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Novel Dinuclear (μ-Hydrido)(μ-alkylideneamido)ruthenium Complexes, $[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}L)(\mu\text{-}H)(\mu\text{-}N{=}CHR)$ (R = Me, Et; L = MeCN, Arene), as Precursors of Active Species for Bimetallic Activation. Dehydrogenative Coupling of Ethylene in a Dinuclear Ruthenium Complex

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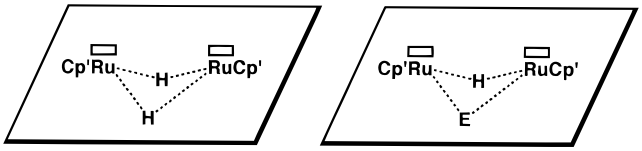
Summary: The dinuclear ruthenium tetrahydride $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_2]_2$ reacts with acetonitrile or propionitrile in the presence of an arene such as toluene or naphthalene to generate the (μ-hydrido)(μ-alkylideneamido)ruthenium complex $(Cp'Ru)_2(\mu\text{-}L)(\mu\text{-}H)(\mu\text{-}N{=}CHR)$ (L = (arene); Cp′ = η^5-C_5Me_5). The reaction of the (μ-alkylideneamido)ruthenium complex with ethylene gives the bis(ethylene)ruthenium complex $[Cp'Ru(\eta^2\text{-}CH_2{=}CH_2)]_2(\mu\text{-}H)(\mu\text{-}N{=}CHCH_3)$, which undergoes dehydrogenative coupling of the ethylene ligand to yield the μ-η^2:η^2-s-cis-butadiene complex $(Cp'Ru)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}CH_2{=}CHCH{=}CH_2)(\mu\text{-}H)(\mu\text{-}N{=}CHCH_3)$.

For a multinuclear transition-metal complex having strong interaction among metals through direct metal−metal bonds or bridging ligands, the substrate can be activated in an effective and characteristic manner due to the cooperative action of the metal centers. Thus, activation of substrates by multinuclear complexes has been one of the focuses of recent studies in the field of organometallic chemistry.[1]

As a part of our current studies of activation of substrates on the reaction field provided by multinuclear complexes, we have partially reported the synthesis and reactivities of the di- and trinuclear polyhydride complexes $[Cp'Ru(\mu\text{-}H)_2]_2$ (**1**; Cp′ = η^5-C_5Me_5)[2] and $(Cp'Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ (**2**).[3] Complex **1** readily gives rise to a pair of unsaturated sites on each of the metal centers upon thermal excitation or hydrogen transfer to an olefin. We have successfully demonstrated examples of bimetallic activation, which is the characteristic manner of activation of substrates achieved by the concerted action of two metal centers. If the bridging ligand **E** is introduced into the dinuclear complex, the reaction field of the complex is affected both electronically and sterically by this ligand. The reaction field of the dinuclear complex could, therefore, be modified with regard to reactivity and selectivity.



Although there have been several reported examples of insertion of nitrile into a transition-metal−hydride bond, yielding alkylideneamide complexes,[4] the resulting complexes have hardly been studied in relation to bimetallic activation. Here we report the synthesis and reactivities of novel dinuclear μ-hydride−μ-alkylideneamide complexes of ruthenium as precursors of the active species for the bimetallic activation. Dehydrogenative coupling of ethylene on the reaction field of this complex, yielding a μ-η^2:η^2-butadiene complex, is also described.

Treatment of **1** with acetonitrile in diethyl ether at room temperature smoothly leads to the formation of the (alkylideneamido)ruthenium complex **3a**, $(Cp'Ru)_2(CH_3CN)_2(\mu\text{-}H)(\mu\text{-}N{=}CHCH_3)$, as a result of insertion of CH_3CN into a Ru−H bond.[5] The coordinated CH_3CN molecules in **3a** are readily replaced with arenes, such

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(1) For dinuclear ruthenium complexes, see, for example: Haines, R. J. In *Comprehensive Organometallic Chemistry II*: Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 7, p 625.

