Reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NCCH_3)_2$ with $Me_3SiC{\equiv}CR$. Synthesis and Structural Characterization of Mononuclear Ruthenium Bis(vinylidene) and Vinylvinylidene Complexes

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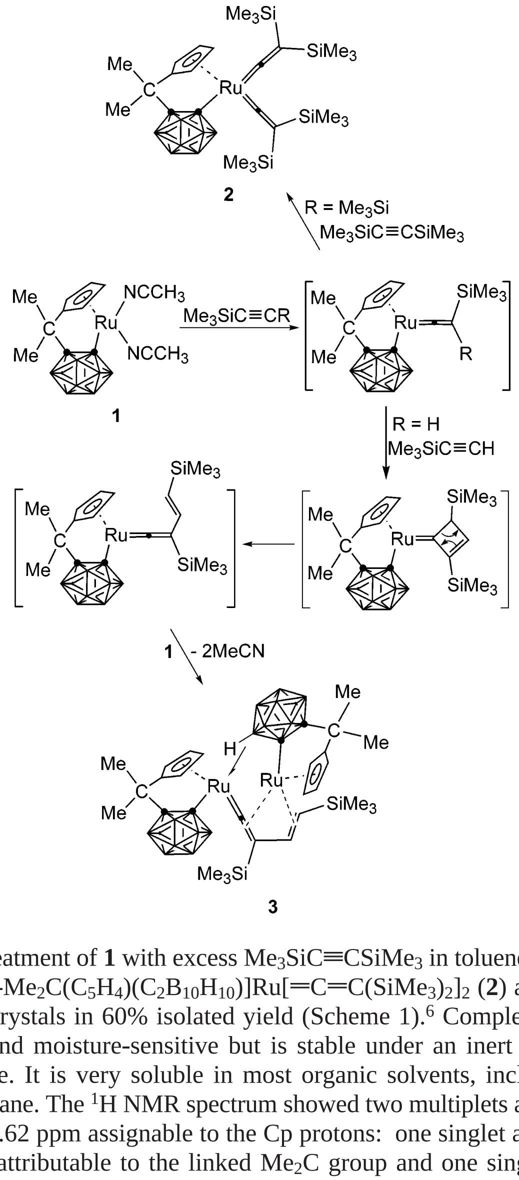
Summary: The substituent R plays a crucial role in the reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NCCH_3)_2$ with $Me_3SiC{\equiv}CR$. If R = Me_3Si, this reaction led to the isolation of the first mononuclear bis(vinylidene)metal complex. If R = H, a vinylvinylidenemetal complex was generated.

It has become apparent that transition-metal-catalyzed organic transformation of alkynes often involves vinylidene intermediates.[1] Vinylidene complexes, which can be mono-, di-, or polynuclear, are known for most transition metals and may be prepared by a variety of methods.[2] The most pertinent route to mononuclear vinylidenes involves the reaction of an alkyne with a transition-metal substrate. The alkynes can be terminal or internal with alkyl/aryl/silyl substituents.[3] Although the chemistry of (vinylidene)metal complexes has been extensively investigated, mononuclear bis(vinylidene) complexes remain unknown.[1−3] A mononuclear bis(vinylidene) species was proposed as a reactive intermediate in the formation of tetrakis(trimethylsilyl)butatriene in 1979.[4] We have isolated an unprecedented ruthenium bis(vinylidene) complex from the reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NCCH_3)_2$ (**1**)[5] with silylalkyne. This finding is reported in this communication.

