Synthesis and Characterization of Dibromo-Containing Ruthenium(IV) η^3-Allyl and Ruthenium(IV) η^4-Diene Complexes. Formation of $[Ru(\eta^5\text{-}C_5Me_5)Br_3]^-$ and $[Ru(\eta^5\text{-}C_5Me_5)Br_3]_2$

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The reaction of Br_2 with $Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-diene})Br$ (diene = 1,3-butadiene (**1a**), 2-methyl-1,3-butadiene (**1b**), 1,3-hexadiene (**1c**)), $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-diene})Br$ (diene = 1,3-butadiene (**2a**), 2-methyl-1,3-butadiene (**2b**), 3-methyl-1,3-pentadiene (**2c**), 1,3-hexadiene (**2d**), 1-methoxy-1,3-butadiene (**2e**), 2,4-hexadiene (**2f**), phenyl-1,3-pentadiene (**2g**), diphenyl-1,3-butadiene (**2h**), 1,3-cyclohexadiene (**2i**), 2,3-dimethoxy-1,3-butadiene (**2j**), 2,3-dimethyl-1,3-butadiene (**2k**), 1,2-dimethylenecyclohexane (**2l**)), and $Ru(\eta^5\text{-}C_5Me_4Et)(\eta^4\text{-diene})Br$ (diene = 2,4-hexadiene (**3**)) has been studied. 1,3-Butadiene and mono-, and 1,2-disubstituted-1,3-butadiene complexes afford bromo-substituted Ru(IV) *anti* η^3-allyl complexes in high yields. This process involves addition of bromine on the *exo* face of the diene ligand taking place regioselectively at the terminal carbon bearing no substituent. Unexpectedly, bromination of **2d** yields the dibromoruthenium(IV) η-(1−3)-hexa-1,4-dien-3-yl complex (**6**). In the course of this process HBr is liberated involving the intermediacy of bromo-substituted Ru(IV) η^3-allyl complexes. The molecular structure of **6** has been determined. 1,4-Disubstituted-1,3-butadiene complexes **2f**−**h** and **3** react with Br_2 to form bromo-substituted Ru(IV) η^3-allyl complexes **10a**−**c** and **11** adopting exclusively the *syn* configuration. These compounds are not stable in solution and decompose to give either a dibromoruthenium(IV) η-(1−3)-hexa-1,4-dien-3-yl complex, as a result of HBr elimination, or the dimeric Ru(IV) complexes $[Ru(\eta^5\text{-}C_5Me_5)Br_3]_2$ (**13**) and $[Ru(\eta^5\text{-}C_5Me_4Et)Br_3]_2$ (**14**), respectively. In order to explain the observed stereochemistry and reactivity of complexes **10a**−**c** and **11** a weak three-center $4e^-$ C−Br···Ru interaction is proposed. In case of **2i**, bromination leads to the formation of the complex salt $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)][Ru(\eta^5\text{-}C_5Me_5)Br_3]$ (**15**) and of the dimeric Ru(III) complex $[Ru(\eta^5\text{-}C_5Me_5)Br_2]_2$. **15** features a novel monomeric $17e^-$ half-sandwich Ru(III) complex as counteranion. The molecular structure of **15** has been determined. By contrast, bromination of 2,3-disubstituted-1,3-butadiene complexes **2j**,**k** affords the novel cationic Ru(IV) η^4-diene complexes $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-diene})Br_2]Br$ (diene = 2,3-dimethoxy-1,3-butadiene (**16a**), 2,3-dimethyl-1,3-butadiene (**16b**)). Complexes **16a**,**b** are not stable in solution in the presence of Br^-. On replacement of the bromide counterion by $CF_3SO_3^-$ the stable complexes **17a**,**b** are obtained. The molecular structures of both **16a** and **17a** have been determined. Complexes **16** and **17** appear to be the first late transition-metal complexes approaching a σ^2,π-metallacyclopentene structure.

Introduction

Transition metal complexes containing conjugated dienes are numerous and constitute an important class of organometallic compounds. There is considerable current interest in such complexes due to their applications in organic synthesis.[2] Quite elaborate is the organic chemistry of iron complexes of conjugated dienes.[2] The chemistry of ruthenium diene complexes, however, has developed only recently including ruthenium-mediated [2 + 4] cycloadditions between a conjugated diene and acetylene[3] and stoichiometric and catalytic dimerization reactions of 1,3-dienes with $Ru(\eta^5\text{-}C_5R_5)(\eta^4\text{-diene})$ (R = H, Me; diene = 1,3-butadiene, 2-methyl-1,3-butadiene).[4]

As part of our current interest in the chemistry of ruthenium diene complexes we have previously reported[5,6] on the oxidative addition of Br_2 to complexes of the type $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-diene})Br$. The products of

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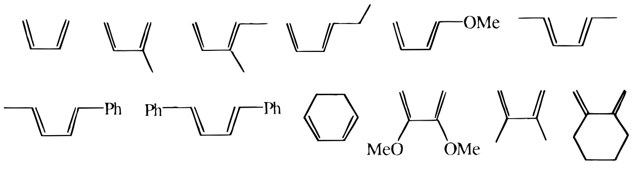
this reaction vary with the substituents of the diene moiety. In the case of 2,4-cyclopentadienone, 1,3-butadiene, and 2-methyl-1,3-butadiene neutral dibromoruthenium(IV) η^3-allyl complexes are readily formed. For 2,3-dimethyl-1,3-butadiene, in contrast, a novel cationic dibromoruthenium(IV) η^4-diene complex is obtained being the first group 8 transition metal diene complex approaching a metallacyclopentene structure. In view of these findings, and to aid the interpretation of these results, we have extended our studies and report on the oxidative addition of Br_2 to a variety of Ru(η^5-C_5R_5)(η^4-diene)Br (R = H, Me) complexes where diene is



X-ray structures of representative complexes and decomposition products are given.

Experimental Section

General Information. Manipulations were performed under an inert atmosphere of purified nitrogen by using standard Schlenk techniques and/or a glovebox. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[7] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC 250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to residual solvent protons. Microanalyses were done by the Microanalytical Laboratories, University of Vienna. Ru(η^5-C_5H_5)(η^4-diene)Br (diene = 1,3-butadiene (**1a**), 2-methyl-1,3-butadiene (**1b**) 1,3-hexadiene (**1c**)),[8] Ru(η^5-C_5Me_5)(η^4-diene)Br (diene = 1,3-butadiene (**2a**), 2-methyl-1,3-butadiene (**2b**), 3-methyl-1,3-pentadiene (**2c**), 1,3-hexadiene (**2d**), 1-methoxy-1,3-butadiene (**2e**), 2,4-hexadiene (**2f**), phenyl-1,3-pentadiene (**2g**), diphenyl-1,3-butadiene (**2h**), 1,3-cyclohexadiene (**2i**), 2,3-dimethoxy-1,3-butadiene (**2j**), 2,3-dimethyl-1,3-butadiene (**2k**), 1,2-dimethylene-cyclohexane (**2l**)),[9] and Ru(η^5-C_5Me_4Et)(η^4-diene)Br (diene = 2,4-hexadiene (**3**))[9] have been synthesized according to literature methods.

Synthesis. (η^5-Cyclopentadienyl)dibromo(η-(1−3)-4-bromo-1-buten-3-yl)ruthenium(IV) (4a). To a stirred solution of **1a** (250 mg, 0.833 mmol) in CH_2Cl_2 (20 mL) at −60 °C, Br_2 (1 equiv), in CH_2Cl_2 (5 mL), was added dropwise within a period of 30 min. The volatiles were then removed under vacuum. The remaining red solid was washed with anhydrous diethyl ether and dried under vacuum. Yield: 300 mg (78%). Anal. Calcd for $C_9H_{11}Br_3Ru$: C, 23.50; H, 2.41; Br, 52.11. Found: C, 23.45; H, 2.48; Br, 52.03. ^1H NMR (δ, acetone-d_6/dmso-d_6 (9:1), 20 °C): 5.93 (s, 5H), 5.80−5.68 (m, 1H, H^3), 4.84−4.77 (m, 1H, H^4), 4.59 (d, 1H, J = 11.3 Hz), 4.44 (dd, 1H, J = 6.6 Hz, J = 1.6 Hz), 4.05 (dd, 1H, J = 9.3 Hz, J = 3.7 Hz), 3.57 (dd, 1H, J = 12.8 Hz, J = 9.3 Hz). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6/dmso-d_6 9:1, 20 °C): 95.5 (C_5H_5), 95.5, 80.8, 59.4, 32.6 (CH_2Br).

(η^5-Cyclopentadienyl)dibromo(η-(1−3)-4-bromo-2-methyl-1-buten-3-yl)ruthenium(IV) (4b). This complex was synthesized analogously to **4a** with **1b** as starting material. Yield: 75%. Anal. Calcd for $C_{10}H_{13}Br_3Ru$: C, 25.34; H, 2.76; Br, 50.57. Found: C, 25.43; H, 2.72; Br, 50.39. ^1H NMR (δ, CD_2Cl_2, 20 °C): 5.96 (s, 5H), 5.21 (m, 1H), 4.67 (s, 1H), 4.09 (dd, 1H, J = 9.1 Hz, J = 3.6 Hz), 4.0 (d, 1H, J = 1.7 Hz), 3.60 (dd, 1H, J = 12.8 Hz, J = 9.1 Hz), 2.26 (s, 3H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 108.7, 96.0 (C_5H_5), 76.9, 57.3, 36.8 (CH_2Br), 21.2 (Me).

(η^5-Cyclopentadienyl)dibromo(η-(2−4)-1-bromo-2-hexen-4-yl)ruthenium(IV) (4c). This complex was synthesized analogously to **4a** with **1c** as starting material. Yield: 83%. Anal. Calcd for $C_{11}H_{15}Br_3Ru$: C, 27.07; H, 3.10; Br, 49.12. Found: C, 27.03; H, 3.01; Br, 49.23. ^1H NMR (δ, CD_2Cl_2, 20 °C): 5.69 (s, 5H), 5.50 (m, 1H), 5.00 (m, 1H), 4.61 (dd, 1H, J = 6.8 Hz, J = 11.6 Hz), 3.78 (dd, 1H, J = 11.9 Hz, J = 6.8 Hz), 3.40 (dd, 1H, J = 11.6 Hz, J = 11.9 Hz), 2.32−2.25 (m, 2H), 1.06 (t, 3H).

(η^5-Pentamethylcyclopentadienyl)dibromo(η-(1−3)-4-bromo-1-buten-3-yl)ruthenium(IV) (5a). This complex was synthesized analogously to **4a** with **2a** as starting material. Yield: 330 mg (92%). Anal. Calcd for $C_{14}H_{21}Br_3Ru$: C, 31.72; H, 3.99; Br, 45.22. Found: C, 31.79; H, 4.02; Br, 45.32. ^1H NMR (δ, $CDCl_3$, 20 °C): 5.90−5.60 (m, 1H), 5.48−5.35 (m, 1H), 4.38 (m, 1H), 3.59 (m, 1H), 2.98−2.86 (m, 2H), 1.57 (s, 15H).