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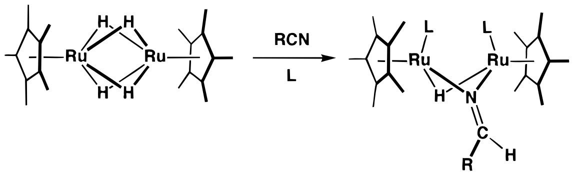
Scheme 1



3a: R = CH_3, L = CH_3CN
3b: R = CH_3, L = 1/2 ($C_6H_5CH_3$)
3c: R = CH_3, L = 1/2 ($C_{10}H_8$)
4b: R = C_2H_5, L = 1/2 ($C_6H_5CH_3$)
4c: R = C_2H_5, L = 1/2 ($C_{10}H_8$)

as toluene and naphthalene, to form the alkylideneamide complex $(Cp'Ru)_2(\mu\text{-}\eta^2{:}\eta^2\text{-arene})(\mu\text{-H})(\mu\text{-N=CHCH}_3)$ (**3b**, arene = $C_6H_5CH_3$; **3c**, arene = $C_{10}H_8$), in which the arene molecule is coordinated in a μ-η^2:η^2 fashion. Similar μ-alkylideneamide complexes $(Cp'Ru)_2(\mu\text{-}\eta^2{:}\eta^2\text{-arene})(\mu\text{-H})(\mu\text{-N=CHC}_2\text{H}_5)$ (**4b**, arene = $C_6H_5CH_3$; **4c**, arene = $C_{10}H_8$) are synthesized in excellent yields by the reaction of **1** with propionitrile in the presence of the corresponding arene. The results are summarized in Scheme 1.

These μ-alkylideneamide complexes are characterized on the basis of the ^{1}H and ^{13}C NMR spectra as well as the analytical data. The ^{1}H and ^{13}C NMR data are comparable to those reported for dinuclear μ-alkylideneamide complexes.[4e−j] The characteristic resonances for the =CH− group next to the bridging nitrogen atom appeared in the region of δ 7.0−8.3 ppm in the ^{1}H NMR and δ 155−175 ppm in the ^{13}C NMR, respectively. Definitive proof of the structure of **4c** was provided by X-ray crystallography.[6] The structure shown in Figure 1 is fully consistent with the spectral data and clearly depicts the formation of the alkylideneamide bridge as a result of the insertion of the propionitrile into the Ru−H bond.

The μ-alkylideneamide complex **3** or **4** can easily open a pair of vacant coordination sites in solution to generate an active species for bimetallic activation.

Complex **3a** readily reacts with 1 atm of ethylene in tetrahydrofuran at ambient temperature for 3 h to generate a bis(η^2-ethylene)ruthenium complex, $[Cp'Ru(\eta^2\text{-CH}_2\text{=CH}_2)]_2(\mu\text{-H})(\mu\text{-N=CHCH}_3)$ (**5**; Scheme 2). Complex **5** was isolated in 97% yield as a yellow-orange microcrystalline solid after chromatographic purification on Al_2O_3. The ^{1}H and ^{13}C NMR and ^{1}H−^{13}C HSC spectra of **5** showed the coordinated two ethylene molecules to be inequivalent. The signals for the eight protons of the coordinated ethylenes were separately observed at relatively high field (δ 0.19−2.71). Treatment of **4b** with ethylene yields the corresponding bis(ethylene) complex **6**.

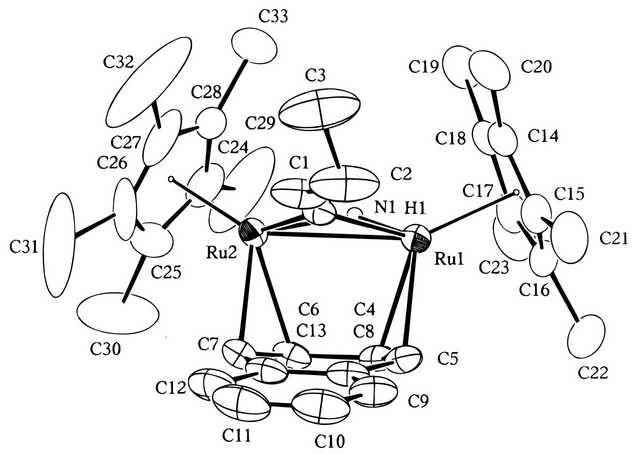
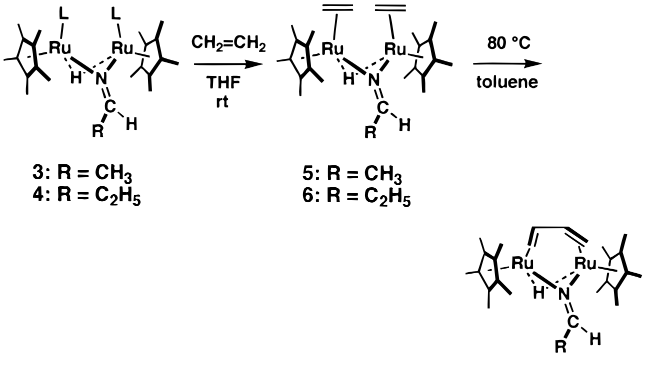