Scheme 1



Treatment of **1** with excess $Me_3SiC{\equiv}CSiMe_3$ in toluene gave $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru[{=}C{=}C(SiMe_3)_2]_2$ (**2**) as yellow crystals in 60% isolated yield (Scheme 1).[6] Complex **2** is air- and moisture-sensitive but is stable under an inert atmosphere. It is very soluble in most organic solvents, including *n*-hexane. The ^1H NMR spectrum showed two multiplets at 4.90 and 4.62 ppm assignable to the Cp protons: one singlet at 1.29 ppm attributable to the linked Me_2C group and one singlet at 0.30 ppm corresponding to the $SiMe_3$ protons. The characteristic Ru=C carbons were observed at 310.7 ppm in the ^{13}C NMR spectrum. The ^{11}B NMR exhibited a 1:1:1:2 pattern. These spectroscopic data suggested that **2** should have a highly symmetrical structure in solution. Its solid-state structure was

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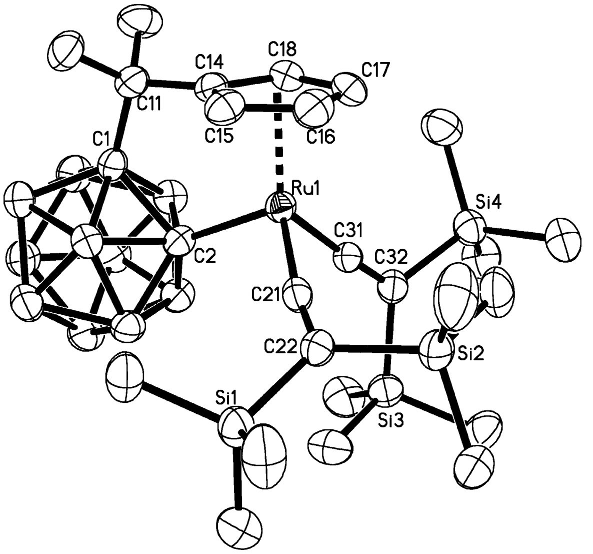

Figure 1. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru[{=}C{=}C(SiMe_3)_2]_2$ (**2**). Selected distances (Å) and angles (deg): Ru−C2 = 2.105(4), Ru−C14 = 2.280(4), Ru−C15 = 2.273(4), Ru−C16 = 2.252(4), Ru−C17 = 2.253(4), Ru−C18 = 2.283(4), Ru−C21 = 1.888(4), Ru−C31 = 1.903(4), C21−C22 = 1.289(5), C31−C32 = 1.267(5); Ru−C21−C22 = 168.6(3), Ru−C31−C32 = 177.1(3), C21−Ru−C31 = 90.1(1), Si1−C22−Si2 = 120.1(2), Si3−C32−Si4 = 119.0(2), C14−C11−C1 = 108.4(3).

