing Molecules

The cation $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ reacted in aqueous solution with hydrazine at room temperature to give the dicationic complex $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}H_2NNH_2)]^{2+}$, in which one hydrido bridge is replaced by a hydrazine ligand (Scheme 4). This cation can be isolated as the hexafluorophosphate or the triflate salt.[60]

Heating of this complex with aqueous hydrazine at reflux resulted in the formation of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}H_2NNH_2)(\mu_2\text{-}NH_2)]^{2+}$, which contains in addition to the hydrazine bridge an amido bridge. When this reaction was carried out at room temperature, a hydrazido intermediate, $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}H_2NNH_2)(\mu_2\text{-}\eta^1\text{-}NHNH_2)]^{2+}$, was isolated as the mixed sulfate−hexafluorophosphate salt (Scheme 4).[60]

It has been assumed that the second hydrazine molecule enters the complex to give not a hydrazine ($\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}H_2NNH_2$) ligand, but a hydrazido ($\mu_2\text{-}NHNH_2$) ligand, in which the N−N bond

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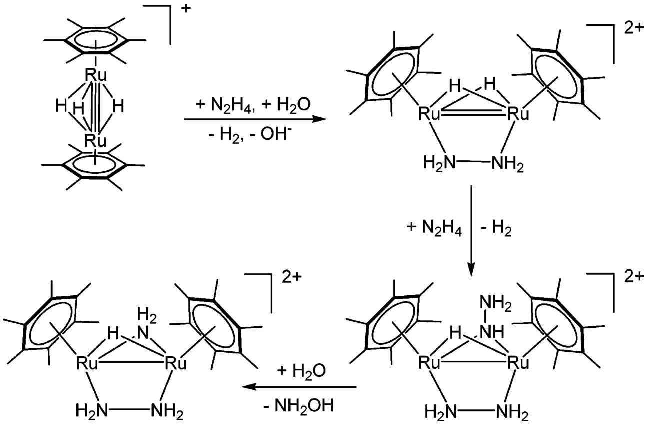
(58) Tschan, M. J.-L.; Chérioux, F.; Therrien, B.; Süss-Fink, G. *Eur. J. Inorg. Chem.* **2004**, 2405−2411.

(59) Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508−3516.

(60) Jahncke, M.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1997**, *565*, 97−103.

Scheme 4. Reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with Hydrazine in Aqueous Solution To Give $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}H_2NNH_2)]^{2+}$, $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}H_2NNH_2)(\mu_2\text{-}\eta^1\text{-}NHNH_2)]^{2+}$, and $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}H_2NNH_2)(\mu_2\text{-}NH_2)]^{2+}$



is weakened due to the 3e donor properties of the bridging nitrogen atom, so that it breaks to give a μ_2-NH_2 ligand.

A structural comparison of the hydrazine dihydrido complex and the hydrazine hydrido amido complex shows the expected lengthening of the ruthenium−ruthenium distance from 2.6925(7) Å in $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}H_2NNH_2)]^{2+}$ to 2.8555(8) Å in $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}H_2NNH_2)(\mu_2\text{-}NH_2)]^{2+}$, which is a consequence of replacing a 1e donor ligand by a 3e donor ligand in a bridging position.