Figure 1. Molecular structure of $(Cp'Ru)_2(\mu\text{-}\eta^2{:}\eta^2\text{-C}_{10}\text{H}_8)(\mu\text{-H})(\mu\text{-N=CHC}_2\text{H}_5)$ (**4c**). The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg) are as follows: Ru1−Ru2 = 2.8103(8), Ru1−N1 = 2.037(4), Ru2−N1 = 2.016(4), N1−C1 = 1.272(7), C4−C5 = 1.409(7), C4−C6 = 1.475(7), C6−C7 = 1.424(7); Ru2−Ru1−N1 = 45.8(1), Ru1−Ru2−N1 = 46.4(1), Ru1−N1−Ru2 = 87.8(2), Ru1−N1−C1 = 141.8(5), Ru2−N1−C1 = 130.3(5), C5−C4−C6 = 119.0(5), C4−C6−C7 = 117.8(5).

Scheme 2



3: R = CH_3
4: R = C_2H_5

5: R = CH_3
6: R = C_2H_5

7: R = CH_3
8: R = C_2H_5

Pyrolysis of the bis(ethylene) complex smoothly proceeds to form a μ-η^2:η^2-s-*cis*-butadiene complex as the sole product via a dehydrogenative coupling reaction of the coordinated ethylene molecules. When **5** was heated in toluene at 80 °C for 17 h, the μ-η^2:η^2-s-*cis*-butadiene complex $(Cp'Ru)_2(\mu\text{-}\eta^2{:}\eta^2\text{-CH}_2\text{=CHCH=CH}_2)(\mu\text{-H})(\mu\text{-N=CHCH}_3)$ (**7**) was exclusively formed. Pyrolysis of **6** gave a similar μ-η^2:η^2-s-*cis*-butadiene complex, $(Cp'Ru)_2(\mu\text{-}\eta^2{:}\eta^2\text{-CH}_2\text{=CH-CH=CH}_2)(\mu\text{-H})(\mu\text{-N=CHCH}_2\text{CH}_3)$ (**8**), in quantitative yield. The butadiene complexes **7** and **8** are directly synthesized from the corresponding alkylideneamide complexes **5** and **6**, respectively, by treatment with ethylene (1 atm) in refluxing toluene. The molecular structure of **8** was verified by means of X-ray diffraction studies (Figure 2).[7] The values of 1.413(8) and 1.374(8) Å for the C(1)−C(2) and C(3)−C(4) distances, respectively, lie within the range of those for the C−C double bonds of the bridging butadiene ligand coordinated in the di- and trinuclear complexes.[8] The

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(5) Experimental details for **3a**: a 50-mL Schlenk tube was charged with 123 mg (0.257 mmol) of **1** and 10 mL of diethyl ether; 1 mL (31 mmol) of freshly distilled acetonitrile was added, and the reaction mixture was stirred at room temperature for 20 min. Removal of the solvent under reduced pressure followed by washing of the residual solid with 1 mL of acetonitrile gave 150 mg (97%) of **3a** as dark yellow crystalline solids.

