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Ruthenium Polyhydrido Clusters Having a Bridging Alkylzinc Group, $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)]_3(\mu_3\text{-}ZnR)_n(\mu_3\text{-}H)_{2-n}$ and $[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}ZnR)_n(\mu\text{-}H)_{4-n}$ (R = Me and Et; n = 1 and 2)

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Novel triruthenium polyhydrido complexes having triply bridging alkylzinc ligands, $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}ZnR)(\mu_3\text{-}H)$ (**3a**: R = Me, **3b**: R = Et) and $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}ZnEt)_2$ (**4a**: R = Me, **4b**: R = Et), are obtained by the reaction of $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (**2**) with a stoichiometric amount of the corresponding dialkylzinc ZnR_2. X-ray diffraction studies of **3b** and **4a** display the structural identity of those that have a triply bridging alkylzinc ligand. The X-ray studies as well as ^1H NMR spectroscopy reveal the existence of bonding interactions between the μ_3-zinc and the Ru-bound hydrido ligands in **3** and **4**. In the variable-temperature ^1H NMR study of **3b**, activation parameters, $\Delta S^\ddagger$ and $\Delta H^\ddagger$, for the coordination-site exchange process among the hydrido ligands were estimated at -1.5 ± 1.3 cal mol^{-1} K^{-1} and 15.0 ± 0.4 kcal mol^{-1}, respectively. The reaction of a diruthenium tetrahydrido complex, $(Cp'Ru)_2(\mu\text{-}H)_4$ (**1**), with an equimolar amount of dialkylzinc yields $(Cp'Ru)_2(\mu\text{-}ZnR)(\mu\text{-}H)_3$ (**5a**: R = Me, **5b**: R = Et). Di-μ-alkylzinc complexes, $(Cp'Ru)_2(\mu\text{-}ZnR)_2(\mu\text{-}H)_2$ (**6a**: R = Me, **6b**: R = Et), are formed in the reaction of **1** with twice the molar amount of dialkylzinc. The crossover reaction between **5b** and 1 equiv of dimethylzinc proved the *cis*-geometry of the bridging alkylzinc ligands in **6**. The variable-temperature ^1H NMR experiment of **5** demonstrated fluxionality of the hydrido ligands, and the activation parameters were estimated at $\Delta S^\ddagger = -5.8 \pm 2.0$ cal mol^{-1} K^{-1} and $\Delta H^\ddagger = 11.0 \pm 0.5$ kcal mol^{-1} for **5a** and $\Delta S^\ddagger = -12.4 \pm 1.8$ cal mol^{-1} K^{-1} and $\Delta H^\ddagger = 9.6 \pm 0.5$ kcal mol^{-1} for **5b** by the line-shape analysis.

Introduction

Reaction chemistry of transition metal cluster complexes has been one of the fascinating subjects in the field of inorganic and organometallic chemistry, and the study of the reactivity of cluster complexes has been increasing in the past two decades.[1] We have thus far synthesized a new class of η^5-C_5Me_5 polyhydride cluster complexes of transition metals, such as $(Cp'Ru)_2(\mu\text{-}H)_4$ (**1**; Cp′ = η^5-C_5Me_5) and $\{(Cp'Ru)(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (**2**),[2,3] and demonstrated several novel types of reactions stemming from the synergic effect of the adjacent metal centers.[4] The reactivity of the cluster complex depends primarily on the stereoelectronic environment of the reaction field. A change in the electronic environment of the reaction field deeply affects the course of the reaction, and the development of a reasonable and efficient method to control electron density at the metal site of the polyhydrido cluster has, therefore, been one of the main research targets in our group. At last, we arrived at the conclusion that introduction of a bridging ligand to the metal core of the cluster enabled control over the reactivity of the cluster complexes as a result of perturbation of the electron density at the metal centers due to polarization of the metal−ligand bond.

It is necessary to introduce the bridging ligand into only one face of the metal core. Otherwise, the reaction fields are covered over with the bridging ligands and there would be insufficient space for coordination and activation of the substrate to the metal site. We have, thus far, devoted ourselves to developing an efficient and reasonable synthetic method of producing a series of the clusters that have a bridging heteroatom ligand and successfully achieved the synthesis of μ-phosphido, μ-alkylidenamido, and μ_3-borylene complexes.[5] In these clusters, the metal centers are likely positively charged due to the difference in the electronegativity between the metal and the heteroatom.