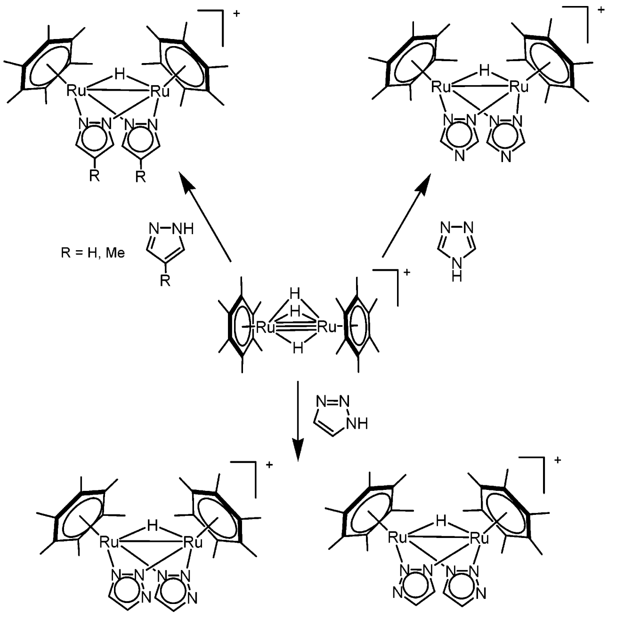
The reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with nitrogen-containing heterocycles such as pyrazole and triazole in water leads with replacement of two hydrido bridges by two deprotonated heterocyclic μ_2-η^1:η^1-N,N-coordinated ligands to form the corresponding pyrazolato and triazolato complexes, see Scheme 5.[61] In all cases, the pyrazolato or triazolato bridges function as 3e donor ligands; therefore the replacement of two μ_2-H ligands (1e donors) by two μ_2-η^1:η^1-N,N-coordinated ligands (3e donors) reduces the formal ruthenium−ruthenium bond order from 3 to 1.

All cations can be isolated easily from the aqueous solution by precipitation as their hexafluorophosphate salts. It is interesting to note that with 1,2,3-triazole the reaction produced two isomers, one containing the two triazolato ligands in parallel orientation, and the other one containing the two triazolato ligands in antiparallel orientation. Precipitation with KPF_6 gave a 1:1 mixture of both isomers of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-}N_3C_2H_2)_2][PF_6]$.[61]

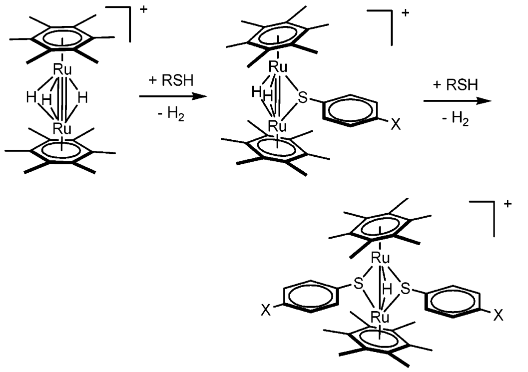
7. Reactions with Sulfur-Containing Molecules

The trihydrido cation $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ reacts also with thiols and thiophenols. The reaction with 1 equiv of RSH ($R = 1,4\text{-}C_6H_4\text{-}X$; X = Me, Br) in ethanol was found to give a mixture of the mono- and dithiolato-substituted complexes $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}S\text{-}1,4\text{-}C_6H_4\text{-}X)]^+$ and $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}S\text{-}1,4\text{-}C_6H_4\text{-}X)_2]^+$ in a 3:1 ratio (see Scheme 6).[62] The durene analogues (η^6-arene = η^6-1,2,4,5-$C_6H_2Me_4$), obtained in the same way, contained a 4:1 molar ratio of mono- and disubstituted products.

Scheme 5. Reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with Various Pyrazoles and Triazoles in Aqueous Solution To Give the Corresponding Bis(μ_2-η^1:η^1-*N,N*-pyrazolato) and Bis(μ_2-η^1:η^1-*N,N*-triazolato) Derivatives



Scheme 6. Reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with Thiophenol Derivatives To Give $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}S\text{-}1,4\text{-}C_6H_4\text{-}X)]^{2+}$ and $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}S\text{-}1,4\text{-}C_6H_4\text{-}X)_2]^{2+}$ ($R = p\text{-}C_6H_4\text{-}X$; X = Me, Br)