(6) Complex **4c** crystallized from pentane in the triclinic system, space group $P\bar{1}$ (No. 2), with a = 11.144(2) Å, b = 16.361(3) Å, c = 8.644(2) Å, α = 96.17(2)°, β = 105.24(2)°, γ = 82.48(2)°, V = 1503.2(5) Å^3, Z = 2, and D_{calc} = 1.453 g cm^{-3}. Intensity data were collected at 23 °C on a Rigaku AFC-5R four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) in the 5° < 2θ < 50° range. The data were processed using the TEXSAN crystal structure analysis package operated on a IRIS Indigo computer. Neutral atom scattering factors were obtained from the standard sources.[12] In the reduction of the data, Lorentz/polarization corrections and empirical absorption corrections based on azimuthal scans were applied to the data. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4136 observed reflections ($I > 3.00\sigma(I)$) and 329 variable parameters and converged with unweighted and weighted agreement factors of R = 0.037 and R_w = 0.036.

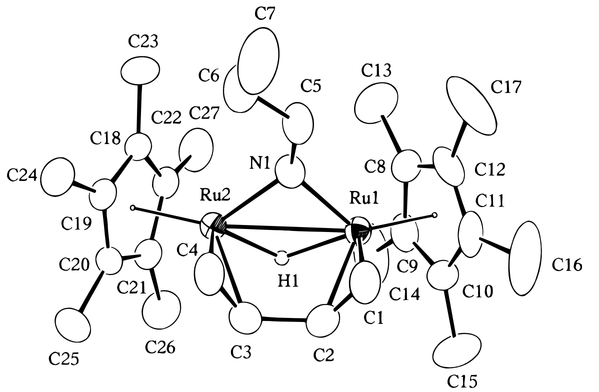
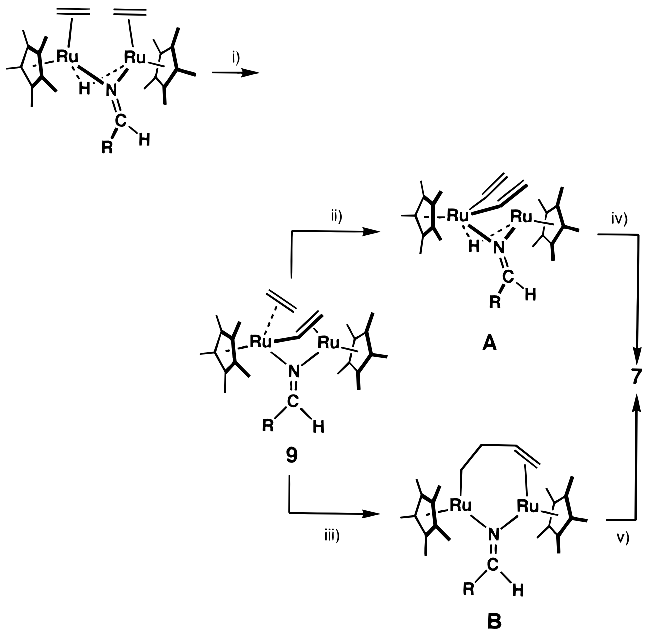


Figure 2. Molecular structure of $(Cp'Ru)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}C_4H_6)(\mu\text{-}H)(\mu\text{-}N{=}CHC_2H_5)$ (**8**). The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg) are as follows: Ru1−Ru2 = 2.8385(7), Ru1−N1 = 2.009(4), Ru2−N1 = 2.013(4), N1−C5 = 1.283(6), C1−C2 = 1.374(8), C2−C3 = 1.520(7), C3−C4 = 1.413(8); Ru2−Ru1−N1 = 45.2(1), Ru1−Ru2−N1 = 45.1(1), Ru1−N1−Ru2 = 89.8(2), Ru1−N1−C5 = 131.5(4), Ru2−N1−C5 = 138.4(5), C1−C2−C3 = 123.8(6), C2−C3−C4 = 122.6(6).

Scheme 3[a]



[a] Legend: (i) C−H activation, $-H_2$; (ii) C−H activation; (iii) insertion of CH_2CH_2 into Ru−C; (iv) reductive elimination; (v) β-H elimination.

C(2)−C(3) distance of 1.520(7) Å corresponds to a C−C single bond and indicates the localization of π electrons in the coordinated butadiene.