(η^5-Pentamethylcyclopentadienyl)dibromo(η-(1−3)-4-bromo-2-methyl-1-buten-3-yl)ruthenium(IV) (5b). This complex was synthesized analogously to **4a** with **2b** as starting material. Yield: 96%. Anal. Calcd for $C_{15}H_{23}Br_3Ru$: C, 33.11; H, 4.26; Br, 44.05. Found: C, 32.96; H, 4.17; Br, 44.06. ^1H NMR (δ, CD_2Cl_2, 20 °C): 5.07 (ddd, 1H, H^3, $^3J_{35}$ = 12.9 Hz, $^3J_{34}$ = 3.8 Hz, $^4J_{23}$ = 1.9 Hz), 3.79 (d, 1H, H^2, $^4J_{23}$ = 1.9 Hz), 3.73 (dd, 1H, H^4, $^2J_{45}$ = 8.5 Hz, $^3J_{34}$ = 3.8 Hz), 3.01 (dd, 1H, H^5, $^3J_{35}$ = 12.9 Hz, $^2J_{45}$ = 8.5 Hz), 2.97 (s, 1H, H^1), 2.40 (s, 3H), 1.74 (s, 15H). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2, 20 °C): 108.2, 105.5 (C_5Me_5), 71.4, 56.4, 35.3 (CH_2Br), 22.4 (Me), 11.1 (C_5Me_5).

(η^5-Pentamethylcyclopentadienyl)dibromo(η-(2−4)-1-bromo-3-methyl-2-penten-4-yl)ruthenium(IV) (5c). This complex was synthesized analogously to **4a** with **2c** as starting material. Yield: 97%. Anal. Calcd for $C_{16}H_{25}Br_3Ru$: C, 34.43; H, 4.51; Br, 42.95. Found: C, 34.51; H, 4.55; Br, 42.73. ^1H NMR (δ, $CDCl_3$, 20 °C): 5.38 (dd, 1H, J = 4.1 Hz, J = 13.1 Hz), 3.72 (dd, 1H, J = 3.9 Hz, J = 8.7 Hz), 3.56 (m, 1H), 3.01 (dd, 1H, J = 8.7 Hz, J = 13.1 Hz), 2.36 (s, 3H), 1.75 (s, 15H), 1.66 (d, 3H, J = 6.4 Hz).

(η^5-Pentamethylcyclopentadienyl)dibromo([2,3-*E*,4,5-*Z*]-η-(1−3)-hexa-1,4-dien-3-yl)ruthenium(IV) (6). To a stirred solution of **2d** (450 mg, 1.135 mmol), 1 g of Na_2SO_4, and 1 g of $NaHCO_3$ in CH_2Cl_2 (20 mL) at −60 °C, Br_2 (1 equiv), in CH_2Cl_2 (5 mL), was added dropwise within a period of 30 min. The mixture was then warmed to room temperature. Solid materials were removed by filtration, and the volatiles were removed under vacuum. The remaining red solid was washed with anhydrous diethyl ether and dried under vacuum. Yield: 406 mg (75%). Anal. Calcd for $C_{16}H_{24}Br_2Ru$: C, 40.27; H, 5.07; Br, 33.49. Found: C, 40.22; H, 5.11; Br, 33.41. ^1H NMR (δ, $CDCl_3$, 20 °C): 6.28 (ddd, 1H, H^5, $^3J_{56}$ = 11.2 Hz, $^3J_{45}$ = 11.0 Hz, ^4J = 1.7 Hz), 6.12 (m, 1H, H^6), 5.18 (ddd, 1H, H^3, $^3J_{23}$ = 6.0 Hz, $^3J_{34}$ = 10.5 Hz, $^3J_{13}$ = 9.6 Hz), 4.27 (d, 1H, H^2, $^3J_{23}$ = 6.0 Hz), 3.67 (dd, 1H, H^4, $^3J_{34}$ = 10.5 Hz, $^3J_{45}$ = 11.0 Hz), 2.18 (d, 1H, H^1, $^3J_{13}$ = 9.6 Hz), 1.64 (s, 15H), 1.61 (dd, 3H, ^4J = 1.7 Hz, ^3J = 6.7 Hz). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 131.6, 131.3, 103.3 (C_5Me_5), 93.8, 83.7, 60.9, 14.8, 10.2 (C_5Me_5).

(η^5-Pentamethylcyclopentadienyl)dibromo(η-(2−4)-1-oxo-2-buten-4-yl)ruthenium(IV) (7). This complex was synthesized analogously to **4a** with **2e** as starting material. Yield: 94%. Anal. Calcd for $C_{14}H_{20}Br_2ORu$: C, 36.15; H, 4.33; Br, 34.35. Found: C, 36.08; H, 4.34; Br, 34.22. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.55 (d, 1H, H^5, $^3J_{34}$ = 7.3 Hz), 5.87 (ddd, 1H, H^3, $^3J_{34}$ = 6.6 Hz, $^3J_{23}$ = 6.8 Hz, $^3J_{13}$ = 10.6 Hz), 5.39 (ddd,

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1H, H^4, $^3J_{34} = 6.6$ Hz, $^3J_{45} = 7.3$ Hz, $^4J_{24} = 1.7$ Hz), 4.56 (dd, 1H, H^2, $^3J_{23} = 6.8$ Hz, $^4J_{24} = 1.7$ Hz), 3.22 (d, 1H, H^1, $^3J_{13} = 10.6$ Hz), 1.79 (s, 15H). ^{13}C{^{1}H} NMR (δ, CDCl$_3$, 20 °C): 196.6, 107.1 ($C_5\mathrm{Me}_5$), 99.3, 74.0, 60.0, 10.7 (C_5Me_5).

[(η^5-Pentamethylcyclopentadienyl)dibromo(η-(1−3)-4-(triethylammonio)-2-methyl-1-buten-3-yl)ruthenium(IV)] Bromide (8). To a solution of **5b** (250 mg, 0.472 mmol) in CH$_2$Cl$_2$ (10 mL), triethylamine (97 μL, 0.538 mmol) was added, and the mixture was stirred for 30 min. On addition of diethyl ether a red precipitate was formed, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 240 mg (79%). Anal. Calcd for C$_{21}$H$_{38}$Br$_3$NRu: C, 39.09; H, 5.94; N, 2.17; Br, 37.15. Found: C, 38.99; H, 5.92; N, 2.12; Br, 37.02. ^{1}H NMR (δ, CD$_3$NO$_2$, 20 °C): 4.67 (d, 1H, $J = 12.3$ Hz), 3.84 (s, 1H), 3.50 (q, 6H), 3.25 (dd, 1H, $J = 13.8$ Hz, $J = 2.6$ Hz), 3.20 (s, 1H), 2.66 (t, 1H, $J = 13.8$ Hz, $J = 12.3$ Hz), 2.56 (s, 3H), 1.86 (s, 15H), 1.38 (t, 9H). ^{13}C{^{1}H} NMR (δ, CD$_3$NO$_2$, 20 °C): 110.8, 108.6 ($C_5\mathrm{Me}_5$), 60.3, 58.6, 54.6, 47.3, 22.6 (Me), 11.5 (C_5Me_5), 7.6.

[(η^5-Pentamethylcyclopentadienyl)dibromo(η-(1,2,3)-4-pyridiniumyl-2-methyl-1-buten-3-yl)ruthenium(IV)] Bromide (9). This complex was synthesized analogously to **8** but with pyridine as the nucleophile. Yield: 99%. Anal. Calcd for C$_{20}$H$_{28}$Br$_3$NRu: C, 38.54; H, 4.53; N, 2.25; Br, 38.46. Found: C, 38.49; H, 4.45; N, 2.17; Br, 38.18. ^{1}H NMR (δ, CD$_3$CN, 20 °C): 8.89 (d, 2H), 8.54 (t, 1H), 8.07 (t, 2H), 4.75 (d, 1H, $J = 13.3$ Hz), 4.64 (d, 1H, $J = 12.6$ Hz), 3.89 (t, 1H, $J = 12.6$ Hz), 3.89 (s, 1H), 3.36 (s, 1H), 2.23 (s, 3H), 1.86 (s, 15H). ^{13}C{^{1}H} NMR (δ, CD$_3$NO$_2$/dmso-d_6, 20 °C): 146.2, 144.8, 128.5, 107.4, 106.7 ($C_5\mathrm{Me}_5$), 66.5, 58.7, 54.6, 21.6 (Me), 10.7 (C_5Me_5).

(η^5-Pentamethylcyclopentadienyl)dibromo([3,4-*E*]-η-(2−4)-5-bromo-2-hexen-4-yl)ruthenium(IV) (10a). This complex was synthesized analogously to **4a** with **2f** as starting material. Yield: 78%. Anal. Calcd for C$_{16}$H$_{25}$Br$_3$Ru: C, 34.43; H, 4.51; Br, 42.95. Found: C, 34.35; H, 4.49; Br, 43.15. ^{1}H NMR (δ, CD$_2$Cl$_2$, 20 °C): 5.48 (m, 1H, H^1, $^3J = 6.7$ Hz, $^3J_{12} = 10.1$ Hz), 5.07 (t, 1H, H^3, $^3J_{34} = 9.6$ Hz, $^3J_{23} = 9.9$ Hz), 2.70 (t, 1H, H^2, $^3J_{12} = 10.1$ Hz, $^3J_{23} = 9.9$ Hz), 2.68 (m, 1H, H^4, $^3J_{34} = 9.6$ Hz, $^3J = 6.1$ Hz), 1.72 (d, 3H, $^3J = 6.5$ Hz), 1.71 (d, 3H, $^3J = 6.1$ Hz), 1.65 (s, 15H). ^{13}C{^{1}H} NMR (δ, CD$_3$CN, 20 °C): 104.5 ($C_5\mathrm{Me}_5$), 98.3, 82.6, 81.6, 57.1, 26.2 (Me), 19.0 (Me), 10.2 (C_5Me_5).

(η^5-Pentamethylcyclopentadienyl)dibromo([3,4-*E*]-η-(2−4)-1-bromo-1-phenyl-2-penten-4-yl)ruthenium(IV) (10b). Using an analogous procedure as for **10a** with **2g** as starting material resulted in the formation of a mixture of **10b** (ca. 60−80%) and **13**. Attempts to recrystallize **10b** from CH$_2$Cl$_2$ led to the quantitative formation of **13**. ^{1}H NMR (δ, CD$_2$Cl$_2$, 20 °C): 7.66 (dd, 2H), 7.43−7.29 (m, 3H), 6.89 (d, H^1, H^1, $J = 11.2$ Hz), 5.29 (t, 1H, H^3, $J = 10.5$ Hz), 3.19 (t, 1H, H^2, $J = 10.5$ Hz, $J = 11.2$ Hz), 2.71−2.60 (m, 1H, H^4), 1.71 (d, 3H, $J = 6.4$ Hz), 1.27 (s, 15H).