If 2 equiv (or more) of RSH was used, the reaction with $[(\eta^6\text{-arene})_2Ru_2(\mu_2\text{-}H)_3]^+$ gave exclusively the dithiolato complexes $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}S\text{-}1,4\text{-}C_6H_4\text{-}X)_2]^+$ and $[(\eta^6\text{-}1,2,4,5\text{-}C_6H_2Me_4)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}S\text{-}1,4\text{-}C_6H_4\text{-}X)_2]^+$.[62] The trithiolato complexes $[(\eta^6\text{-arene})_2Ru_2(\mu_2\text{-}SR)_3]^+$ are not accessible from the trihydrido precursor. They have, however, been prepared by starting from the chloro precursor $[(\eta^6\text{-arene})_2Ru_2(\mu_2\text{-}Cl)_2Cl_2]$.[63,64]

In the case of the reactions of the hexamethylbenzene derivatives with *p*-bromothiophenol, the complete series of cationic complexes $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}S\text{-}1,4\text{-}C_6H_4\text{-}Br)]^+$, $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}S\text{-}1,4\text{-}C_6H_4\text{-}Br)_2]^+$, and $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}S\text{-}1,4\text{-}C_6H_4\text{-}Br)_3]^+$ has been isolated as the tetrafluoroborate salts and structurally characterized. This allows a comparison of the ruthenium−ruthenium distances with respect to that in $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ (Chart 3).

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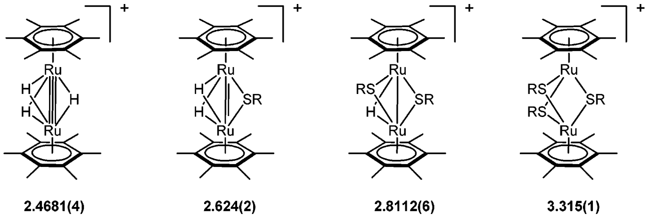
(61) Jahncke, M.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1998**, *561*, 227−235.

(62) Tschan, M. J.-L.; Therrien, B.; Ludvíc, J.; Štěpnička, P.; Süss-Fink, G. *J. Organomet. Chem.* **2006**, *691*, 4304−4311.

(63) Chérioux, F.; Therrien, B.; Süss-Fink, G. *Eur. J. Inorg. Chem.* **2003**, 1043−1047.

(64) Chérioux, F.; Therrien, B.; Sadki, S.; Comminges, C. *J. Organomet. Chem.* **2005**, *690*, 2365−2371.

Chart 3. Comparison of the Ru−Ru Distances (Å) in the Series $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ (30e), $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_2(\mu_2\text{-}S\text{-}1,4\text{-}C_6H_4\text{-}Br)]^+$ (32e), $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}S\text{-}1,4\text{-}C_6H_4\text{-}Br)_2]^+$ (34e), and $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}S\text{-}1,4\text{-}C_6H_4\text{-}Br)_3]^+$ (36e)

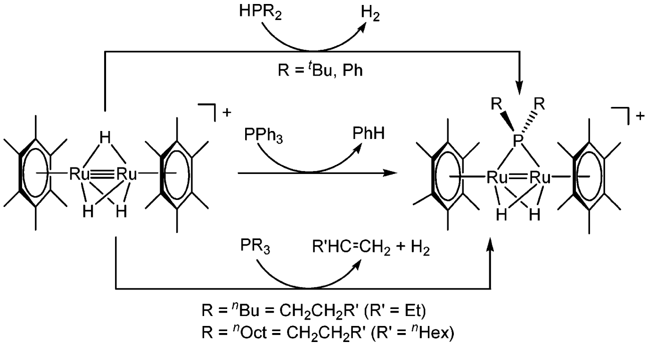


The increase of the Ru−Ru distances in this series parallels the increase in the electron count in these dinuclear complexes from 30 to 36. In the context of the EAN rule, this tendency may be interpreted in terms of a decrease in the bond order from a metal−metal triple bond to a metal−metal double bond to a metal−metal single bond and finally to no metal−metal bond at all. However, a bond order and overlap population analysis, which we carried out recently in collaboration with Daul using density function theory (DFT), showed this interpretation to be just a formalism.[65]