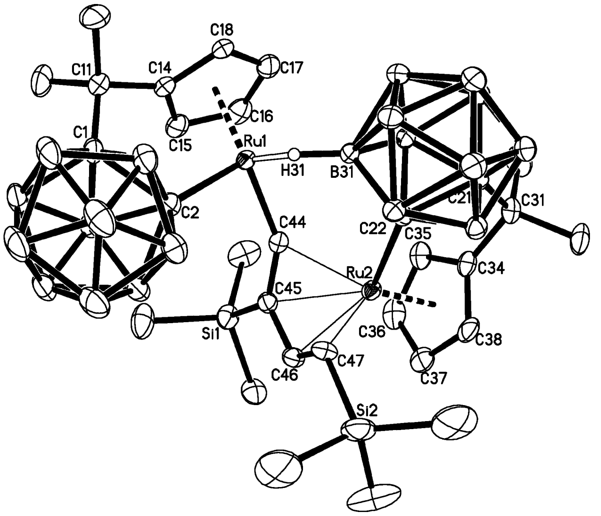

Figure 2. Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru\{\mu\text{-}\eta^4\text{-}[{=}C{=}C(SiMe_3)CH{=}CH(SiMe_3)]\}Ru[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]$ (**3**). Selected distances (Å) and angles (deg): Ru1−C2 = 2.116(1), Ru1−C14 = 2.221(1), Ru1−C15 = 2.196(1), Ru1−C16 = 2.260(1), Ru1−C17 = 2.287(1), Ru1−C18 = 2.270(1), Ru1−B31 = 2.345(1), Ru1−C44 = 1.890(1), C44−C45 = 1.387(2), C45−C46 = 1.443(2), C46−C47 = 1.395(2), Ru2−C22 = 2.132(1), Ru2−C34 = 2.217(1), Ru2−C35 = 2.234(1), Ru2−C36 = 2.220(1), Ru2−C37 = 2.217(1), Ru2−C38 = 2.216(1), Ru2−C44 = 2.163(1), Ru2−C45 = 2.188(1), Ru2−C46 = 2.154(1), Ru2−C47 = 2.265(1); Ru1−C44−C45 = 150.0(1), C44−C45−C46 = 113.9(1), C44−C45−Si1 = 126.6(1), C46−C45−Si1 = 119.5(1), C45−C46−C47 = 121.9(1), C46−C47−Si2 = 121.0(1).

confirmed by single-crystal X-ray analyses[7] and shown in Figure 1. Complex **2** has a three-legged piano-stool geometry with the two vinylidene groups in cis positions. The average Ru−C_5 ring distance of 2.268(4) Å and Ru−C(cage) distance of 2.105(4) Å are similar to the corresponding values observed in $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(X_2)$ (X_2 = Lewis base) complexes.[8] The Ru═C distances of 1.888(4)/1.903(4) Å, the C═C distances of 1.289(5)/1.267(5) Å, and the Ru═C═C angles of 168.6(3)/177.1(3)° are close to those observed in other vinylideneruthenium complexes, for example, 1.845(4) Å, 1.301(5) Å, and 177.2(3)° in $RuCl_2\{{=}C{=}C(SiMe_3)Ph\}(dcpmp)$,[9a] 1.850(3) Å, 1.289(5) Å, and 171.6(3)° in $[Cp^*Ru{=}C{=}CHSiMe_3(PMe^iPr_2)_2][B\{3,5\text{-}C_6H_3\text{-}(CF_3)_2\}_4]$,[9b] and 1.85(2) Å, 1.29(2) Å, and 173(1)° in $Cp^*RuCl({=}C{=}C)(PPh_3)$.[9c] The C(21)−Ru−C(31) angle of 90.1(1)° falls in the range 83−96° found in $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(X_2)$ (X = $P(OEt)_3$, $NCCH_3$, NH_2Pr^n) complexes.[5]

Complex **2** is thermally stable, even in refluxing toluene, and did not show any activity toward internal alkynes, due most likely to steric reasons. The impact of the sterically demanding Me_3Si groups in the formation of **2** was further demonstrated in the following experiment. Reaction of **1** with excess $Me_3SiC{\equiv}CH$ in toluene afforded the green (vinylvinylidene)ruthenium complex $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru\{\mu\text{-}\eta^4\text{-}[{=}C{=}C(SiMe_3)CH{=}CH(SiMe_3)]\}Ru[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]$ (**3**) in 57% isolated yield (Scheme 1).[6] Complex **3** is air- and moisture-sensitive but remains intact under an inert atmosphere. It is soluble in polar solvents such as THF, CH_2Cl_2, and toluene but is insoluble in *n*-hexane. Complex **3** was fully characterized by various spectroscopic techniques and elemental analyses.[6] The characteristic Ru═C carbon was observed at 320.8 ppm in the ^{13}C NMR spectrum. The unique B−H→Ru proton was found at −8.88 ppm as a broad quartet with J_{BH} = 81 Hz in the ^1H NMR spectrum.[10] A single-crystal X-ray diffraction study[7] revealed that **3** is a dinuclear complex consisting of the vinylvinylideneruthenium moiety $[\eta^5{:}\sigma\text{-}Me_2C\text{-}$