The decomposition of **10b** was also monitored by ^{1}H NMR spectroscopy. A 5-mm NMR tube was charged with the crude product and was capped with a septum. CD$_2$Cl$_2$ (0.5 mL) was added by syringe, and the sample was transferred to a NMR probe. ^{1}H NMR spectra were recorded showing the quantitative formation of phenyl-1,3-pentadiene.

(η^5-Pentamethylcyclopentadienyl)dibromo([3,4-*E*]-η-(2−4)-1-bromo-1,4-diphenyl-2-penten-4-yl)ruthenium(IV) (10c). Using an analogous procedure as for **10a** with **2h** as starting material resulted in the formation of a mixture of **10c** (ca. 60−80%) and **13**. Attempts to recrystallize **10c** from CH$_2$Cl$_2$ resulted in complete decomposition to give **13**. ^{1}H NMR (δ, CD$_2$Cl$_2$, 20 °C): 7.62 (d, 4H), 7.36−7.26 (m, 6H), 6.95 (d, 1H, H^1, $J = 9.8$ Hz), 5.75 (dd, 1H, H^3, $J = 10.8$ Hz, $J = 9.3$ Hz), 3.78 (d, 1H, $J = 10.8$ Hz), 3.31 (dd, 1H, $J = 9.3$ Hz, $J = 9.8$ Hz), 1.27 (s, 15H).

The decomposition of **10c** was also monitored by ^{1}H NMR spectroscopy showing the liberation of diphenyl-1,3-butadiene.

(η^5-Tetramethylethylcyclopentadienyl)dibromo(η-(2−4)-5-bromo-2-hexen-4-yl)ruthenium(IV) (11). Using an analogous procedure as for **10a** with **3** as starting material resulted in a mixture of **11** and **14**. No attempts were made to separate these complexes. ^{1}H NMR (δ, CDCl$_3$, 20 °C): 5.51 (m, 1H), 5.11 (t, 1H, $J = 9.7$ Hz), 2.73 (m, 2H), 1.92 (q, 2H), 1.73 (s, 6H), 1.71 (s, 6H), 1.69 (d, 6H, $J = 4.4$ Hz), 1.18 (t, 3H).

(η^5-Pentamethylcyclopentadienyl)dibromo([*E*,*E*]-η-(1−3)-hexa-1,4-dien-3-yl)ruthenium(IV) (12). **10a** (122 mg, 0.219 mmol) was dissolved in 10 mL of CH$_2$Cl$_2$. AgCF$_3$SO$_3$ (56 mg, 0.218 mmol) was added, and the mixture was stirred for 1 h. The resulting precipitate of AgBr was removed by filtration. On addition of diethyl ether a red precipitate was formed which was collected on a glass frit, washed with diethyl ether and dried under vacuum. Yield: 76 mg (73%). Anal. Calcd for C$_{16}$H$_{24}$Br$_2$Ru: C, 40.27; H, 5.07; Br, 33.49. Found: C, 40.13; H, 5.19; Br, 33.35. ^{1}H NMR (δ, CD$_3$CN, 20 °C): 6.41−6.32 (m, 1H, H^6), 6.00 (ddd, 1H, H^5, $^3J_{56} = 14.5$ Hz, $^3J_{45} = 10.4$ Hz, $^4J = 1.6$ Hz), 5.29 (ddd, 1H, H^3, $^3J_{23} = 6.3$ Hz, $^3J_{34} = 10.6$ Hz, $^3J_{13} = 10.2$ Hz), 4.46 (d, 1H, H^2, $^2J_{23} = 6.3$ Hz), 3.93 (dd, 1H, H^4, $^3J_{45} = 10.4$ Hz, $^3J_{34} = 10.6$ Hz), 2.50 (d, 1H, H^1, $^3J_{13} = 10.2$ Hz), 1.70 (dd, 3H, $^4J = 1.6$ Hz, $^3J = 6.8$ Hz), 1.64 (s, 15H). ^{13}C{^{1}H} NMR (δ, CD$_2$Cl$_2$, 20 °C): 140.5, 130.9, 106.3 ($C_5\mathrm{Me}_5$), 95.2, 92.4, 66.1, 19.6 (Me), 9.8 (C_5Me_5).

Bis(μ-bromo)bis[(η^5-pentamethylcyclopentadienyl)-dibromoruthenium(IV)] (13). Method a. 13 was prepared by following a published procedure.[10] **Method b.** A solution of either **10b** or **10c** in CH$_2$Cl$_2$ was set aside for crystallization by vapor diffusion with diethyl ether. After 1 day a dark red precipitate was formed, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 75%. Anal. Calcd for C$_{20}$H$_{30}$Br$_6$Ru$_2$: C, 25.23; H, 3.18; Br, 50.36. Found: C, 25.99; H, 3.21; Br, 50.73. ^{1}H NMR (δ, dmso-d_6, 20 °C): 1.47 (s, 15H).

Bis(μ-bromo)bis[(η^5-tetramethylethylcyclopentadienyl)-dibromoruthenium(IV)] (14). Method a. 14 was prepared according to the literature but with [Ru(η^5-C$_5$Me$_4$Et)Br$_2$]$_2$ as starting material.[10] Yield: 93%. **Method b.** A solution of **11** in CH$_2$Cl$_2$ was set aside for crystallization by vapor diffusion with diethyl ether. Within 1 day dark red crystals were formed which were suitable for an X-ray diffraction study. Yield: 89%. Anal. Calcd for C$_{22}$H$_{34}$Br$_6$Ru$_2$: C, 26.96; H, 3.50; Br, 48.92. Found: C, 26.87; H, 3.36; Br, 49.24. ^{1}H NMR (δ, dmso-d_6, 20 °C): 1.86 (q, 2H), 1.61 (s, 6H), 1.57 (s, 6H), 1.13 (t, 3H).

Reaction of Br$_2$ with [η^5-Pentamethylcyclopentadienyl)bromo(η^4-2,4-cyclohexadiene)ruthenium(II). Formation of (η^5-Pentamethylcyclopentadienyl)(η^6-benzene)-ruthenium(II) (η^5-Pentamethylcyclopentadienyl)tribromoruthenate(III) (15). Using an analogous procedure as for **4a** with **2i** as starting material resulted in the formation of **15** and [Ru(η^5-C$_5$Me$_5$)Br$_2$]$_2$[11] in a ratio of about 1:1. ^{1}H NMR (δ, CDCl$_3$, 20 °C): 7.43 (s, 6H); 2.40 (s, 15H), 1.89 (s, 30H). A solution containing **15** and [Ru(η^5-C$_5$Me$_5$)Br$_2$]$_2$ in CH$_2$Cl$_2$ was set aside for crystallization by vapor diffusion with diethyl ether. Within 1 day dark red crystals of morphologically different appearance were formed. They were separated manually and crystallographically analyzed.

[(η^5-Pentamethylcyclopentadienyl)dibromo(η^4-2,3-dimethoxybutadiene)ruthenium(IV)] Bromide (16a). This complex was synthesized analogously to **4a** with **2j** as starting material. Yield: 98%. Anal. Calcd for C$_{16}$H$_{25}$Br$_3$O$_2$Ru: C, 32.56; H, 4.27; Br, 40.62. Found: C, 32.65; H, 4.29; Br, 40.55. ^{1}H NMR (δ, CD$_3$CN, 20 °C): 4.24 (s, 6H), 3.92 (d, 2H, $^2J = 6.1$ Hz), 2.61 (d, 2H, $^2J = 6.1$ Hz), 1.97 (s, 15H).

[(η^5-Pentamethylcyclopentadienyl)dibromo(η^4-2,3-dimethylbutadiene)ruthenium(IV)] Bromide (16b). This complex was synthesized analogously to **4a** with **2k** as starting material.[6] Yield: 93%. Anal. Calcd for C$_{16}$H$_{25}$Br$_3$Ru: C,

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Table 1. Crystallographic Data[a]

	6	**14**	**15**	**16a**·CH_2Cl_2	**17a**
formula	$C_{16}H_{24}Br_2Ru$	$C_{11}H_{17}Br_3Ru$	$C_{26}H_{36}Br_3Ru_2$	$C_{17}H_{27}Br_3Cl_2O_2Ru$	$C_{17}H_{25}Br_2F_3O_5RuS$
fw	477.24	490.05	790.42	675.09	659.32
cryst size, mm	0.11 × 0.18 × 0.20	0.06 × 0.15 × 0.35	0.17 × 0.19 × 0.80	0.06 × 0.11 × 0.18	0.06 × 0.28 × 0.56
space group	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)	*Pnma* (No. 62)	*Pnma* (No. 62)	$\mathrm{P}2_1/c$ (No. 14)
a, Å	17.459(4)	8.544(3)	19.511(5)	13.810(3)	9.562(3)
b, Å	13.624(4)	13.003(5)	12.732(3)	10.128(2)	8.328(3)
c, Å	7.383(2)	12.756(4)	11.512(3)	17.065(4)	29.120(9)
β, deg		93.44(1)			94.22(1)
V, Å^3	1756.1(8)	1414.6(9)	2859.7(12)	2386.8(9)	2312.6(13)
Z	4	4	4	4	4
ρ_{calc}, g cm^{-3}	1.805	2.301	1.836	1.879	1.894
T, K	300	299	295	295	294
μ(Mo Kα), mm^{-1}	5.43	9.55	5.26	5.91	4.27
abs corr	analytical	empirical	empirical	analytical	analytical
transm fact., min/max	0.47/0.60	0.86/1.16	0.93/1.13	0.53/0.72	0.32/0.78
$\theta_{\max}$, deg	25	24	25	24	25
index ranges	$-20 \leq h \leq 20$	$0 \leq h \leq 9$	$0 \leq h \leq 23$	$0 \leq h \leq 15$	$0 \leq h \leq 11$
	$0 \leq k \leq 16$	$0 \leq k \leq 14$	$0 \leq k \leq 15$	$0 \leq k \leq 11$	$0 \leq k \leq 9$
	$0 \leq l \leq 8$	$-10 \leq l \leq 10$	$0 \leq l \leq 13$	$0 \leq l \leq 19$	$-34 \leq l \leq 34$
no. reflns measd	3358	2241	3619	2171	4675
no. of unique reflns	3102	1986	2641	1999	4113
no. of reflns > $4\sigma(F)$	2265	1327	1691	1194	2861
no. of params	183	137	156	127	270
$R(F)$ ($F > 4\sigma(F)$)[a]	0.048	0.043	0.041	0.034	0.049
$R(F)$ (all data)	0.084	0.085	0.085	0.092	0.083
w$R(F^2)$ (all data)[b]	0.078	0.074	0.087	0.084	0.134
diff Four. peaks min/max, eÅ^{-3}	−0.35/0.44	−0.53/0.45	−0.57/0.69	−0.65/0.62	−0.70/0.72

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{0.5}$.

34.43; H, 4.51; Br, 42.95. Found: C, 34.45; H, 4.48; Br, 42.78. ^{1}H NMR (δ, acetone-d_6, 20 °C): 3.97 (d, 2H, $^2J = 4.5$ Hz), 3.12 (d, 2H, $^2J = 4.5$ Hz), 2.07 (s, 6H), 1.82 (s, 15H).