8. Reactions with Phosphorus-Containing Molecules

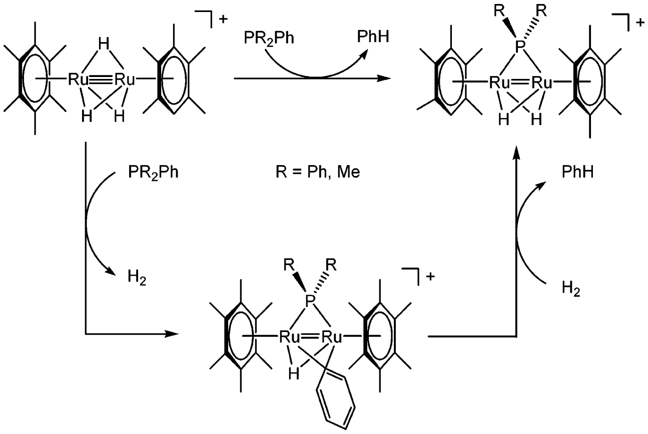
The reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with diaryl- or dialkylphosphines PR_2H gave, as expected, the cationic phosphido derivatives $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}H)_2]^+$ (R = Ph, ^{t}Bu).[66] Surprisingly, such phosphido complexes also are accessible in high yield by the reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with the corresponding triarylphosphines or even with trialkylphosphines (PPh_3, P^nBu_3, P^nOct_3) by facile carbon−phosphorus bond cleavage[66] (see Scheme 7).

Scheme 7. Reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with Secondary and Tertiary Phosphines to Give the Monophosphido Derivatives $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}H)_2]^+$



There is a fundamental difference in the reactions of triarylphosphines and trialkylphosphines. PPh_3 reacted with $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ to give benzene as a side product, whereas the reaction with aliphatic phosphines led via β-elimination to an olefin and molecular hydrogen, which was verified in the case of tri-*n*-octylphosphine, where the *n*-oct-1-ene formed was unambiguously identified.[66] In the case of mixed aryl−alkyl tertiary phosphines, such as PMe_2Ph, it is always the aryl group which is eliminated, as the arene, while the alkyl substituents stay on the phosphorus atom of the phosphido bridge.

Scheme 8. Isolation of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}H)(\mu_2\text{-}Ph)]^+$ (R = Ph, Me) as Tetrafluoroborate Salts as Intermediates from the Reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with PPh_3 or PMe_2Ph



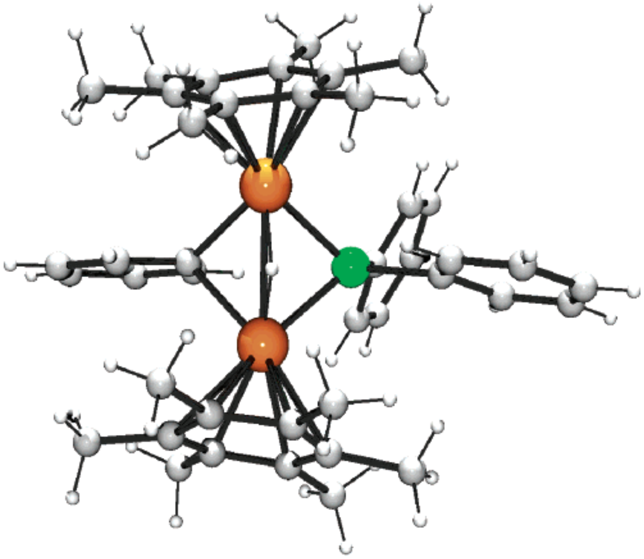


Figure 3. Molecular structure of the cation $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)(\mu_2\text{-}Ph)]^+$.

