# A Triple-Decker Complex with a Central Metallabenzene**

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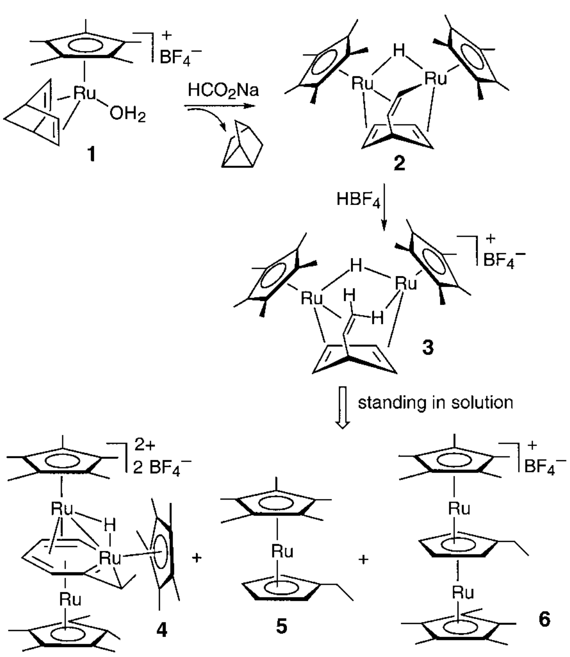
It was established in the 1980s that benzene can act as a bridging ligand to form triple-decker complexes.[1, 2] Recent studies on the chemistry of metallabenzenes revealed that transition metal containing metallabenzenes can display chemical properties similar to those of benzene.[3] For example, they can undergo electrophilic substitution reactions[4] and can form $\eta^6$-metallabenzene complexes.[5] These results imply that metallabenzenes may also function as bridging ligands in triple- or poly-decker complexes. However, such complexes have not yet been reported, although the possibility of obtaining triple-decker complexes with a central metallabenzene was suggested in 1994.[5e] Here we describe the synthesis and characterization of the first triple-decker complex with a central metallabenzene.

Treatment of [Cp*Ru(H$_2$O)(nbd)]BF$_4$ (**1**; Cp* = $\eta^5$-C$_5$Me$_5$, nbd = norbornadiene)[6] with HCO$_2$Na in dry THF produced the bimetallic complex **2** along with nortricyclene and a small amount of the known complex [Cp*RuH(nbd)] (Scheme 1).[7] Analytically pure samples of **2** were obtained by column chromatography. The structure of **2** was deduced on the basis of its mass spectrum and $^1$H as well as $^{13}$C{$^1$H} NMR spectroscopic data. The ion peak at $m/z = 566$ corresponding to the composition $\{Cp^*_2Ru_2(C_7H_8)\}$ suggests that **2** is a bimetallic complex. The $^1$H and $^{13}$C{$^1$H} NMR data indicate that **2** is a fluxional hydride complex. The room-temperature $^1$H NMR spectrum in C$_6$D$_6$ displayed a hydride signal at $\delta = -16.57$ and a broad Cp* signal at $\delta = 1.88$. However, the $^1$H NMR spectrum at 250 K in CD$_2$Cl$_2$ showed a sharp hydride signal at $\delta = -16.85$ and two Cp* signals at $\delta = 1.77$ and 1.85, that is, the two Ru atoms in **2** are inequivalent at this temperature. The presence of the bridging C$_7$H$_7$ ligand is supported by its $^{13}$C and $^1$H NMR spectroscopic data. In particular, the $^{13}$C{$^1$H} NMR spectrum at 250 K in CD$_2$Cl$_2$ showed the signals of the $\alpha$- and $\beta$-CH groups of the $\mu$-$\sigma$,$\pi$-vinylic group at $\delta = 156.31$ and 60.84, respectively; that of the bridgehead CH group at $\delta = 47.02$; and those of the olefinic CH groups of the cyclopentadiene at $\delta = 26.24$, 49.86, 58.86, and 66.37. In the $^1$H NMR spectrum, the signals of the $\alpha$- and $\beta$-CH groups of the $\mu$-$\sigma$,$\pi$-vinylic group were observed at $\delta = 5.94$ and 3.91, that of the bridgehead proton at $\delta = 3.47$, and those of the olefinic protons of the cyclopentadiene at $\delta = 1.82$ (1 H), 2.59 (1 H), and 2.65 (2 H). The $^{13}$C shift of $\delta = 156.31$ and the $^1$H shift of $\delta = 5.94$ are comparable to those of the $\alpha$-CH groups of other $\mu$-$\sigma$,$\pi$-vinylic ligands.[8] Although the detailed mechanism is not yet clear, the bridging ligand in **2** is apparently formed by C–C bond cleavage of a norbornadiene ligand. Cleavage of C–C bonds of norbornadiene by late transition metal complexes to give fulvene or vinylcyclopentadiene species has been reported.[6, 7, 9]



Scheme 1. Preparation of the triple-decker complex **4**.