[(η^5-Pentamethylcyclopentadienyl)dibromo(η^4-2,3-dimethoxybutadiene)ruthenium(IV)] Trifluoromethanesulfonate (17a). **16a** (330 mg, 0.559 mmol) was dissolved in 10 mL of CH_2Cl_2. $AgCF_3SO_3$ (144 mg, 0.560 mmol) was added, and the mixture was stirred for 1 h. The resulting precipitate of AgBr was removed by filtration. On addition of diethyl ether a red precipitate was formed, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 350 mg (95%). Anal. Calcd for $C_{17}H_{25}Br_2F_3O_5RuS$: C, 30.97; H, 3.82; Br, 24.24. Found: C, 31.05; H, 3.84; Br, 24.15. ^{1}H NMR (δ, CD_3CN, 20 °C): 4.23 (s, 6H), 3.86 (d, 2H, $^2J = 6.1$ Hz), 2.03 (d, 2H, $^2J = 6.1$ Hz), 1.93 (s, 15H). ^{13}C{^{1}H} NMR (δ, CD_3CN, 20 °C): 153.5, 114.9 (C_5Me$_5$), 62.6 (OMe), 51.3, 11.7 (C$_5$*Me*$_5$).

[(η^5-Pentamethylcyclopentadienyl)dibromo(η^4-2,3-dimethylbutadiene)ruthenium(IV)] Trifluoromethanesulfonate (17b). This complex was synthesized analogously to **17a** with **16b** as starting material.[6] Yield: 74%. Anal. Calcd for $C_{17}H_{25}Br_2F_3O_3RuS$: C, 32.55; H, 4.02; Br, 25.47. Found: C, 32.46; H, 4.08; Br, 26.78. ^{1}H NMR (δ, acetone-d_6, 20 °C): 3.65 (d, 2H, $^2J = 1.7$ Hz), 2.72 (s, 6H, Me), 2.53 ppm (d, 2H, $^2J = 1.7$ Hz), 2.16 (s, 15H). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2, 20 °C): 140.7, 116.0 (C_5Me$_5$), 72.0, 22.2 (Me), 12.4 (C$_5$*Me*$_5$).

Reaction of Br_2 with [(η^5-Pentamethylcyclopentadienyl)bromo(η^4-dimethylenecyclohexane)ruthenium(II) (2l). Following the protocol for **17a**, bromination of **2l** led only to the formation of several intractable materials.

X-ray Structure Determination for 6, 14, 15, 16a·CH_2Cl_2, and 17a. Crystal data and experimental details are given in Table 1. X-ray data were collected on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.716\,09$ Å) radiation, and the $\theta-2\theta$ scan technique (**6**, **14**, **15**, **16a**·CH_2Cl_2) or the ω-scan technique (**17a**). Three representative reference reflections were measured every 120 min and used to correct for crystal decay and system instability. Corrections for Lorentz and polarization effects and for absorption were applied. The structures were solved by direct methods.[12] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions.[13] The structures were refined against F^2. Final positional parameters are given in Tables 2−6.

Table 2. Atomic Positional and Isotropic Displacement Parameters (Å^2 × 10^3) for Ru(η^5-C$_5$Me$_5$)(η^3−CH$_2$CHCHCH=CHCH$_3$)Br$_2$ (6)

	x	y	z	U_{eq}[a]
Ru	0.05749(4)	0.16107(4)	0.30774(8)	40(1)
Br(1)	−0.06609(6)	0.07104(6)	0.22554(14)	77(1)
Br(2)	0.11887(7)	0.02673(7)	0.11610(14)	76(1)
C(1)	0.0966(5)	0.2500(6)	0.5374(9)	38(2)
C(2)	0.1491(4)	0.1706(6)	0.5115(10)	46(2)
C(3)	0.1109(5)	0.0823(6)	0.5526(10)	44(2)
C(4)	0.0334(5)	0.1049(6)	0.5938(11)	48(2)
C(5)	0.0245(5)	0.2099(6)	0.5796(11)	51(2)
C(6)	0.1165(5)	0.3562(5)	0.5498(10)	62(2)
C(7)	0.2339(4)	0.1808(6)	0.4810(12)	64(3)
C(8)	0.1435(5)	−0.00186(6)	0.5632(12)	74(3)
C(9)	−0.0239(5)	0.0343(6)	0.6595(13)	82(3)
C(10)	−0.0490(5)	0.2638(6)	0.6269(12)	75(3)
C(11)	−0.00092(5)	0.2831(6)	0.1964(13)	54(2)
C(12)	0.435(6)	0.2522(6)	0.0749(11)	57(3)
C(13)	0.1205(6)	0.2708(6)	0.1158(11)	63(3)
C(14)	0.1866(7)	0.2462(9)	0.00060(15)	87(3)
C(15)	0.2518(7)	0.2975(10)	−0.0007(16)	101(4)
C(16)	0.2661(7)	0.3884(10)	0.0998(17)	138(5)

[a] $U_{\mathrm{eq}} = {}^1/_3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*(\mathbf{a}_i\mathbf{a}_j)$.

Results and Discussion

1,3-Butadiene and Monosubstituted- and 1,2-Disubstituted-1,3-Butadiene Complexes. As shown in Scheme 1, new bromo-substituted Ru(IV) η^3-allyl complexes **4a−c** and **5a−c** can be synthesized in high yields by reacting **1a−c** and **2a−c** with stoichiometric

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(13) Sheldrick, G. M. SHELXL93 Program for crystal structure refinement, University of Göttingen, Germany, 1993.

Table 3. Atomic Positional and Isotropic Displacement Parameters (Å^2 × 10^3) for [Ru(η^5-C_5Me_5)Br_3]$_2$ (14)

	x	*y*	*z*	U_{eq}[a]
Ru(1)	0.59066(8)	0.48101(5)	0.35983(5)	34(1)
Br(1)	0.66900(9)	0.50845(7)	0.55360(7)	52(1)
Br(2)	0.79534(14)	0.61888(8)	0.34214(8)	77(1)
Br(3)	0.43857(14)	0.59730(8)	0.23109(8)	82(1)
C(1)	0.5861(11)	0.3153(5)	0.3808(6)	41(2)
C(2)	0.5100(9)	0.3395(6)	0.2798(7)	39(2)
C(3)	0.6224(9)	0.3810(5)	0.2160(6)	33(2)
C(4)	0.7683(10)	0.3803(6)	0.2755(6)	39(2)
C(5)	0.7454(11)	0.3408(7)	0.3744(6)	47(2)
C(6)	0.5145(14)	0.2547(6)	0.4669(7)	91(4)
C(7)	0.3445(10)	0.3151(8)	0.2435(8)	84(4)
C(8)	0.6073(11)	0.4075(7)	0.1021(6)	61(3)
C(9)	0.9250(9)	0.4041(7)	0.2356(7)	64(3)
C(10)	0.8770(12)	0.3182(8)	0.4553(7)	89(4)
C(11)	0.5372(18)	0.1384(7)	0.4474(8)	138(6)

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\mathbf{a}_i\mathbf{a}_j)$.

Table 4. Atomic Positional and Isotropic Displacement Parameters (Å^2 × 10^3) for [Ru(η^5-C_5Me_5)(η^6-C_6H_6][Ru(η^5-C_5Me_5)Br_3] (15)

	x	*y*	*z*	U_{eq}[a]
Ru(1)	0.46009(3)	0.75	0.15402(5)	49(1)
C(1)	0.5618(4)	0.75	0.2303(6)	55(2)
C(2)	0.5261(3)	0.6605(5)	0.2690(4)	58(2)
C(3)	0.4674(3)	0.6948(4)	0.3331(4)	56(1)
C(4)	0.6286(4)	0.25	0.1652(7)	90(3)
C(5)	0.5457(4)	0.5460(5)	0.2508(6)	88(2)
C(6)	0.4180(3)	0.6250(6)	0.3959(6)	101(3)
C(7)	0.4670(4)	0.6986(6)	−0.0288(5)	91(2)
C(8)	0.4174(5)	0.6435(6)	0.0238(6)	96(3)
C(9)	0.3636(4)	0.6933(7)	0.0817(6)	110(4)
Ru(2)	0.33163(3)	0.25	0.27514(5)	55(1)
Br(1)	0.45599(5)	0.25	0.33877(10)	108(1)
Br(2)	0.35274(5)	0.10766(6)	0.12659(6)	108(1)
C(11)	0.2198(4)	0.25	0.2951(7)	74(3)
C(12)	0.2476(3)	0.1584(5)	0.3511(5)	64(2)
C(13)	0.2928(3)	0.1932(4)	0.4410(4)	54(1)
C(14)	0.1685(5)	0.25	0.1977(9)	146(6)
C(15)	0.2291(4)	0.0473(6)	0.3293(6)	102(3)
C(16)	0.3289(3)	0.1257(5)	0.5261(5)	81(2)

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\mathbf{a}_i\mathbf{a}_j)$.

Table 5. Atomic Positional and Isotropic Displacement Parameters (Å^2 × 10^3) for [Ru(η^5-C_5Me_5)(η^4-$CH_2COMeCOMeCH_2$)Br_2]Br·CH_2Cl_2 (16a·CH_2Cl_2)

	x	*y*	*z*	U_{eq}[a]
Ru	0.40973(5)	0.25	0.32048(4)	39(1)
Br(1)	0.30434(5)	0.41371(8)	0.24827(4)	62(1)
Br(2)	0.55103(8)	0.25	0.59907(6)	63(1)
C(1)	0.5111(6)	0.25	0.2203(5)	42(2)
C(2)	0.5332(4)	0.3641(6)	0.2668(4)	43(2)
C(3)	0.5670(4)	0.3212(6)	0.3409(3)	40(2)
C(4)	0.4859(7)	0.25	0.1352(5)	57(3)
C(5)	0.5355(4)	0.5041(7)	0.2397(4)	54(2)
C(6)	0.6103(4)	0.4062(7)	0.4021(3)	49(2)
C(7)	0.3930(4)	0.3818(7)	0.4208(3)	47(2)
C(8)	0.3012(4)	0.3194(7)	0.4229(3)	48(2)
O	0.2151(3)	0.3781(5)	0.4182(2)	55(1)
C(9)	0.2097(5)	0.5184(8)	0.4310(4)	81(3)
C(10)	0.1576(8)	0.25	0.6661(8)	102(5)
Cl(1)	0.2778(3)	0.25	0.6386(3)	128(2)
Cl(2)	0.0789(4)	0.25	0.5877(2)	152(2)

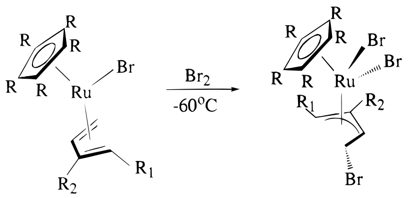
[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij} a_{\mathbf{i}}^* a_j^* (\mathbf{a}_i\mathbf{a}_j)$.