Although no intermediary species could be detected by ^1H NMR, we can propose several possible reaction paths leading to the formation of **7**. One of the plausible reaction paths is shown in Scheme 3, which involves an initial oxidative addition of a C−H bond of the ethylene ligand, yielding the vinyl−ethylene complex **9**. Activation of the C−H bond of the ethylene coordinated in **9** and subsequent reductive coupling of the resulting two vinyl groups would form the butadiene complex **7** by way of the divinyl complex **A**. There is no precedent for such a coupling reaction of two vinyl groups as far as the dinuclear complex is concerned. However, examples of the reductive coupling of two vinyl ligands have already been reported for a mononuclear complex.[9] Another possible route to **7** from **9** would involve insertion of the ethylene molecule into the Ru−C bond to yield the $\eta^1{:}\eta^2$-butenyl complex **B**, which would undergo β-H elimination to give **7**.

To isolate the intermediate vinyl−ethylene complex **9**, the reaction of **5** with 1 atm of acetylene was carried out. The reaction smoothly proceeded in toluene at room temperature to result in the quantitative formation of **9** *via* an insertion reaction of the acetylene molecule into the Ru−H bond. Insertion of acetylene into the Ru−H bond was proved by the labeling experiment using acetylene-d_2.[10] Quantitative conversion of **9** into **7** upon heating in benzene at 55 °C was confirmed by means of ^1H and ^{13}C NMR spectroscopy.[11]

As reported previously, the dinuclear tetrahydride-bridged complex **1** reacted with excess ethylene to generate a dinuclear 2,5-dimethylruthenacyclopentadiene complex as the sole product *via* an intermediary vinyl−ethylene complex.[2h] These results show that there is a marked contrast between the reactivity of the dinuclear alkylideneamide-bridged complex **3** or **4** toward ethylene and that of the tetrahydride complex **1**.

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Supporting Information Available: Tables giving spectral (including ^1H and ^{13}C NMR spectral assignments of **3a**−**c**, **4b**,**c**, and **5**−**9**) and X-ray (for **4c** and **8**) data (45 pages). Ordering information is given on any current masthead page.

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[7] Complex **8** crystallized from THF in the orthorhombic system, space group *Pbca* (No. 61), with $a = 15.166(7)$ Å, $b = 25.605(5)$ Å, $c = 13.590(6)$ Å, $V = 5277(3)$ Å^3, $Z = 8$, and $D_{calc} = 1.469$ g cm^{-3}. Data collection, solution, and refinement were carried out as in ref 6. The final cycle of full-matrix least-squares refinement was based on 3415 observed reflections ($I > 3.00\sigma(I)$) and 275 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.035$ and $R_w = 0.028$.

[8] (a) Sasse, H. E.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1972**, *392*, 167. (b) Tachikawa, M.; Shapley, J. R.; Haltiwanger, R. C.; Pierpont, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 4651. (c) Pierpont, C. G. *Inorg. Chem.* **1978**, *17*, 1976. (d)(King, J. A., Jr.; Vollhardt, K. P. C. *Organometallics* **1983**, *2*, 684. (e) Lewandos, G. S.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1987**, 2703. (f) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 198.

[9] See, for example: (a) Czisch, P.; Erker, G.; Korth, H.-G.; Sustmann, R. *Organometallics* **1984**, *3*, 945. (b) Chang, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4298.

[10] Treatment of **7** (116 mg, 0.203 mmol) with excess C_2D_2 (1 atm) in THF at room temperature for 30 min afforded **9** (116 mg, 99%) as dark purple solids. Distribution of deuterium in **9** was determined on the basis of the integrated ^1H NMR spectrum. The deuterium was distributed only in the vinyl group, and the occupancies of deuterium were 0.94, 0.30, and 0.70 at the α-position, β-position (*cis* to Ru), and β-positin (*trans* to Ru), respectively. This result indicates that **9** is mainly formed by way of insertion of acetylene into the Ru−H bond.

[11] An NMR tube was charged with 17 mg (0.030 mmol) of **9** and 0.6 mL of benzene-d_6. The tube was sealed and heated to 55 °C. The reaction was monitored by ^1H NMR spectrometry. After 60 min, the yield of **7** reached 43%. With the reaction time, a progressive increase in the intensity of the signal for **7** and significant decrease in those for **9** were observed. After 170 min, the yield of **7** reached 81%. After 6.5 h, the signals attributable to **9** disappeared and the yield of **7** reached 100%. The ^{13}C NMR spectrum measurement also confirmed the exclusive formation of **7** in the pyrolysis of **9**.

[12] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1975; Vol. 4.