An intermediate of the reaction of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with PPh_3 was isolated, $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}H)(\mu_2\text{-}Ph)]^+$ as its tetrafluoroborate salt (see Scheme 8). The single-crystal X-ray structure analysis revealed a bridging phenyl ligand coordinated in a μ_2-η^1 fashion to the diruthenium backbone (see Figure 3). The distances between the bridgehead carbon atom of the bridging phenyl ligand and the two ruthenium atoms are 2.264(5) and 2.236(5) Å.[66]

In line with this observation, it is not surprising that trimethylphosphine does not react in the same way, since β-elimination is not possible with the methyl group; instead, three PMe_3 molecules replace a η^6-C_6Me_6 ligand on one of the two ruthenium atoms to give $[(\eta^6\text{-}C_6Me_6)(PMe_3)_3Ru_2(\mu_2\text{-}H)_3]^+$.[67]

9. Synthesis of Trinuclear Clusters

The reaction of the dinuclear cation $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ with the mononuclear cation $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ in aqueous

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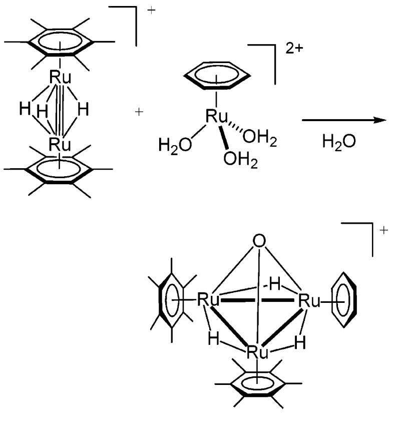
(65) Penka Fowe, E.; Therrien, B.; Süss-Fink, G.; Daul, C. Manuscript in preparation.

(66) Tschan, M. J.-L.; Chérioux, F.; Karmazin-Brelot, L.; Süss-Fink, G. *Organometallics* **2005**, *24*, 1974−1981.

(67) Tschan, M. J.-L.; Chérioux, F.; Therrien, B.; Süss-Fink, G. Submitted for publication in *Eur. J. Inorg. Chem.*

Scheme 9. Synthesis of the Trinuclear Cluster $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ from the Dinuclear Precursor $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ and the Mononuclear Complex $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ in Aqueous Solution

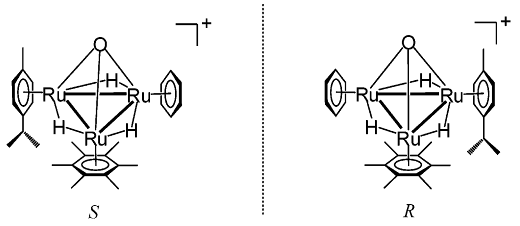


solution resulted in the formation of the trinuclear cluster cation $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ (see Scheme 9). The triruthenium framework is capped by a μ_3-oxo ligand stemming from an aquo ligand. In this reaction, the triaquo complex $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ is generated in situ from an aqueous solution of the chloro precursor $[(\eta^6\text{-}C_6H_6)_2Ru_2(\mu_2\text{-}Cl)_2Cl_2]$ used in excess, in order to avoid side-product formation. Upon addition of $NaBF_4$, the trinuclear complex precipitated as the tetrafluoroborate salt, $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)][BF_4]$.[68]

It is noteworthy that the arene ligands in the trinuclear cluster cations obtained by this reaction can be varied a great deal. However, for steric reasons, it is impossible to have three η^6-hexamethylbenzene ligands on the triruthenium skeleton. On the other hand, with three η^6-benzene ligands, the trinuclear cluster is not stable either, so that neither the cation $[(\eta^6\text{-}C_6H_6)_3Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ nor the cation $[(\eta^6\text{-}C_6Me_6)_3Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ has been so isolated thus far.