Table 6. Atomic Positional and Isotropic Displacement Parameters (Å^2 × 10^3) for [Ru(η^5-C_5Me_5)(η^4-$CH_2COMeCOMeCH_2$)Br_2]CF_3SO_3 (17a)

	x	*y*	*z*	U_{eq}[a]
Ru	0.27943(5)	0.44750(7)	0.1517(2)	43(1)
Br(1)	0.29483(9)	0.38929(11)	0.23676(3)	63(1)
Br(2)	0.29393(9)	0.73639(10)	0.17876(3)	66(1)
C(1)	0.5113(7)	0.4408(10)	0.1516(3)	55(2)
C(2)	0.4584(8)	0.5162(10)	0.1092(3)	61(2)
C(3)	0.3795(8)	0.4006(10)	0.0835(3)	57(2)
C(4)	0.3842(8)	0.2540(9)	0.1084(3)	55(2)
C(5)	0.4649(7)	0.2784(10)	0.1507(2)	54(2)
C(6)	0.6129(8)	0.5144(13)	0.1876(3)	89(3)
C(7)	0.5008(11)	0.6746(11)	0.0920(4)	90(3)
C(8)	0.3231(11)	0.4176(13)	0.0344(3)	94(3)
C(9)	0.3352(10)	0.0949(10)	0.0900(3)	84(3)
C(10)	0.5103(10)	0.1504(11)	0.1837(3)	84(3)
C(11)	0.1247(7)	0.2539(10)	0.1475(3)	63(2)
C(12)	0.0384(7)	0.3770(11)	0.1642(3)	61(2)
C(13)	0.0351(8)	0.5262(12)	0.1409(3)	66(2)
C(14)	0.1166(7)	0.5351(12)	0.1017(3)	72(2)
O(1)	−0.0287(6)	0.3698(7)	0.2017(2)	76(2)
O(2)	−0.0336(6)	0.6425(8)	0.1601(3)	92(2)
C(15)	−0.0456(11)	0.2152(13)	0.2234(4)	101(3)
C(16)	−0.0628(11)	0.7902(14)	0.1333(5)	136(5)
S	0.7653(4)	0.2370(5)	0.0666(1)	118(1)
O(3)	0.7825(12)	0.1623(18)	0.1097(3)	200(6)
O(4)	0.6239(10)	0.2511(24)	0.0429(4)	256(9)
O(5)	0.8208(22)	0.3818(16)	0.0616(6)	290(11)
C(17)	0.8496(16)	0.1474(38)	0.0288(4)	220(13)
F(1)	0.8214(12)	0.1579(15)	−0.0138(3)	207(5)
F(2)	0.9747(12)	0.1122(23)	0.0464(5)	325(10)
F(3)	0.7925(19)	−0.0345(13)	0.0288(4)	259(8)

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij}\ a_i^* a_j^* (\mathbf{a}_i\mathbf{a}_j)$.

Scheme 1



1a R = H; $R_1 = R_2$ = H
1b R = H; R_1 = H, R_2 = Me
1c R = H; R_1 = Et, R_2 = H
2a R = Me; $R_1 = R_2$ = H
2b R = Me; R_1 = H, R_2 = Me
2c R = Me; $R_1 = R_2$ = Me

4a R = H; $R_1 = R_2$ = H
4b R = H; R_1 = H, R_2 = Me
4c R = H; R_1 = Et, R_2 = H
5a R = Me; $R_1 = R_2$ = H
5b R = Me; R_1 = H, R_2 = Me
5c R = Me; $R_1 = R_2$ = Me

amounts of Br_2 at −60 °C in CH_2Cl_2. The reactions involve addition of bromine on the face of the cisoid η^4-diene group opposite to the metal center and regioselectively at the terminal carbon atom bearing no substituent. Addition on η^4-diene complexes with an internal substituent (**1b**, **2b**,**c**) occurs such that the substituent ends up on the central allyl carbon atom. Under these reaction conditions, the addition is kinetically controlled resulting in the sole formation of *anti* η^3-allyl isomers (as drawn). At elevated temperatures, however, isomerization to the thermodynamically favored *syn* products takes place.[14] All complexes are stable to air in the solid state and also for extended periods in solution. **4a**−**c** and **5a**−**c** have been fully characterized by elemental analyses and ^{1}H NMR spectroscopy. Where solubility has permitted (**4a**,**b**, **5b**) $^{13}C\{^1H\}$ NMR spectra have also been recorded. The ^{1}H NMR spectra of **4a**−**c** and **5a**−**c** all show the expected singlet resonances for the C_5H_5 and C_5Me_5 rings appearing in the ranges 5.69−5.96 ppm and 1.74−1.80 ppm, respectively, while characteristic multiplet resonances assignable to the allyl ligands are observed in the expected ranges. The signals of the CH_2Br protons are observed in the range 4.0−3.5 ppm. The $^{13}C\{^1H\}$

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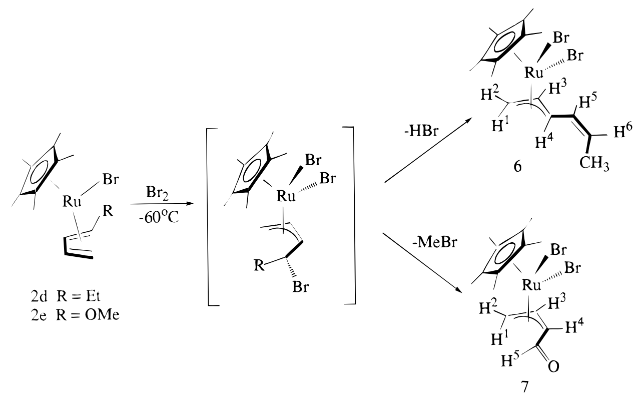
[14] Masuda, K.; Saitoh, M.; Aoki, K.; Itoh, K. *J. Organomet. Chem.* **1994**, *473*, 285.

Scheme 2



NMR spectra of **4a**,**b** and **5b** contain no surprising features with the resonance of the sp^3 carbon atom bearing the bromide substituent observed in the range of 32.6−36.8 ppm. Proof of the stereospecific *exo* addition was reached from X-ray crystallography as shown previously.[6]

Bromination of **2d**,**e** gave, on workup, complexes **6** and **7** in 75 and 94% yield (Scheme 2). In the course of this process HBr and MeBr, respectively, are liberated involving apparently the intermediacy of a bromo-substituted Ru(IV) η^3-allyl complex where bromine attack had taken place at the substituted terminal carbon atom of the η^4-diene ligand. Moreover, the elimination of HBr is accompanied by isomerization to the more stable *syn* product (as drawn in Scheme 2).

The rest of the ligand adopts *cis* stereochemistry. Complexes **6** and **7** have been characterized by ^{1}H and ^{13}C{^{1}H}NMR spectroscopy. In the ^{1}H NMR spectrum of **6**, a sharp singlet at 1.64 ppm is observed for the C_5Me_5 ring; the resonance for the central allyl proton appears as a double double doublet centered at 5.18 ppm ($^3J_{34}$ = 10.5 Hz, $^3J_{13}$ = 9.6 Hz, $^3J_{23}$ = 6.0 Hz). The proton coupling constant $^3J_{34}$ = 10.5 Hz suggests that the geometry around the C^3-C^4 bond has *syn* configuration. The stereochemistry of the olefin part of the ligand is apparent from the coupling constant $^3J_{56}$ = 11.2 Hz consistent with a *cis* arrangement. The ^{1}H NMR spectrum of **7** agrees with the postulated structure. The central allyl proton is found as a double double doublet centered at 5.87 ppm ($^3J_{13}$ = 10.6 Hz, $^3J_{23}$ = 6.8 Hz, $^3J_{34}$ = 6.6 Hz). However, the coupling constant of $^3J_{34}$ = 6.6 Hz unequivocally places the CHO substituent *anti* with respect to the allyl moiety.

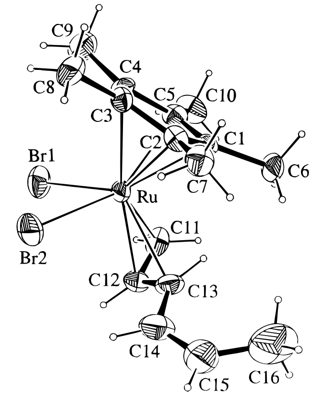
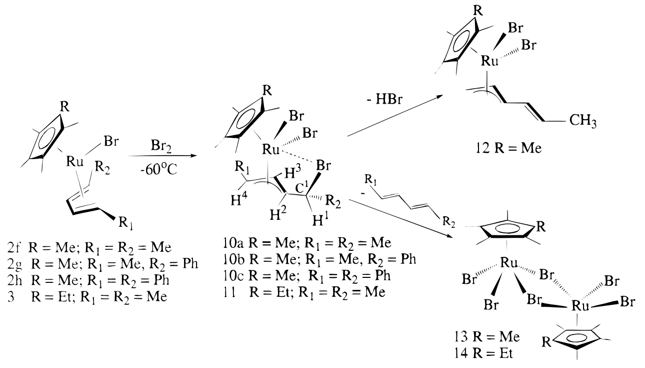


Figure 1. ORTEP drawing of Ru(η^5-C_5Me_5)(η^3-$CH_2CHCHCH{=}CHCH_3$)Br_2 (**6**). Selected bond lengths (Å) and angles (deg): Ru−Br(1) 2.555(1), Ru−Br(2) 2.550(1), Ru−C(1−5)$_{av}$ 2.241(8), Ru−C(11) 2.190(7), Ru−C(12) 2.135(8), Ru−C(13) 2.335(9), C(11)−C(12) 1.352(11), C(12)−C(13) 1.401(12), C(13)−C(14) 1.450(13), C(14)−C(15) 1.338(15); Br(1)−Ru−Br(2) 83.02(4), C(11)−C(12)−C(13) 117.0(8).

Scheme 3



The structure of **6** has been confirmed by X-ray crystallography as depicted in Figure 1. Positional parameters are given in Table 2 with important bond distances and angles reported in the caption. The olefin substitutent takes the *syn* position. The enyl function of the allyl ligand is bonded asymmetrically to the metal with the Ru−C bonds to the unsubstituted terminal and central allyl carbon atoms C(11) and C(12) (2.190(7) and 2.135(8) Å, respectively) being distinctly shorter than Ru−C bond to the third allyl carbon atom C(13) (2.335(9) Å). The Ru−Br(1) and Ru−Br(2) bond distances are nearly identical being 2.555(1) and 2.550(1) Å, respectively. The asymmetric bonding of the allyl moiety to the metal center is in good agreement with observations on the related μ-(1−3)-hexa-1,4-dien-3-yl complexes of Mo(η^3-$CH_2CHCHCH{=}CHCH_3$)$(CH_3CN)_2(CO)_2$Br and Fe(η^3-$CH_2CHCHCH{=}CHCH_3$)(η^5-C_5H_5)(CO) both with all-trans-type C_6 chains.[15,16]

Reactions of 5b with NEt$_3$ and Pyridine. Preliminary studies on the reactivity of bromo-substituted Ru(IV) η^3-allyl complexes show that the halide of the allyl moiety is readily replaced by other nucleophiles. To illustrate the procedure, complex **5b** has been subjected to the action of the bases pyridine and NEt_3. **5b** is cleanly converted to new complexes readily identified by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy as the cationic pyridinium- and triethylammonium-substituted Ru(IV) *anti* η^3-allyl complexes **8** and **9**, respectively. During substitution the sp^3 carbon atom configuration appears to be retained consistent with the occurrence of a S_N1 type of mechanism. A similar complex, the cationic pyridinium-substituted Ru(IV) η^3-cyclopentenoyl complex [Ru(η^5-C_5H_5)(η^3-$C_5H_4ONC_5H_5$)Br_2]Br has been reported previously.[4]

1,4-Disubstituted-1,3-Butadiene Complexes. Treatment of complexes **2f**−**h** and **3** with Br_2 leads to the formation of Ru(IV) η^3-allyl complexes **10a**−**c** and **11**, where, surprisingly, all adopt the *syn* configuration (Scheme 3). With the exception of **10a**, unfortunately, none of these complexes could be obtained in pure form. **10a** has been characterized by elemental analysis, and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Inability to obtain

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[15] Paz-Sandoval, M. A.; Saaredra, P. J.; Pomposo, G. D.; Joseph-Nathan, P.; Powell, P. *J. Organomet. Chem.* **1990**, *387*, 265.