Protonation of **2** with HBF$_4$ produced the bimetallic complex **3**, which was previously obtained by protonation of [Cp*RuH(nbd)] with HBF$_4$.[7] In attempts to grow crystals of **3**, we found that the complex is unstable and was converted to other species in solution. When a solution of **3** in Et$_2$O/CH$_2$Cl$_2$ was stored at room temperature for a week, a brown crystalline solid and a brown solution were produced. The solid was identified as the triple-decker complex **4**. From the solution, the ruthenocene **5** and the ethylcyclopentadienyl-bridged triple-decker complex **6** were isolated.

Complexes **5** and **6** were readily characterized by their MS and NMR spectroscopic data. For example, the CI-MS of **5** showed the molecular ion peak at $m/z = 330$ corresponding to the composition of $\{Cp^*Ru(C_7H_9)\}$. The $^1$H and $^{13}$C{$^1$H} NMR spectra of **5** displayed the characteristic signals of $\eta^5$-C$_5$Me$_5$ and $\eta^5$-C$_5$H$_4$Et. The $^1$H NMR spectrum of **6** showed the Cp* signal at $\delta = 1.93$, and the $^{13}$C{$^1$H} NMR spectrum of **6** showed Cp* signals at $\delta = 10.46$ and 86.49. The presence of bridging C$_5$H$_4$Et in **6** is supported by the $^1$H NMR spectrum (in CD$_2$Cl$_2$), which showed ethyl signals at $\delta = 1.23$ (CH$_3$) and $\delta = 2.63$ (CH$_2$) as well as C$_5$H$_4$ signals at $\delta = 4.12$ and 4.27. Consistent with the structure, the $^{13}$C{$^1$H} NMR spectrum (in CD$_2$Cl$_2$) showed ethyl signals at $\delta = 10.94$ (CH$_3$) and 19.84 (CH$_2$) as well as C$_5$H$_4$ signals at $\delta = 55.17$ (CH), 56.29 (CH), and 76.20 (C). The bridging C$_5$H$_4$Et ligand in **6** is presumably formed by insertion of the vinylcyclopentadiene ligand into the Ru–H bond of **3** followed by hydrogen shift. The first

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cyclopentadienyl-bridged triple-decker complex was discovered by Werner et al. about 30 years ago.[10] Closely related ruthenium triple-decker complexes such as $[(Cp^*Ru)_2(\mu\text{-}C_5R_5)]^+$ (R = H, Me) are known and were prepared by different routes.[11]

The most interesting product is the triple-decker complex **4**, which contains a bridging metallabenzene. Its structure was established by X-ray diffraction (Figure 1).[12] The complex contains a central six-membered metallacycle, which is $\eta^6$-bonded to Ru3 with a Ru3–Ru1 distance of 2.9386(9) Å and an average Ru3–C distance of 2.223 Å. Except for C1, all the atoms of the central metallacycle are also bonded to Ru2, with an Ru2–Ru1 distance of 2.9065(9) Å and an average Ru2–C distance of 2.294 Å. The distance between Ru2 and C1 (2.699(10) Å) is too long for a normal covalent Ru–C bond. A hydrogen atom bridges Ru1 and Ru2. The Ru1–Ru2 and Ru3–Ru1 bond lengths are close to those of reported Ru–Ru single bonds.[5a–d] The atoms Ru1 and C2–C5 are coplanar, with a maximum deviation from the least-squares plane of −0.0391 Å for C3. The atom C1 lies 0.3872 Å out of the plane and is tilted toward Ru3. The Ru1–C1 and Ru1–C5 bond lengths are essentially equal and are within the range of those reported for $\eta^6$-ruthenabenzenes.[5a–d] As expected, the Ru1–C1 and Ru1–C5 bonds are shorter than the Ru1–C6 bond. There is no short–long bond alternation in the C1–C5 carbon chain. This structural feature indicates that the middle metallacycle has a delocalized electronic structure.