A wide range of trinuclear (arene)ruthenium complexes has been synthesized simply by modifying the two building blocks, by introduction of different functional groups either in the dinuclear or in the mononuclear precursor.[35,69−75] Typical examples are the complexes $[\{\eta^6\text{-}C_6H_5[\text{*}CH(CH_3)CH_2OH]\}(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$, which possesses a chiral functional group,[70] $[(\eta^6\text{-}C_6H_5\text{-}CH_2CH_2OCOFc)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$, which contains a tethered ferrocenyl (Fc) substituent, and $[(\eta^6\text{-}1,2\text{-}MeC_6H_4\text{-}COOCH_2CH_2OCOCMe{=}CH_2)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$, which contains a polymerizable side chain.[75] Mixed osmium−diruthenium clusters such as $[(\eta^6\text{-}C_6H_6)Os(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ have also been obtained by this method.[76]

Chart 4. *S* and *R* Enantiomers of the Intrinsically Chiral Cluster Cation $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$, Containing a Tetrahedral Ru_3O Skeleton with Four Different Vertices



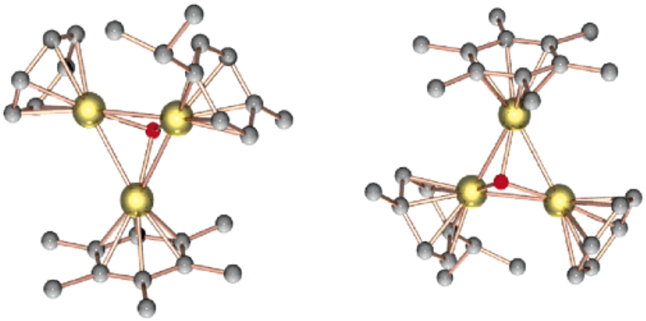


Figure 4. The two enantiomers (*S*)- and (*R*)-$[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$, present in the crystal of the hexafluorophosphate salt.

10. Synthesis of Intrinsically Chiral Triruthenium Oxo Clusters

The synthetic method which we developed for the synthesis of trinuclear arene ruthenium cations in aqueous solution (Scheme 9) allows the assembly of intrinsically chiral triruthenium oxo clusters: if there are three different η^6-arene ligands coordinated to the three ruthenium atoms, the molecule is chiral because the tetrahedral Ru_3O skeleton presents four different vertices (Chart 4). The strategy involves the reaction of a dinuclear precursor containing two different arene ligands, $[(\eta^6\text{-}arene^1)(\eta^6\text{-}arene^2)Ru_2(\mu_2\text{-}H)_3]^+$, with a mononuclear complex, $[(\eta^6\text{-}arene^3)Ru(H_2O)_3]^{2+}$, containing another different arene ligand. An ideal asymmetric diruthenium precursor is the easily accessible mixed *p*-cymene−hexamethylbenzene complex $[(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)(\eta^6\text{-}C_6Me_6)Ru_2(\mu_2\text{-}H)_3]^+$.[35]

The first intrinsically chiral Ru_3O cluster that we synthesized according to this method was the cation $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$, prepared from $[(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)(\eta^6\text{-}C_6Me_6)Ru_2(\mu_2\text{-}H)_3]^+$ and the benzene derivative $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ in aqueous solution. The trinuclear cation crystallized as the hexafluorophosphate salt, and the single-crystal structure analysis revealed indeed both enantiomers to be present in the racemic crystal (see Figure 4).[35]

However, the separation of the *R* and *S* enantiomers of this cluster turned out to be unsuccessful in our hands. We tried fractional crystallization of the cationic enantiomers in the presence of chiral anions such as L-(+)-tartrate and (−)-camphor-10-sulfonate from acetone solution, HPLC on chiral phases, or ion-exchange chromatography in the presence of chiral ions. In no case did the chiral cluster $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ separate into the enantiomers. Therefore, we decided to introduce a chiral auxiliary group R* tethered to one of the three different arene ligands, so that the clusters formed are obtained as a diastereomer mixture (see Scheme 10).

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[68] Faure, M.; Jahncke, M.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *Polyhedron* **1999**, *18*, 2679−2685.

[69] Vieille-Petit, L.; Therrien, B.; Süss-Fink, G.; Ward, T. R. *J. Organomet. Chem.* **2003**, *684*, 117−123.

[70] Vieille-Petit, L.; Therrien, B.; Süss-Fink, G. *Eur. J. Inorg. Chem.* **2003**, 3707−3711.