[16] Lee, G.-H.; Peng, S.-M.; Lush, S.-F.; Liao, M.-Y.; Liu, R.-S. *Organometallics* **1987**, *6*, 2094.

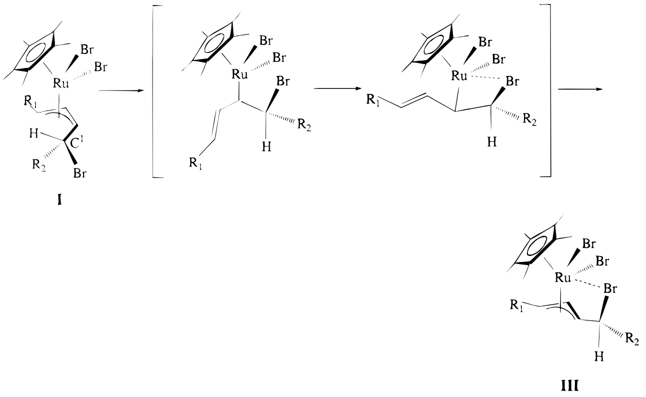
a pure sample of **10b**,**c** and **11** precluded suitable microanalyses, and characterization was only by ^{1}H NMR spectroscopy. Structural evidence will, thus, be discussed mainly with reference to **10a**. The assignments of the proton resonances were aided by detailed double resonance experiments.

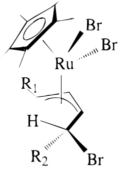
The ^{1}H NMR spectrum of **10a** resembles that for **3a**−**c** and **4a**−**c** with the major difference being a substantial downfield shift for the aliphatic proton H^1 resonating at 5.48 (m, 1H, $^3J_{12}$ = 10.1 Hz, ^3J = 6.7 Hz) (*cf.* the respective proton resonances of **3a**−**c** and **4a**−**c**, which appear in the range 3.5−4.0 ppm, and thus, the deshielding of H^1 cannot be explained merely by the −I effect of the bromine substituent). A sharp singlet at 1.65 ppm is observed for the C_5Me_5 ligand while the remaining allylic protons resonate at 5.07 (t, 1H, H^3, $^3J_{23}$ = 9.9Hz, $^3J_{34}$ = 9.6 Hz), 2.70 (t, 1H, H^2, $^3J_{12}$ = 10.1 Hz, $^3J_{23}$ = 9.9 Hz), and 2.68 ppm (m, 1H, H^4, $^3J_{34}$ = 9.6 Hz, ^3J = 6.1 Hz), respectively. The resonances of the methyl groups are observed as two doublets centered at 1.72 (d, 3H, ^3J = 6.5 Hz) and 1.71 ppm (d, 3H, ^3J = 6.1 Hz). The proton coupling constant of $^3J_{23}$ = 9.9 Hz unequivocally proves that the 1-bromoethyl moiety takes the *syn* configuration around the C^2−C^3 bond. The downfield shift of H^1 is even more pronounced for **10b**,**c**, where the proton resonances are observed at 6.89 and 6.95 ppm, respectively. Bromine attack in **10b** took place exclusively at the carbon atom adjacent to the phenyl substituent. The ^{13}C{^{1}H} NMR spectrum of **10a** exhibits the characteristic three-signal pattern of the enyl fragment appearing at 98.3, 82.6, and 57.1 ppm, while resonances of C_5Me_5 ring and the methyl substituents of the allyl ligand are found in the usual ranges. Surprisingly, however, the resonance of the carbon atom C^1 is drastically shifted downfield to 81.6 ppm (*cf.* **4a**,**b** and **5b** exhibit the resonance of C^1 between 32.6 and 36.8 ppm).

10a−**c** and **11** are unstable in solution releasing free diene (as monitored by ^{1}H NMR spectroscopy) and forming the dimeric complexes **13** and **14**, respectively. **13** and **14** are poorly soluble in all common solvents and are deposited as microcrystalline precipitates in high yield. The synthesis of **13** by reacting [Ru(η^5-C_5Me_5)Br_2]$_2$[11] with Br_2 (1 equiv) in CH_2Cl_2 has been reported previously[10] but has been formulated as polymeric [Ru(η^5-C_5Me_5)Br_3]$_n$. **14** can be prepared in analogous fashion with [Ru(η^5-C_5Me_4Et)Br_2]$_2$[17] as the precursor. While **10b**,**c** and **11** are converted to **13** and **14** within a matter of minutes, **10a** persists in solution for a few hours and eventually yields, in addition to **13** as the major decomposition product, complex **12** in about 20% yield as the result of HBr elimination. More conveniently, however, **12** can be obtained in 73% yield by treatment of **10a** with 1 equiv of Ag^+, introduced as the $CF_3SO_3^-$ salt, in CH_2Cl_2 at room temperature.

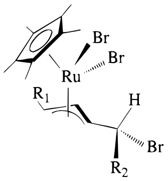
The reasons for depicting the intermediate products **10a**−**c** and **11** as done in Scheme 3 are as follows. The structure to be assumed should accommodate the NMR spectroscopic results and allow concurrent conversion to **13** and **14** as well as **12**. Neither the Ru(IV) *anti* η^3-allyl nor the Ru(IV) *syn* η^3-allyl formulations **I** and **II** conform to the strong deshielding of H^1 and C^1. Thus, for an adequate description of the bonding situation in **10a**−**c** and **11** a weak C^1−Br···Ru interaction is proposed leading to structure **III** where the allyl adopts a *syn* conformation.

Scheme 4

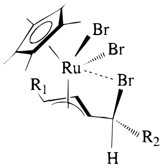




I



II



III

The formation of **III** may proceed via an *anti syn* isomerization of the initially formed complex **I** being presumably the kinetic product of the bromination of **2f**−**h** and **3**. The underlying mechanism may be the dissociation of the terminus bearing the bromoalkyl substituent to give an η^1-allyl intermediate followed by rotation around the C^2−C^3 and C^1−C^2 bonds. This transformation leads to a vacant coordination site on the metal which can be occupied by the bromide substituent of the sp^3 carbon atom leading to a weak 4e$^-$ three-center C^1−Br···Ru bond. Due to this interaction charge is removed from both C^1 and H^1 which consequently attain higher positive partial charges.**10a**−**c** and **11**, therefore, may be envisioned as “arrested” intermediates along the two observed decomposition pathways. The formation of the dimeric complexes **13** and **14**, however, appears to be favored. It is possible to speculate that **10a**−**c** and **11** are not 20e$^-$ intermediates, if the shift of electron density from the C^3−C^2···C^1 interaction to a C^1−Br···Ru interaction is concerted.

The dimeric nature of **14** has been established by X-ray crystallography (Figure 2). Positional parameters are given in Table 3 with important bond distances and angles reported in the caption. **14** consists of two symmetry-equivalent ruthenium cations in half-sandwich four-legged piano stool environments which are linked via a shared Br(1)−Br(1) edge. The overall architecture of this molecule is novel. With regard to the ruthenium coordination, however, **14** is similar to the monomeric anion [Ru(η^5-C_5Me_5)Br_4]$^-$ described recently.[6] Mean bond distances and bond angles in **14** compare well with those found in the monomeric complex.

Treatment of **2i** with Br_2 (1 equiv) in CH_2Cl_2 at −60 °C affords, on workup, a mixture of complex salt **15** together with the known dimeric Ru(III) complex [Ru(η^5-C_5Me_5)Br_2]$_2$ (Scheme 5).[17] **15** contains the cationic

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(17) Koelle, U.; Kossakowski, J.; Klaff, N.; Wesemann, L.; Englert, U.; Herberich, G. E. *Angew. Chem.* **1991**, *103*, 732.

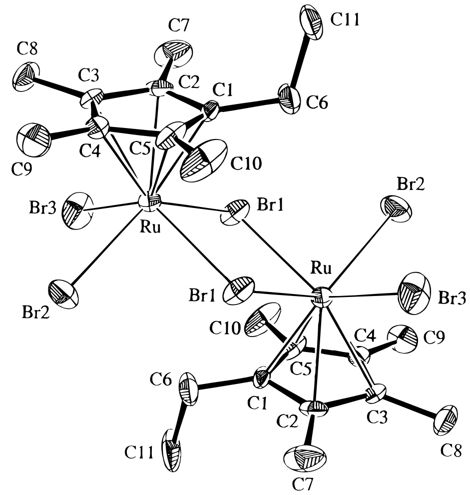
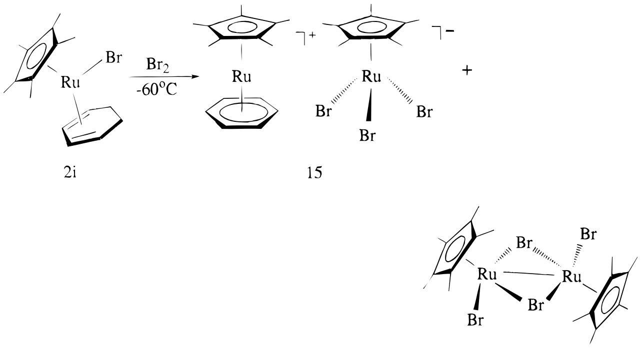


Figure 2. ORTEP drawing of $[Ru(\eta^5\text{-}C_5Me_4Et)Br_3]_2$ (**14**). Selected bond lengths (Å) and angles (deg): Ru−Br(1) 2.547(1), Ru−Br(2) 2.524(1), Ru−Br(3) 2.533(1), Ru−C(1−5)$_{av}$ 2.243(8); Br(1)−Ru−Br(1′) 75.88(4), Br(1)−Ru−Br(2) 81.03(4), Br(2)−Ru−Br(3) 81.33(5), Br(1)−Ru−Br(3′) 79.76(4), Br(1)−Ru−Br(3) 129.81(4), Br(2)−Ru−Br(1′) 128.93(4).