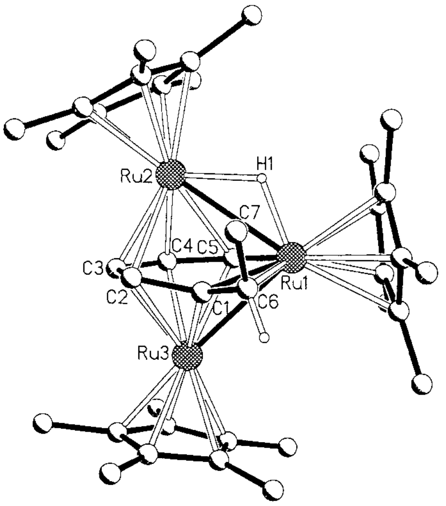

Figure 1. Molecular structure of **4**. Selected bond lengths [Å] and angles [°]: Ru1-Ru2 2.9065(9), Ru1-Ru3 2.9386(9), Ru1-C1 2.043(8), Ru1-C5 2.055(7), C1-C2 1.410(10), C2-C3 1.463(11), C3-C4 1.400(10), C4-C5 1.358(9), C1-C6 1.392(11), C6-C7 1.467(12), Ru1-C6 2.219(9), Ru1-H1 1.70(6), Ru2-H1 2.00(6), Ru2-C1 2.699(10), Ru2-C2 2.339(7), Ru2-C3 2.195(7), Ru2-C4 2.248(7), Ru2-C5 2.395(7), Ru3-C1 2.126(9), Ru3-C2 2.274(7), Ru3-C3 2.215(7), Ru3-C4 2.200(8), Ru3-C5 2.299(8); C1-Ru1-C5 82.2(3), C2-C1-Ru1 130.1(7), C3-C2-C1 120.4(7), C4-C3-C2 121.5(6), C5-C4-C3 125.0(7), C4-C5-Ru1 132.9(6), C1-Ru1-C6 37.8(3), C5-Ru1-C6 120.0(3), C2-C1-C6 139.6(8), C6-C1-Ru1 78.0(5), C1-C6-C7 121.5(9), C1-C6-Ru1 64.2(5), C7-C6-Ru1 121.0(7), Ru2-Ru1-Ru3 75.91(2).

Consistent with the solid-state structure, the $^{13}C\{^1H\}$ NMR spectrum showed three sets of Cp* signals. The $^{13}C$ signals of the bridging ligand were observed at $\delta = 24.36$ (C7), 37.42 (C2), 41.52 (C6), 54.02 (C4), 64.83 (C3), 146.89 (C5), and 168.32 (C1). In the $^1H$ NMR spectrum (in $CD_2Cl_2$), the hydride peak was observed at $\delta = -13.51$; the three Cp* signals (1:1:1 intensity) were located at $\delta = 1.91$, 1.93, and 2.39; and the signals of the bridging ligand appeared at $\delta = 1.40$ ($CH_3$), 4.06 (C6H), 5.26 (C2H), 5.46 (C4H), 7.13 (C3H), and 8.20 (C5H).

In the 30-valence-electron triple-decker complex $[\{(\eta^6\text{-mesitylene})Cr\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-mesitylene})]$,[1b] the central arene molecule is $\eta^6$-bonded to both metal centers. The central metallabenzene in **4** is bonded $\eta^5$ to Ru2 and $\eta^6$ to Ru3. Such a structural feature is understandable, because the hydrido ligand bridging Ru1 and Ru2 allows Ru2 to attain 18 valence electrons without forming a bond to C1. "Slipped" triple-decker complexes were previously reported for electron-rich systems, for example, $[(Cp^*Co)_2\{\mu\text{-}(\eta^4{:}\eta^4\text{-cumene})\}]$;[13a] $[\{(\eta^5\text{-}C_5H_2tBu_3)Co\}_2(\mu\text{-}\eta^4{:}\eta^4\text{-toluene})]$;[2b] $[(CpRu)_2(\mu\text{-}\eta^5{:}\eta^5\text{-cot})]$,[13b] $[(CpRh)_2(\mu\text{-}\eta^5{:}\eta^5\text{-cot})](PF_6)_2$,[13c] and $[(\eta^8\text{-cot})Ti)_2\text{-}\{\mu\text{-}\eta^5{:}\eta^5\text{-cot})\}]$ (cot = 1,3,5,7-cyclooctatetraene).[13d]

Complex **4** is the first well-characterized triple-decker complex with a bridging metallabenzene ligand. Triple-decker complexes with bridging benzene,[1, 2] a heterobenzene containing a main group element (e.g., borabenzenes),[14] and inorganic benzene analogues (e.g., $P_6$, metallaboranes)[15] have all been made. Conversion of **3** to **4** is also interesting, as it involves C–C bond cleavage of vinylcyclopentadiene (formed from norbornadiene) under mild conditions. Metal-promoted C–C bond activation is of much current interest.[16] Cleavage of a C–C bond of cyclopentadiene was observed in the reaction of cyclopentadiene with the trinuclear ruthenium cluster $[(Cp^*Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$.[17] While this work was in progress, Suzuki et al. reported that reaction of $[(Cp^*Ru)_2(\mu\text{-}H)_4]$ with norbornadiene at 60 °C gives $[(Cp^*Ru)_2(\mu\text{-}\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_4CH_2CH_3)(H)]$.[5d]

In summary, we have prepared the first triple-decker complex with a bridging metallabenzene by C–C bond activation of norbornadiene under mild conditions. We are currently studying the mechanism of these interesting transformations and preparing other triple-decker complexes with bridging metallabenzenes.