[71] Vieille-Petit, L.; Unternährer, S.; Therrien, B.; Süss-Fink, G. *Inorg. Chim. Acta* **2003**, *355*, 335−339.

[72] Vieille-Petit, L.; Therrien, B.; Süss-Fink, G. *Acta Crystallogr.* **2003**, *E59*, m669−m670.

[73] Vieille-Petit, L.; Therrien, B.; Süss-Fink, G. *Inorg. Chim. Acta* **2004**, *357*, 3437−3442.

[74] Vieille-Petit, L.; Karmazin-Brelot, L.; Labat, G.; Süss-Fink, G. *Eur. J. Inorg. Chem.* **2004**, 3907−3912.

[75] Vieille-Petit, L.; Therrien, B.; Buryak, A.; Severin, K.; Süss-Fink, G. *Acta Crystallogr.* **2004**, *E60*, m1909−m1911.

[76] Romakh, V. B.; Therrien, B.; Süss-Fink, G. *Inorg. Chim. Acta* **2006**, *359*, 907−911.

Scheme 10. Synthesis of Intrinsically Chiral Cluster Cations $[(\eta^6\text{-}C_6H_5R)(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ from $[(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)(\eta^6\text{-}C_6Me_6)Ru_2(\mu_2\text{-}H)_3]^+$ and $[(\eta^6\text{-}C_6H_5R)Ru(H_2O)_3]^{2+}$ in Aqueous Solution

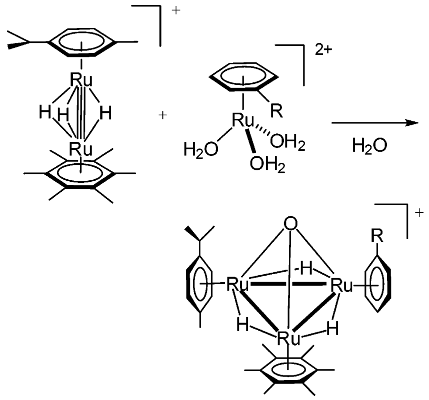
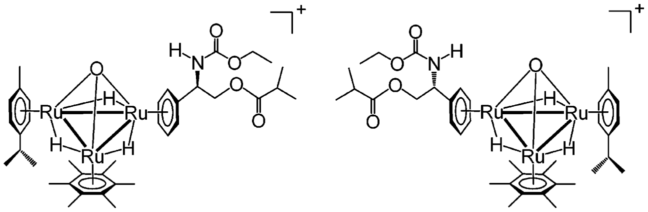


Chart 5. *S,S* and *R,S* Diastereomers of the Intrinsically Chiral Cluster Cation $[\{\eta^6\text{-}C_6H_5((S)\text{-}CH(NHCO_2Et)CH_2OCOPr^i)\}(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ Containing an *S*-Configured Substituent



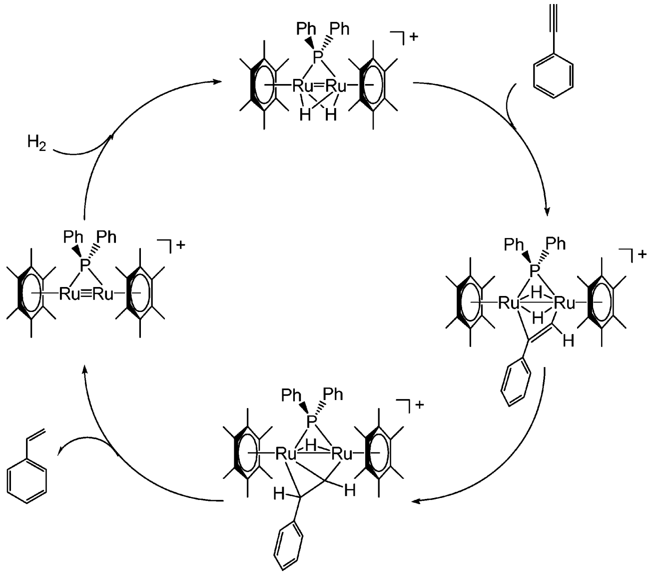
Several intrinsically chiral cluster cations containing the chiral auxiliary group R* at one of the arene ligands were prepared. The separation of the diastereomers obtained was successful only in the case of $[\{\eta^6\text{-}C_6H_5((S)\text{-}CH(NHCO_2Et)CH_2OCOPr^i)\}(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}1,4\text{-}{}^iPrC_6H_4Me)Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$ (Chart 5), which was separated by thin-layer chromatography on silica gel into the R_{Ru_3O},S_C and S_{Ru_3O},S_C diastereomers.[35] This was the first case where the intrinsically chiral Ru_3O cluster core has been enantiotopically separated.