Scheme 5



sandwich $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^+$ [18] and the novel anionic Ru(III) complex $[Ru(\eta^5\text{-}C_5Me_5)Br_3]^-$ as the counterion.

This latter ion could not be characterized by NMR spectroscopy because of the paramagnetic nature of this 17e$^-$ molecule. The proton resonances of the diamagnetic cationic part of **15**, slightly broadened and somewhat downfield shifted, appear as singlets at 7.43 (s, 6H) and 2.40 ppm (s, 15H) (*cf.* the ^{1}H NMR spectrum of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]PF_6$[18] exhibits two sharp singlets at 6.18 and 2.20 ppm). The second product was identified as $[Ru(\eta^5\text{-}C_5Me_5)Br_2]_2$ by ^{1}H NMR spectroscopy and X-ray crystallography.[17,19] The dimer exhibits a singlet resonance at 1.89 ppm and is in line with literature-reported values.[17] The formation of **15** along with $[Ru(\eta^5\text{-}C_5Me_5)Br_2]_2$ in the same reaction may be due to an equilibrium $[Ru(\eta^5\text{-}C_5Me_5)Br_2]_2 + 2Br^- \leftrightarrow 2[Ru(\eta^5\text{-}C_5Me_5)Br_3]^-$ shifted to the right in the presence of the large cation $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^+$.

A structural view of **15**, as determined by X-ray diffraction, is depicted in Figure 3. Positional parameters are given in Table 4 with important bond distances and angles given in the caption. **15** consists of the cationic sandwich complex $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)]^+$ and the anionic half-sandwich complex $[Ru(\eta^5\text{-}C_5Me_5)Br_3]^-$ both with crystallographic mirror symmetry. The structure of the tribromo complex corresponds well to a trigonal pyramid with C_5Me_5 at the apex and the three bromide atoms at the base. The Ru−Br distances are in the expected range (Ru(2)−Br(1) = 2.535(1) Å, Ru(2)−Br(2) = 2.526(1) Å). These values are comparable to the Ru−Br(terminal) distances in the Ru(III) complex $[Ru(\eta^5\text{-}C_5Me_5)Br_2]_2$ being 2.543(2) Å (*cf.* the bond distance of the Ru−Br(bridging) bond is 2.479(2) Å).[17,19]

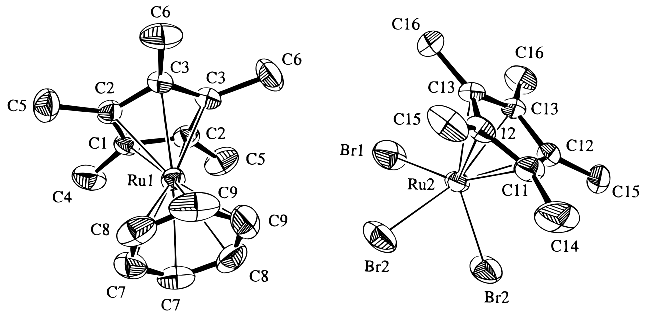
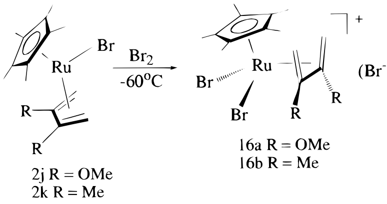


Figure 3. ORTEP drawing of $[Ru(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6H_6)][Ru(\eta^5\text{-}C_5Me_5)Br_3]$ (**15**). Selected bond lengths (Å) and angles (deg): Ru(1)−C(1−3)$_{av}$ = 2.174(6), Ru(1)−C(7−9)$_{av}$ = 2.192(6), Ru(2)−Br(1) 2.535(1), Ru(2)−Br(2) 2.526(1), Ru(2)−C(11−13)$_{av}$ 2.189(6); Br(1)−Ru(2)−Br(2) 92.27(3), Br(2)−Ru(2)−Br(2′) 91.71(4).

Scheme 6



2,3-Disubstituted-1,3-Butadiene Complexes. Reaction of Br_2 with **2j**,**k** does not lead to η^3-allyl compounds but instead gives the novel Ru(IV) η^4-diene complexes **16a**,**b** in 98 and 93% isolated yield, respectively (Scheme 6). This formulation is based on elemental analysis, ^{1}H NMR spectroscopic data, and an X-ray structure determination of **16a**. By contrast, **2l** gave only a mixture of intractable materials.

The $^{13}C\{^1H\}$ NMR spectrum was not available due to both the poor solubility and instability of **16a**,**b** in solution. The ^{1}H NMR spectra of **16a**,**b** in CD_3CN display the characteristic resonances of the diene ligand. The *syn* and *anti* protons of **16a** give rise to two doublets centered at 3.92 (2H) and 2.61 ppm (2H), respectively. The geminal coupling constant of the CH_2 protons is 6.1 Hz, respectively. This is indicative of an enhanced sp^3 character of the terminal carbon atoms and points to a metallacyclopentene resonance structure rather than that of a classical diene otherwise typical for late transition-metal η^4-diene complexes.[9] [20] The ^{1}H NMR spectrum of **16b** is similar to that of **16a** and is not discussed here.[6] For comparison, the geminal coupling constants for terminal CH_2 of $Zr(\eta^5\text{-}C_5H_5)_2(\eta^4\text{-}CH_2CMeCMeCH_2)$ and $Ta(\eta^5\text{-}C_5Me_5)_2(\eta^4\text{-}CH_2CMeCMeCH_2)Cl_2$ are equal 10.0 and 7.2 Hz, respectively.[20b,e] As noted previously,[6] the solution ^{1}H NMR spectra of **16a**,**b** are

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(18) Chaudret, B.; Jalon, F. A. *J. Chem. Soc., Chem. Commun.* **1988**, 711.

(19) A structure determination of $(Ru(\eta^5\text{-}C_5Me_5)\,Br_2)_2$ carried out by us on crystals of the byproduct according to Scheme 4 gave the same structure as reported in ref 17, except for a larger discrepancy in unit cell dimensions for which we found space group $P2_1/c$, a = 8.412(3) Å, b = 15.666(5) Å, c = 28.148(6) Å, β = 92.19(1)°, and V = 3707(2) Å^3. Our values for $a-c$ are large by about 0.9% than those in ref 17.

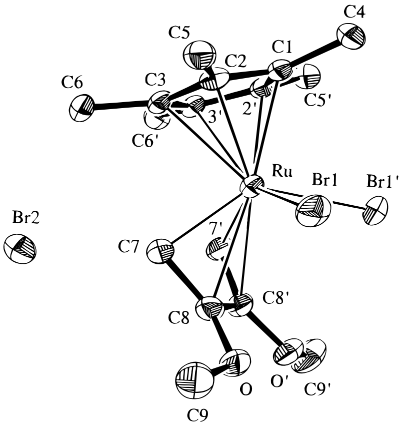

Figure 4. ORTEP drawing of [Ru(η^5-C_5Me_5)(η^4-CH_2-COMeCOMeCH$_2$)Br$_2$]Br·CH$_2$Cl$_2$ (**16a**·CH$_2$Cl$_2$). Selected bond lengths (Å) and angles (deg): Ru−Br(1) 2.527(1), Ru−C(1−5)$_{av}$ 2.259(7), Ru−C(7) 2.182(6), Ru−C(8) 2.408(6), C(7)−C(8) 1.417(8), C(8)−C(8′) 1.406(13), C(8)-O 1.332(7), O−C(9) 1.439(8); Br(1)−Ru−Br(1′) 82.01(4).

solvent dependent tentatively interpreted as an ion-pairing phenomenon. While in low dielectric solvents, such as CDCl$_3$, ion-pairing between the cationic part of **16a** and the counterion is favored, in the moderate dielectric solvents CD$_3$CN and C$_2$D$_5$OD the complexes **16a**,**b** are largely dissociated. Most solvent sensitive are the resonances of the *anti* protons. For example, the resonances of the *anti* protons of **16a** appear as doublets centered at 3.87 (2H, $^2J = 6.1$ Hz), 2.61 (2H, $^2J = 6.1$ Hz), and 2.66 ppm (2H, $^2J = 5.2$ Hz) in CDCl$_3$, CD$_3$CN, and C$_2$D$_5$OD, respectively, while the resonances of the remaining protons are hardly affected. The solid state structure of **16a**·CH$_2$Cl$_2$, which will be discussed in a following paragraph, reveals no significant direct interaction between the metal center and the counterion. The distance between ruthenium and the free Br$^-$ anion is 5.139 Å.

The bromide counterion is readily replaced by CF$_3$SO$_3^-$ upon addition of AgCF$_3$SO$_3$ (1 equiv) in CH$_2$Cl$_2$ giving the stable cationic complexes **17a**,**b** in 95 and 74% isolated yield. Characterization of **17a**,**b** was by elemental analysis, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, and an X-ray diffraction study. The structure of **17b** has been reported earlier.[6]

The ^{1}H NMR spectra of **17a**,**b** closely resemble those of **16a**,**b** which, by contrast, are not very sensitive to solvent. For instance, the resonances of the *anti* protons of **17a** appear as doublets centered at 2.71 (2H, $^2J =$ 5.9 Hz), 2.44 (2H, $^2J = 6.0$ Hz), 2.05 (2H, $^2J = 6.1$ Hz), and 2.26 ppm (2H, $^2J = 6.1$ Hz) in CDCl$_3$, CD$_2$Cl$_2$, CD$_3$CN, and C$_2$D$_5$OD, respectively. This is not unexpected since CF$_3$SO$_3^-$ is only a weakly coordinating ligand. As expected, in the solid state structure of **17a** (Figure 5), which will be discussed in a following paragraph, no direct interaction between the metal center and the CF$_3$SO$_3^-$ counterion is observed. The shortest distances are 4.971 Å to O(5) and 4.934 Å to F(2). The ^{13}C{^{1}H} NMR spectrum of **17a** shows singlets at 153.5 (internal diene C atoms), 114.9 (*C*$_5$Me$_5$), 62.6 (OMe), 51.3 (terminal diene C atoms), and 11.7 ppm (C$_5$*Me*$_5$), respectively. The ^{13}C{^{1}H} NMR spectrum of **17b** is very similar to that of **17a** and is not discussed here. The marked downfield chemical shifts are indicative of the high oxidation state of the ruthenium center.