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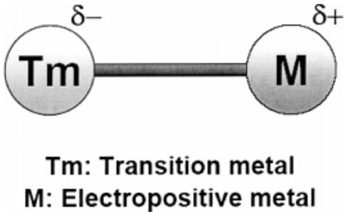
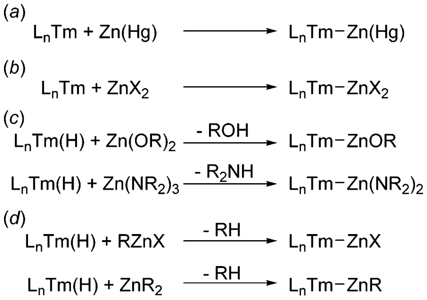
10.1021/om070024f CCC: $37.00

Chart 1



Scheme 1. Bond-Forming Reactions between the Transition Metal and the Zinc Group



Introduction of an electropositive element such as Zn, Mg, and Al into a metal core of the clusters most certainly raised the electron density at the metal center as a result of polarization between ruthenium and the electropositive metal (Chart 1). The reaction field of the cluster would be thus affected electronically and modified with regard to both reactivity and selectivity.

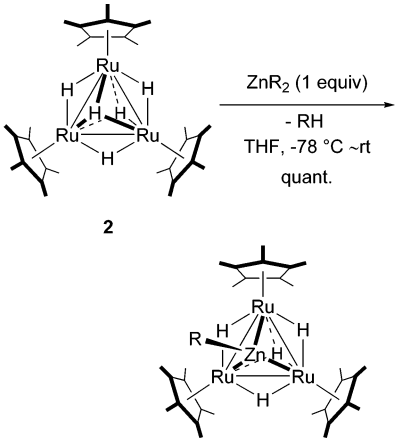
As far as heterobimetallic complexes having a direct bond between the transition metal and the zinc are concerned, there have thus far been several reported examples. The bond-forming reactions between the transition metal and the zinc group are roughly classified as follows: (a) direct reaction of a transition metal compound with zinc amalgam,[6] (b) reaction of a transition metal complex with zinc halide,[7] (c) reaction of a transition metal complex with zinc amide or zinc alkoxide,[8] (d) reaction of a transition metal complex with alkyl zinc halide[9] or zinc alkyls or aryls[10] (Scheme 1). Among these methods, the type d reaction is likely the most promising because we adopt the polyhydride clusters $(Cp'Ru)_2(\mu\text{-}H)_4$ and $(Cp'Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$ as the starting materials.

We examined this method for the synthesis of the triruthenium polyhydride cluster with a triply bridging ZnR ligand. In a previous communication, we partly reported the synthesis and characterization of the first trinuclear polyhydride having a triply bridging ethylzinc ligand, $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}ZnEt)(\mu_3\text{-}H)$.[11]

We report herein the full details of the synthesis and characterization of novel trinuclear and binuclear complexes with a polarized Ru−Zn bond, $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}ZnR)(\mu_3\text{-}H)$ (**3**), $(Cp'Ru)_3(\mu_3\text{-}ZnR)_2(\mu_3\text{-}H)_3$ (**4**), $(Cp'Ru)_2(\mu\text{-}ZnR)(\mu\text{-}H)_3$ (**5**), and $\{Cp'Ru(\mu\text{-}H)\}_2(\mu\text{-}ZnR)_2$ (**6**) (R = Me and Et). Mobility of the hydrido ligands, which is closely correlated to the reactivity of the cluster, has been also studied by means of NMR spectroscopy.

Results and Discussion

Reaction of $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}H)_2$ (2) with Dialkylzinc: Formation of Novel Trinuclear Complexes Having Triply Bridged Alkylzinc Ligands. Treatment of **2** with an equimolar amount of dialkylzinc ZnR_2 (R = Me and Et) in THF with a increase in temperature from −78 °C to room temperature resulted in the quantitative formation of a trinuclear ruthenium hydride complex having a μ_3-alkylzinc ligand, $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}ZnR)(\mu_3\text{-}H)$ (**3a**: R = Me, **3b**: R = Et), accompanied by the elimination of alkanes, methane, and ethane (eq 1). Monitoring the reaction of **2** with an equimolar amount of diethylzinc by means of ^1H NMR spectroscopy confirmed quantitative formation of ethane. Complex **3** is soluble and stable in toluene and THF and is slightly soluble in pentane. Addition of excess methanol to complex **3** resulted in protonolysis to give parent pentahydride **2**.