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[6] Preparation of **2**: a toluene solution (5 mL) of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru(NCCH_3)_2$ (**1**; 86 mg, 0.2 mmol) and bis(trimethylsilyl)acetylene (102 mg, 0.6 mmol) was stirred at room temperature for 24 h. Removal of the solvent gave a yellow solid. Recrystallization from *n*-hexane afforded **2** as yellow crystals (89 mg, 60%), mp 123−124 °C. ^1H NMR (C_6D_6): δ 4.90 (m, 2H, C_5H_4), 4.62 (m, 2H, C_5H_4), 1.29 (s, 6H, $C(CH_3)_2$), 0.30 (s, 36H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 310.7 (Ru═*C*), 112.0 (Ru═C═*C*), 89.0, 84.0 (C_5H_4), 40.6 ($C(CH_3)_2$), 31.4 ($C(CH_3)_2$), 3.0 ($Si(CH_3)_3$). $^{11}B\{^1H\}$ NMR (C_6D_6): δ −1.8 (2B), −4.5 (2B), −6.1 (2B), −7.8 (4B). IR (KBr, cm^{-1}): ν 2553 (vs) (BH), 1631 (m) (C═C). Anal. Calcd for $C_{26}H_{56}B_{10}RuSi_4$: C, 45.24; H, 8.18. Found: C, 45.40; H, 8.60. **3**: a toluene solution (5 mL) of **1** (86 mg, 0.2 mmol) and ethynyltrimethylsilane (59 mg, 0.6 mmol) was stirred at room temperature for 24 h. Removal of the solvent gave a green solid. Recrystallization from toluene afforded **3** as green crystals (102 mg, 57%), mp 165−166 °C. ^1H NMR (CD_2Cl_2): δ 5.53 (m, 1H, C_5H_4), 5.24 (m, 2H, C_5H_4), 4.98 (d, ^3J = 10.8 Hz, 1H, CH), 4.97 (m, 1H, C_5H_4), 4.59 (m, 2H, C_5H_4), 4.27 (m, 1H, C_5H_4), 4.18 (m, 1H, C_5H_4), 1.71 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 0.55 (d, ^3J = 10.8 Hz, 1H, CH), 0.40 (s, 9H, $Si(CH_3)_3$), 0.14 (s, 9H, $Si(CH_3)_3$), −8.88 (q br, J_{BH} = 81 Hz, 1H, B−H→Ru). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 320.8 (Ru═*C*), 136.8, 132.9 (*C*Hcdbd═*C*H), 113.9 (Ru═C═*C*), 93.2, 85.4, 81.4, 80.1, 79.6, 78.0, 68.3 (C_5H_4), 42.3, 41.4 ($C(CH_3)_2$), 32.6, 32.5, 32.4, 31.3 ($C(CH_3)_2$), 1.61, 0.28 ($Si(CH_3)_3$). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −2.7 (3B), −4.7 (3B), −6.2 (2B), −7.8 (4B), −9.1 (4B), −10.1 (4B). IR (KBr, cm^{-1}): ν 2588 (vs) (BH), 1620 (m) (C═C). Anal. Calcd for $C_{30}H_{60}B_{20}Ru_2Si_2$: C, 40.24; H, 6.75. Found: C, 40.51; H, 6.92.

[7] Crystal data for **2** ($C_{26}H_{56}B_{10}RuSi_4$; fw = 690.2): monoclinic, space group $P2_1/n$, $a = 9.413(1)$ Å, $b = 32.694(7)$ Å, $c = 13.215(3)$ Å, $\beta = 110.86(3)°$, $V = 3800.3(1)$ Å^3, $T = 293$ K, $Z = 4$, $d_{calcd} = 1.206$ g/cm^3, R1 = 0.051 ($I > 2\sigma(I)$), wR2(F^2) = 0.132. Crystal data for **3** ($C_{30}H_{60}B_{20}Ru_2Si_2$, fw = 895.3): monoclinic, space group $P2_1/n$, $a = 18.257(1)$ Å, $b = 10.553(1)$ Å, $c = 22.748(1)$ Å, $\beta = 90.27(1)°$, $V = 4382.4(4)$ Å^3, $T = 293$ K, $Z = 4$, $d_{calcd} = 1.357$ g/cm^3, R1 = 0.028 ($I > 2\sigma(I)$), wR2(F^2) = 0.070.