11. Catalytic Potential

The presence of three hydrido ligands in the complexes $[(\eta^6\text{-}arene)_2M_2(\mu_2\text{-}H)_3]^+$, combined with the electron deficiency of these systems, is suggestive of potential catalytic properties for hydrogenation reactions.

The only underivatized compound tested as a hydrogenation catalyst, $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$, indeed showed moderate catalytic activity for the hydrogenation of benzene to cyclohexane under mild conditions.[77] However, it was shown later that the reaction is not catalyzed by hydrido complexes but by metallic ruthenium nanoparticles formed from $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]Cl$ under catalytic conditions.[78] Also in the case of the trinuclear cluster cation $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_2\text{-}H)_3(\mu_3\text{-}O)]^+$, which catalyzes the hydrogenation of benzene under biphasic conditions,[68] and for which a supramolecular mechanism had been proposed,[79] ruthenium(0) nanoparticles have been identified as the true catalytic species.[35,80]

Scheme 11. Tentative Catalytic Cycle for the Hydrogenation of Phenylacetylene Catalyzed by $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)_2]^+$



On the other hand, the phosphido derivative $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)_2]^+$, which selectively catalyzes the hydrogenation of carbon−carbon double and triple bonds without catalyzing the attack on other reducible functions, seems to operate as a molecular catalyst, at least under these mild conditions (60 °C and 50 bar of H_2).[81] The cluster cation $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}\eta^1{:}\eta^2\text{-}CHCHPh)(\mu_2\text{-}H)]^+$, isolated as the tetrafluoroborate salt from the catalytic hydrogenation of phenylacetylene, suggests a reaction course involving initial insertion of the unsaturated substrate into one of the three hydrido bridges of $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)_2]^+$, followed by the transfer of a second one onto the ligand formed; a tentative catalytic cycle is outlined in Scheme 11.

12. Outlook

The dinuclear cations $[(\eta^6\text{-}arene)_2M_2(\mu_2\text{-}H)_3]^+$ (M = Ru, Os) turned out to be valuable complexes for organometallic synthesis. Because of their electron deficiency (30e systems), they are highly reactive and susceptible to addition reactions, and because of their hydrophilicity, they can be handled in organic as well as in aqueous solution. In this respect, they may be considered as bridging the gap between classical coordination compounds and organometallic complexes.

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[77] Bennett, M. A.; Ennett, J. P.; Gell, K. I. *J. Organomet. Chem.* **1982**, *233*, C17−C20.

[78] Wildegren, J. A.; Bennett, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 10301−10310.

[79] Süss-Fink, G.; Faure, M.; Ward, T. R. *Angew. Chem.* **2002**, *114*, 105−108; *Angew. Chem., Int. Ed.* **2002**, *41*, 99−101.

[80] Hagen, C. M.; Vieille-Petit, L.; Laurenczy, G.; Süss-Fink, G.; Finke, R. G. *Organometallics* **2005**, *24*, 1819−1831.

[81] Tschan, M. J.-L.; Süss-Fink, G.; Chérioux, F.; Therrien, B. *Chem. Eur. J.* **2006**, *13*, 292−299.