## *Experimental Section*

**2**: A mixture of **1** (1.0 g, 2.3 mmol) and $HCO_2Na$ (1.0 g, 15 mmol) in dry THF (50 mL) was stirred for 3 h. The solvent of the reaction mixture was evaporated to dryness. The residue was extracted with hexane (50 mL). The extract was concentrated to dryness, and the residue was purified by column chromatography (neutral alumina, eluent: benzene) to give **2** as a brown-yellow solid (0.48 g, 74%). The formation of nortricyclene in the reaction was confirmed by $^1H$ and $^{13}C\{^1H\}$ NMR experiments. $^1H$ NMR (300.13 MHz, $CD_2Cl_2$, 250 K): $\delta = -16.85$ (s, 1H, Ru($\mu$-H)Ru), 1.77 (s, 15H, Cp*), 1.85 (s, 15H, Cp*), 1.82 (m, 1H, =CH), 2.59 (m, 1H, =CH), 2.65 (m, 2H, =CH), 3.47 (dt, $J$(H,H) = 3.7, 4.6 Hz, 1H, CH), 3.91 (dd, $J$(H,H) = 3.7, 5.5 Hz, 1H, =CH), 5.94 (d, $J$(H,H) = 5.5 Hz, 1H, =CHRu); $^1H$ NMR (300.13 MHz, $C_6D_6$, 298 K): $\delta = -16.57$ (s, 1H, Ru($\mu$-H)Ru), 1.88 (br, 30H, Cp*), 2.05 (s, 1H, =CH), 3.02 (s, 3H, =CH), 3.86 (s, 1H, CH), 4.19 (s, 1H, =CH), 6.26 (d, $J$(H,H) = 5.1 Hz, 1H, =CHRu); $^{13}C\{^1H\}$ NMR (75.48 MHz, $CD_2Cl_2$, 250 K): $\delta = 10.24$ (s, Cp*), 10.35 (s, Cp*), 26.24 (s, =CH), 47.02 (s, CH), 49.86 (s, =CH), 58.86 (s, =CH), 60.84 (s, =CH), 66.37 (s, =CH), 89.54 (s, Cp*), 91.90 (s, Cp*), 156.31 (s, =CH-Ru); MS (FAB, NBA matrix): $m/z$ (%): 566 (90) [$M^+$]; C,H analysis (%) calcd for $C_{27}H_{38}Ru_2$: C 57.42, H 6.78; found: C 57.26, H 6.63.