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$(C_5H_4)(C_2B_{10}H_{10})]Ru[{=}C{=}C(SiMe_3)CH{=}CH(SiMe_3)]$ and the $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru$ fragment, as shown in Figure 2. One Ru atom is η^4-bound to the two C=C double bonds of the vinylvinylidene group, and the other one is coordinated to the B−H bond of the cage. Both Ru atoms adopt a three-legged piano-stool geometry if each C=C is viewed as one coordination site. The average Ru(1)−C_5 ring distance of 2.247(1) Å and Ru(1)−C(cage) distance of 2.116(1) Å are very close to the Ru(2)−C_5 ring distance of 2.221(1) Å and Ru(2)−C(cage) distance of 2.132(1) Å and to those of 2.268(4) and 2.105(4) Å in **2**. The Ru(1)=C(44) distance of 1.890(1) Å is almost identical with those of 1.888(4) and 1.903(4) Å in **2**. The Ru(2)−C(44−47) distances range from 2.154(1) to 2.256(1) Å with an average value of 2.193(1) Å, which is quite comparable to that of 2.176(5) Å in $Ru(acac)_2$(2,3-dimethyl-1,3-butadiene)[11a] and 2.221(3) Å in $[CpRu\{\eta^4\text{-}C_4H_3(CH_2)_3\text{-}PPh_2\text{-}\kappa^1N\text{-}NPh\}][PF_6]$.[11b] The Ru(1)−B(31) distance of 2.345(1) Å is almost the same as that of 2.34(1) Å in $Ru_3(\mu\text{-}\sigma{:}\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8)(CO)_6(PMe_2Ph)_2$[10a] and 2.360(5) Å in $Ru_3(\mu\text{-}H)(CO)_8(\eta^5\text{-}7\text{-}CB_{10}H_{11})$.[10b] The Ru(1)−C(44)−C(45) angle of 150.0(1)° is significantly smaller than that of 163.6(7)° in $[TpRu{=}C{=}C(COOMe)CH{=}CHCOOMe(PEt_3)_2][BPh_4]$,[12a] 172(1)° in $[Cp^*Ru\{{=}C{=}CHC(CH_2)Ph\}(PEt_3)_2][BPh_4]$,[12b] and 176.2(4)° in $[(\eta^5\text{-}C_9H_7)Ru\{{=}C{=}C(Me)(1\text{-cyclohexenyl})\}(PPh_3)_2][PF_6]$,[12c] due probably to the coordination of the vinylvinylidene moiety to the Ru(2) atom.

The formation of **2** and **3** may involve the common mono(vinylidene)ruthenium intermediate $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ru[{=}C{=}C(SiMe_3)R]$. If R is a bulky Me_3Si group, the second equivalent of $Me_3SiC{\equiv}CSiMe_3$ approaches the metal center to form the bis(vinylidene) complex **2**.[9a] If R is H, the second equivalent of $Me_3SiC{\equiv}CH$ reacts with the reactive vinylideneruthenium intermediate via [2 + 2] cycloaddition and ring-opening reactions to generate the vinylvinylidene complex **3**.[12a] These transformations are shown in Scheme 1.

In conclusion, a mononuclear bis(vinylidene)metal complex was prepared and structurally characterized for the first time. A sterically demanding ancillary ligand and bulky alkynes are both important components to stabilize bis(vinylidene)metal complexes.

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Supporting Information Available: Text giving details of the syntheses and X-ray studies of **2** and **3**, and CIF files giving X-ray crystallographic data for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The chemical shift of the B−H→Ru proton was reported at −10.08 ppm with J_{BH} = 70 Hz in $Ru_3(\mu\text{-}\sigma{:}\eta^5\text{-}7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8)(CO)_6(PMe_2Ph)_2$ and at −10.31 ppm with J_{BH} = 56 Hz in $Ru_3(\mu\text{-}H)(CO)_8(\eta^5\text{-}7\text{-}CB_{10}H_{11})$; see: (a) Liao, Y.-H.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1996**, *15*, 5102. (b) Ellis, D. D.; Franken, A.; Stone, F. G. A. *Organometallics* **1999**, *18*, 2362.

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