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(1)

3a (R = Me)
3b (R = Et)

Complex **3** was definitely characterized on the basis of the ^1H and ^{13}C NMR spectra. The ^1H NMR spectrum of **3b** exhibited a set of quartet and triplet peaks at δ −0.50 and 1.11 ppm assignable to the methylene and methyl hydrogen of the ethylzinc group, respectively. Generally, a signal of the methylene proton adjacent to an electropositive metal tends to shift upfield. For example, Inoue et al.[12] reported that the resonance signal of the methylene protons of $ZnEt_2$ appeared at δ 0.26 ppm in benzene-d_6. Significant upfield shift (around δ 0.5 ppm) of the methylene signal of ethylzinc derivatives ZnEtR was also reported by van Koten et al.[13] Compared with these values, the corresponding signals for **3b** were observed in significantly

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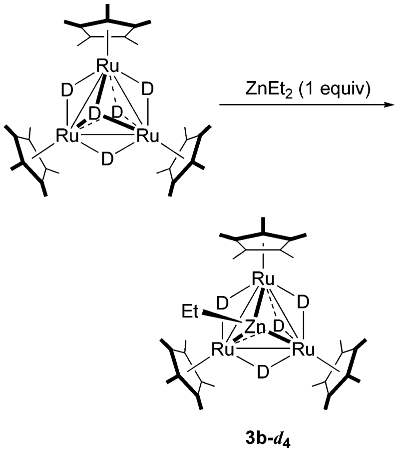
upper field probably due to the shielding effect stemming from the aromatic ring current of the three Cp′ groups.

In the ^{13}C NMR spectrum of **3b**, a signal of the methylene carbon directly bound to the μ_3-zinc atom was observed at δ 20.3 ppm as a triplet with a coupling constant of $J_{CH} = 115.8$ Hz. This J_{CH} value is somewhat smaller than that observed between an sp^3-hybridized carbon nucleus and a proton nucleus and is characteristic of the methyl or methylene group attached to an electropositive metal such as Mg and Zn.

We also confirmed this phenomenon for a μ_3-ethylmagnesium analogue $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}MgEt)(\mu_3\text{-}H)$, of which the methylene carbon signal appeared at δ 4.7 (t, $J_{CH} = 111.0$ Hz) ppm in the ^{13}C NMR spectrum.[11] In addition, Wilke et al. had synthesized a series of Ni−Mg complexes (tmeda)MgR(μ-R)-Ni$(C_2H_4)_2$ (R = Me, Et, ^{n}Pr) and reported that the corresponding coupling constant value lay in the range from 104 to 114 Hz.[14]

In the ^{1}H NMR spectrum of **3b**, resonance signals of the three C_5Me_5 groups were observed to be equivalent at δ 2.00. The ^{13}C NMR spectrum of **3b** exhibited a quartet at δ 13.0 and a singlet at δ 85.4 ppm assignable to the methyl carbons and the ring carbons of the C_5Me_5 ligands, respectively. These results suggested that there was a 3-fold axis perpendicular to the Ru$_3$ plane in the time-averaged structure of **3b**.

Two resonance signals attributable to the hydrides appeared at δ 2.56 (br s, 3 H) and δ −26.97 (br s, 1 H) ppm. These two signals disappeared when the reaction of pentadeuteride complex **2-*d*$_5$** with an equimolar amount of diethylzinc was carried out under the same reaction conditions (eq 2). On the basis of the control experiment, both of these resonance signals were unambiguously assigned to those of the hydrides. The shift of δ 2.56 ppm for the hydrido ligand in **3b** is significantly lower field than that ordinarily observed for the hydrides directly bound to late transition metals. This is most certainly due to a bonding interaction of the hydrido ligands with not only the ruthenium atom but also the zinc atom. Such a downfield shift was reported for zinc hydride species NaHZn$(CH_3)_2$ (δ 3.40) by Shriver et al.[15] This result strongly supports the presence of an electron-deficient bonding interaction among Zn, H, and the two ruthenium atoms in **3b**. As mentioned below, the four-centered interaction was confirmed by means of the X-ray diffraction study of **3b**.