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**4–6**: $HBF_4 \cdot Et_2O$ (0.1 mL) was added to a solution of **2** (0.20 g, 0.35 mmol) in $Et_2O$ (30 mL). The reaction mixture was stirred for 5 min to give an orange solid, which was collected by filtration, washed with $Et_2O$, and dried under vacuum to give **3** (0.15 g, 67 %). Complex **3** (0.20 g, 0.31 mmol) was dissolved in $CH_2Cl_2$ (2 mL), which was then layered with diethyl ether (10 mL). The mixture was allowed to stand for a week to give a brown solution and brown-red needles of **4**, which were collected by filtration, washed with hexane (5 mL), and dried under vacuum (0.080 g, 40 % based on Ru). The mother liquor was evaporated to dryness, and hexane (10 mL) was added to give a brown-yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum to give **6** (0.076 g, 38 % based on Ru). The filtrate was concentrated to dryness, and the residue purified by column chromatography (silica gel, eluent: hexane) to give **5** as a colorless oil (0.015 g, 8% based on Ru). **4**: $^1$H NMR (300.13 MHz, [D$_6$]acetone): $\delta = -13.51$ (d, $J$(H,H) = 1.38 Hz, 1 H, RuH), 1.40 (d, $J$(H,H) = 5.37 Hz, 3 H, $CH_3$), 1.91 (s, 15 H, Cp*), 1.93 (s, 15 H, Cp*), 2.39 (s, 15 H, Cp*), 4.06 (qd, $J$(H,H) = 5.73, 1.38 Hz, 1 H, Ru-C*H*-$CH_3$), 5.26 (d, $J$(H,H) = 5.37 Hz, 1 H, =CH), 5.46 (dd, $J$(H,H) = 7.23, 4.95 Hz, 1 H, =CH), 7.13 (t, $J$(H,H) = 5.13 Hz, 1 H, =CH), 8.20 (d, $J$(H,H) = 7.23 Hz, 1 H, =CH); $^{13}$C{$^1$H} NMR (75.48 MHz, [D$_6$]acetone): $\delta = 9.64$ (s, Cp*), 9.75 (s, Cp*), 10.10 (s, Cp*), 24.36 (s, $CH_3$), 37.42 (s, =CH), 41.52 (s, Ru*C*H$CH_3$), 54.02 (s, =CH), 64.83 (s, =CH), 92.48 (s, Cp*), 106.20 (s, 2 Cp*), 146.89 (s, =CHRu), 168.32 (s, =CRu); elemental analysis (%) calcd for $C_{37}H_{54}B_2F_8Ru_3$: C 45.55, H 5.58; found: C 45.80, H 5.62. **5**: $^1$H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.16$ (t, $J$(H,H) = 7.5 Hz, 3 H, $CH_3$), 1.99 (s, 15 H, Cp*), 2.20 (q, $J$(H,H) = 7.5 Hz, 2 H, $CH_2$), 4.15 (s, 4 H, Cp); $^{13}$C{$^1$H} NMR (75.48 MHz, $CDCl_3$): $\delta = 11.74$ (s, Cp*), 14.63 (s, $CH_3$), 20.81 (s, $CH_2$), 71.81 (s, Cp), 71.91 (s, Cp), 84.32 (s, Cp*), 92.13 (s, Cp); MS (CI): $m/z$ (%): 330 (100) [$M^+$]. **6**: $^1$H NMR (300.13 MHz, $CD_2Cl_2$): $\delta = 1.23$ (t, $J$(H,H) = 7.6 Hz, 3 H, $CH_3$), 1.93 (s, 30 H, Cp*), 2.63 (q, $J$(H,H) = 7.6 Hz, 2 H, $CH_2$), 4.12 (s, 2 H, Cp), 4.27 (s, 2 H, Cp); $^{13}$C{$^1$H} NMR (75.48 MHz, $CD_2Cl_2$): $\delta = 10.46$ (s, Cp*), 10.94 (s, $CH_3$), 19.84 (s, $CH_2$), 55.17 (s, Cp), 56.29 (s, Cp), 76.20 (s, Cp), 86.49 (s, Cp*); elemental analysis (%) calcd for $C_{27}H_{39}BF_4Ru_2$: C 49.70, H 6.02; found: C 50.02, H 5.86.

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[12] Crystal data for **4**: $C_{37}H_{54}B_2F_8Ru_3$, $M_r = 975.63$; triclinic, space group $P\bar{1}$; $a = 9.3162(12)$, $b = 11.6864(15)$, $c = 18.106(2)$ Å, $\alpha = 78.518(3)$, $\beta = 87.415(3)$, $\gamma = 80.060(3)°$, $V = 1902.7(4)$ Å$^3$; $Z = 2$, $\rho_{calcd} = 1.703$ g cm$^{-3}$; 12561 reflections, 8468 independent reflections ($R_{int} = 0.0571$); $R_1 = 0.0560$, $wR_2 = 0.1104$ for 527 parameters and 4100 reflections with $I > 2\sigma(I)$. Crystals of **4** suitable for X-ray diffraction were grown from a solution in $CH_2Cl_2$ layered with diethyl ether. Intensity data were collected on a Bruker SMART CCD Area Detector with graphite-monochromated $Mo_{K\alpha}$ radiation at room temperature. The structure was solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares methods on $F^2$ by using the Bruker SHELXTL (Version 5.10) program package. All non-hydrogen atoms were refined anisotropically. The two $BF_4^-$ counteranions were highly disordered, and their atomic distances (B–F, F···F) were constrained during the structural refinement. The metal-bound hydrido ligand H1 was located in the difference Fourier map and refined with isotropic thermal parameter. The remaining hydrogen atoms were placed in ideal positions and refined with a riding model. CCDC-173137 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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# Synthesis, Structure, and Molecular Orbital Calculations of Chromium(III) and Iron(III) Complexes Containing $\eta^2$-Pyrazolato Ligands[**]

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The coordination chemistry of pyrazolato ligands has been extensively explored, particularly among complexes of the mid to late transition metals.[1] Among the 1656 Group 6–11 complexes containing pyrazolato ligands whose structures

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