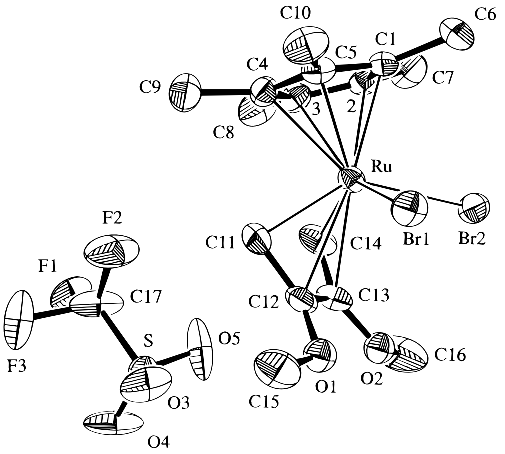

Figure 5. ORTEP drawing of [Ru(η^5-C_5Me_5)(η^4-CH_2-COMeCOMeCH$_2$)Br$_2$]CF$_3$SO$_3$ (**17a**). Selected bond lengths (Å) and angles (deg): Ru−Br(1) 2.521(1), Ru−Br(2) 2.533(1), Ru−C(1−3)$_{av}$ 2.271(7), Ru−C(11) 2.186(7), Ru−C(12) 2.433(7), Ru−C(13) 2.424(8), Ru−C(14) 2.175(7), C(11)−C(12) 1.424(11), C(12)−C(13) 1.416(12), C(13)−C(14) 1.431(11), C(12)-O(1) 1.308(9), C(13)-O(2) 1.318(10), O(1)−C(15) 1.448(11), O(2)−C(16) 1.473(12); Br(1)−Ru−Br(2) 82.95(4).

The structures of **16a** (in the form of **16a**·CH$_2$Cl$_2$) and **17a** have been confirmed by X-ray crystallography (see Figures 4 and 5). Positional parameters are given in Tables 5 and 6 with important bond distances and angles given in the captions. The overall geometric features of the two 2,3-dimethoxy-1,3-butadiene complexes are very similar. Transition-metal s-cis η^4-diene complexes are generally described as resonance hybrids of the limiting forms **a** and **b**. While the bonding of dienes to early transition metals is normally more accurately represented by the σ^2,π-metallacylopentene structure **a**, the vast majority of complexes containing middle and late transition metals adopt the η^4-s-cis-1,3-diene structure **b**. Noteworthily, metallacyclopentene complexes of late transition metals have been postulated as intermediates; e.g., the interconversion of the diene ligand in Co(η^5-C$_5$H$_5$)(η^4-diene) complexes can be explained only by an “envelope-flip” process involving a metallacyclopentene intermediate.[21] Complexes **16** and

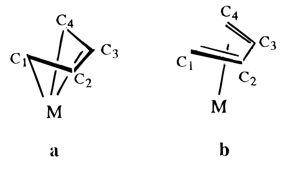

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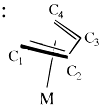
Table 7. Comparison of Bond Distances (Å) in η^4-Diene Complexes

compd	$M-C_{1,4}$	$M-C_{2,3}$	$C_{1,3}-C_{2,4}$	C_2-C_3	ref
$Ti(\eta^5\text{-}C_5Me_5)(B)Cl_2$[a]	2.183(10)	2.284(9)	1.417(14)	1.400(13)	20a
$Zr(\eta^5\text{-}C_5H_5)_2(DB)$[b]	2.300(3)	2.597(3)	1.451(4)	1.398(4)	20b
$Hf(\eta^5\text{-}C_5H_5)_2(DB)$	2.267(5)	2.641(5)	1.472(5)	1.378(8)	20b
$Hf(\eta^5\text{-}C_5Me_5)(DB)(py)Cl_2$	2.276(10)	2.480(10)	1.503(14)	1.384(15)	20c
$Hf(PMe_3)_2(B)Cl_2$	2.303(3)	2.478(3)	1.463(4)	1.401(3)	20d
$Ta(\eta^5\text{-}C_5H_5)(B)Cl_2$	2.257(12)	2.417(12)	1.455(16)	1.375(16)	20e
$Mo(\eta^5\text{-}C_5H_5)(NO)(B)$	2.220(3)	2.338(2)	1.410(4)	1.414(6)	20f
$Mo(\eta^5\text{-}C_5H_5)(B)Cl_2$	2.233(4)	2.319(4)	1.409(6)	1.364(7)	20g
$[Ru(\eta^5\text{-}C_5Me_5)(DOB)Br_2]^+$ (**16a**)[c]	2.182(6)	2.408(6)	1.417(8)	1.406(13)	this work
$[Ru(\eta^5\text{-}C_5Me_5)(DOB)Br_2]^+$ (**17a**)	2.180(7)	2.428(8)	1.427(11)	1.416(12)	this work
$[Ru(\eta^5\text{-}C_5Me_5)(DB)Br_2]^+$ (**17b**)	2.190(7)	2.352(7)	1.396(9)	1.431(15)	6
$[Ru(\eta^5\text{-}C_5Me_5)(MB)(CH_3CN)]^+$ [d]	2.222(4)	2.204(4)	1.393(5)	1.433(5)	20h
$Ru(\eta^5\text{-}C_5Me_5)(B)I$	2.222(3)	2.155(3)	1.404(5)	1.430(5)	9
$Fe(C_8H_{16}N_2)(CO)(DB)$[e]	2.116(2)	2.062(2)	1.409(3)	1.423(3)	20i
$Rh(\eta^5\text{-}C_5H_4Cl)(DOB)$	2.125(5)	2.123(4)	1.430(6)	1.433(5)	20j
$Ru(\eta^6\text{-}C_6Me_6)(PPhMe_2)(C_4H_8)$[f]	2.152(5)	–	1.518(7)	1.513(8)	22

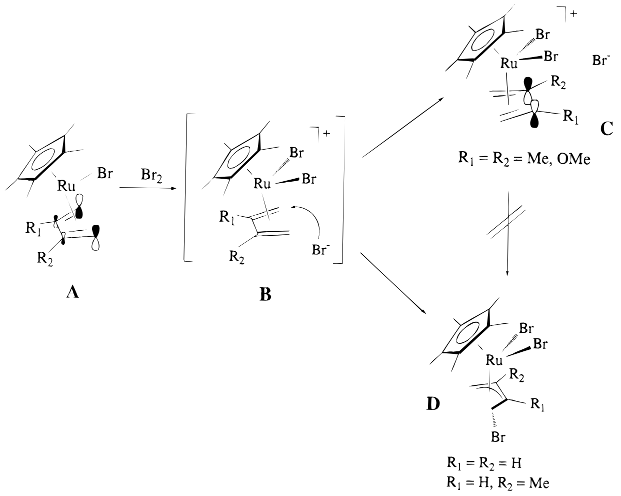
[a] *B* = 1,3-butadiene. [b] *DB* = 2,3-dimethyl-1,3-butadiene. [c] *DOB* = 2,3-dimethoxy-1,3-butadiene. [d] *MB* = 2-methyl-1,3-butadiene. [e] $C_8H_{16}N_2$ = glyoxal bis(isopropylimine). [f] Ruthenacyclopentane:



17 appear to be the first examples of late transition-metal complexes which approach the σ^2,π structural limit **a**. This is evident from the highly asymmetric bonding of the diene, with metal–carbon bonds to the diene termini being shorter by up to 0.248 Å (**17a**) than those to the internal carbon atoms (*cf.* in $Zr(\eta^5\text{-}C_5H_5)_2(\eta^4\text{-}CH_2CMeCMeCH_2)$ the respective difference in metal–carbon bond distances is 0.297 Å[20b]). The ruthenium–carbon bonds to the terminal carbon atoms, on average, are about 2.181 Å while the one to the internal carbon atoms are 2.416 Å. For comparison, in the ruthenacyclopentane complex $Ru(\eta^6\text{-}C_6Me_6)(PPhMe_2)(C_4H_8)$ the ruthenium–carbon σ bond distance is 2.152(5) Å.[21] In the extreme σ^2,π case an inversion of the carbon–carbon distance sequence from that in the free diene is predicted; i.e., coordinated dienes are expected to exhibit a long–short–long rather than a short–long–short pattern of carbon–carbon bond distances. The structures of **16a** and **17a** reveal within the experimental error no significant differences in carbon–carbon distances of the diene moieties (*cf.* in **17b**[6] the internal bond of the diene ligand is only slightly longer (C(8)–C(8′) = 1.431(15) Å) than the terminal bonds (C(7)–C(8) = 1.396(9) Å) but the standard deviations are also comparatively high). Thus, on the basis of both NMR spectroscopy and X-ray crystallography the geometry and bonding situation in **16** and **17** is best described as an intermediate case between the two extremes **a** and **b**. A summary of structural data of some representative η^4-diene complexes is given in Table 7.

Mechanistic Considerations. Scheme 7 presents a mechanistic proposal of the formation of bromo-substituted Ru(IV) η^3-allyl and Ru(IV) η^4-diene complexes. As the first step, the oxidative addition of Br_2 to the neutral Ru(II) η^4-diene complex **A** leads to the cationic Ru(IV) η^4-diene intermediate **B**. The diene moiety of the precursor **A** is *exo* oriented with respect to the bromide ligand (as shown by X-ray crystallography[4,6,9,20h]), and although intermediate **B** cannot be isolated, it is reasonable to assume that **B** also adopts the *exo* configuration. Whether its instability is partly due to unfavorable metal–diene orbital interactions remains unclear, but it does seem likely that the driving force of minimizing repulsions between the substituents of the diene ligand and the C_5Me_5 moiety plays an important role. It has been shown recently that the structurally related Ru(II) η^4-2,3-diphenyl-1,3-butadiene complex $Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}CH_2CPhCPhCH_2)Cl$ is unstable due to repulsive interactions between the phenyl groups of the diene ligand and the C_5Me_5 ring.[9] The lifetime of **B** should, thus, be shortest in case of 2,3-disubstituted-1,3-butadienes so that Br^- cannot attack before rotation of the diene ligand gives the sterically more favorable *endo* isomer **C**. In case of parent 1,3-butadiene and monosubstituted- and 1,2-disubstituted-1,3-butadienes, the lifetime of **B** appears to be high enough so that Br^- can attack to give Ru(IV) *anti* η^3-allyl complexes **D**. This is in accordance with the fact that cationic η^4-diene complexes are typically the most reactive of substrates toward nucleophilic attack undergoing preferential attack at the terminal position.[23] The activation is, at least partly, a consequence of the

Scheme 7



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strong electron-withdrawing effect of the Ru(IV) metal center which dominates at the terminal carbon atoms (*cf*. Davies−Green−Mingos rules).[23] The diene ligand in **C**, however, is not reactive toward nucleophilic attack, and it is likely that species does not lie on the pathway to **D**; i.e., **C** is no intermediate of **D**. Conversion of **C** to **D** has not been observed even in the presence of excess Br^-. In fact, we have shown previously[3] that **16b** reacts with either Br^- or I^- by loss of the diene ligand involving nucleophilic attack at the metal center. Preliminary density functional calculations[24] show that in **C** the frontier orbitals relevant for nucleophilic attack are the p_z orbitals of the internal carbon atoms contributing more strongly to the LUMO (lowest unoccupied molecular orbital) rather than the terminal carbon orbitals as one would expect (see LUMO of **A**).[23] This result further supports the observation that the diene ligand in **C** is not particularly active toward nucleophilic attack. Density functional calculations on a variety of Ru(II) and Ru(IV) diene complexes are in progress and will be the subject of a forthcoming paper.

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Supporting Information Available: Listings of hydrogen atomic coordinates and *U* values, anisotropic temperature factors, complete bond lengths and angles, and least-squares planes for complexes **6**, **14**, **15**, **16a**·CH_2Cl_2, and **17a** (33 pages). Ordering information is given on any current masthead page.

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