(2)

3b-*d*$_4$

Characteristic features of the NMR spectral parameters of **3b**, a small J_{CH} value for the carbon positioned α to the zinc atom and the downfield shift of the signal of the hydride having a bonding interaction with zinc, were also observed in the ^{1}H and the ^{13}C NMR spectra of **3a**. The ^{13}C NMR signal of the methyl carbon attached to the zinc appeared at δ 5.2 ppm with a coupling constant of $J_{CH} = 119.0$ Hz. The ^{1}H NMR spectrum of **3a** revealed two singlet peaks at δ −26.82 (1H) and 2.95 (3H) ppm, and the latter signal was assignable to the μ_3-H ligands capping the Ru$_3$ and the three Ru$_2$Zn planes, respectively.

Introduction of the metal alkyl group into the Ru$_3$ core most certainly induces the change in the electron density at the ruthenium center due to the polarization of the Ru−M bond. As the ^{13}C chemical shift is not governed by only the electron density at the carbon atom, a simple correlation is not always possible between the electron density at the metal center and the chemical shifts of the carbon directly bound to the metal. The ^{13}C NMR chemical shift is, however, sometimes a good standard for estimating the electron density. A positive correlation has been reported between the ^{13}C chemical shifts of the ring carbons of aromatic compounds and the electron density at the carbon.[16] The resonance signal shifts upfield with an increase in electron density. Such a correlation is observed in a series of ruthenium complexes $[RuX(PR_3)_2(\eta^5\text{-}C_5H_5)]^n$ (X = Cl, C$_2$Ph, CO, CN^{t}Bu; R = Me, Ph; n = 0 and +1).[17] The ^{13}C chemical shifts of the ring carbons of the C_5Me_5 groups in **3a** and **3b** are δ 85.6 and 85.4 ppm, respectively, and are almost equal to that in the parent complex **2** (δ 85.7). These values imply that the charge at the ruthenium center in **3a** and **3b** is neutral or slightly positive, although zinc is more electropositive than ruthenium. Induction of cationic charge at the ruthenium center possibly stems from the Lewis acidic character of the zinc. The available data so far are, however, insufficient to prove a correlation between the ^{13}C chemical shift and the electron density statistically.

The line-shape of the two signals of the hydrido ligands that appeared around δ 2.6 and −27 ppm depends upon the temperature, and they significantly broadened with an increase in the temperature. This considerable spectral change strongly implies an exchange process of the hydrides between the Ru$_3$ site and the three Ru$_2$Zn sites. The variable-temperature ^{1}H NMR spectra of **3b**, which evidently demonstrate the fluxionality of the hydrido ligands, are illustrated in Figure 1.

A set of signals that appeared at δ 2.43 and −27.05 ppm were slightly broadened, $w_{1/2}$ = 5.3 and 11.4 Hz, respectively, due to the site-exchange process even at room temperature. With the decrease in the temperature, both peaks sharpened and shifted downfield. At −40 °C, these two hydrido signals are observed at δ 2.69 and −26.98 ppm as doublet peaks with a mutual coupling constant of 2.0 Hz. In spite of lowering the temperature to −60 °C, the line-shapes and the chemical shifts of these signals did not change any more. The spectrum measured at −40 °C was, therefore, concluded to be a slow-limit spectrum. Although these signals significantly broadened, in turn, upon a rise in the temperature to 100 °C, they never coalesced into one peak.

This temperature dependence of the spectra strongly implies the site-exchange process of the hydrido ligands in the μ_3-alkylzinc complex **3**. Simulation of the spectra was carried out on the hydride region by using a gNMR program package, and the result is shown in the right half of Figure 1. According to

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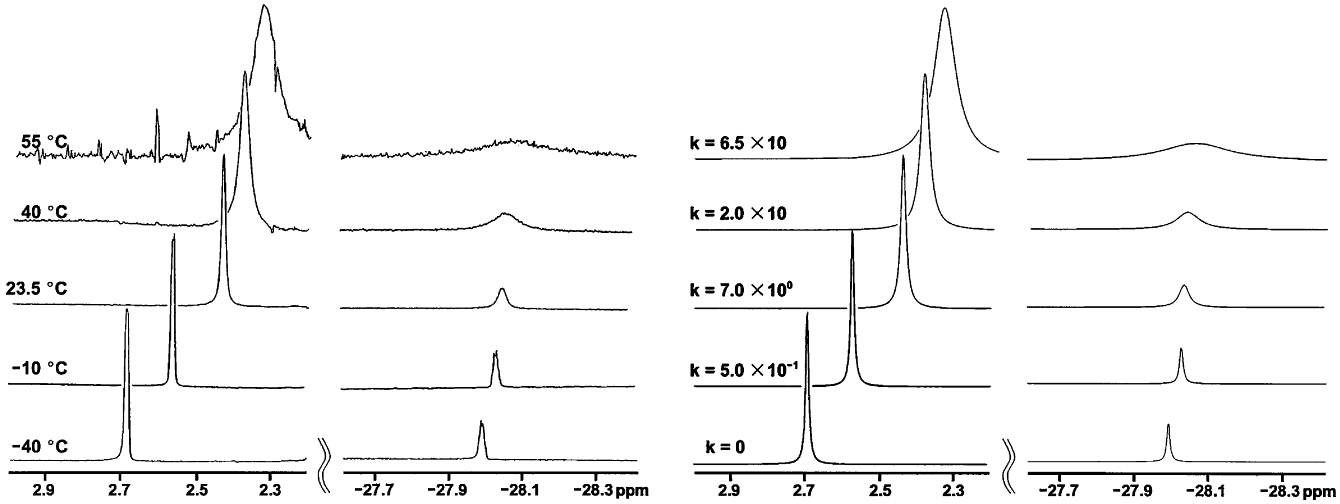
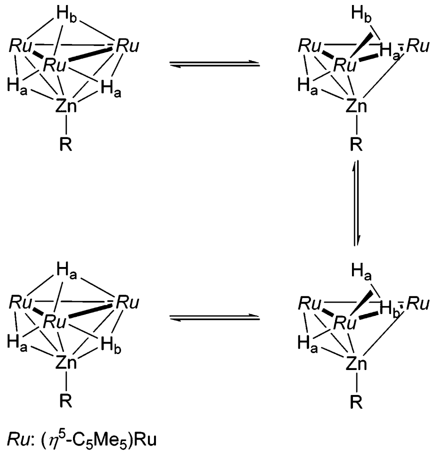


Figure 1. Variable-temperature ^{1}H NMR spectra of $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}ZnEt)(\mu_3\text{-}H)$ (**3b**) showing hydrido signals (left) and results of simulation (right).

Scheme 2. Possible Mechanism for the Site-Exchange of the Hydrido Ligands in 3b[a]

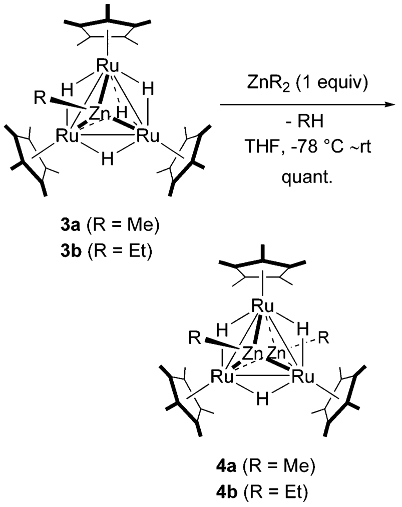


[a] One of the three μ_3-hydrido ligands located above the Ru_2Zn plane is omitted for clarity.

the line-shape analysis of the variable-temperature ^{1}H NMR spectra, the free energy of activation $\Delta G^{\ddagger}$ for this fluxional process for **3b** was estimated at 15.4 ± 0.1 kcal mol^{-1} at 0 °C ($\Delta S^{\ddagger} = -1.5 \pm 1.3$ cal mol^{-1} K^{-1}, $\Delta H^{\ddagger} = 15.0 \pm 0.4$ kcal mol^{-1}). The $\Delta G^{\ddagger}$ value for **3a** was similarly estimated at 15.2 ± 0.1 kcal mol^{-1} at 0 °C ($\Delta S^{\ddagger} = -0.3 \pm 0.7$ cal mol^{-1} K^{-1}, $\Delta H^{\ddagger} = 15.1 \pm 0.2$ kcal mol^{-1}).

Notably, the $\Delta S^{\ddagger}$ values for both **3a** and **3b** are nearly 0 within experimental error, and this indicates that the site-exchange process is most likely an intramolecular process (Scheme 2). The enthalpy of activation, ca. 15 kcal mol^{-1}, for this dynamic process is comparable to that calculated for the site-exchange of the hydride between the terminal and the bridging positions in $Re_2H_2(CO)_9$ (30−40 kJ mol^{-1}) by way of an intermediary η^2-H_2 complex.[18]

It is noteworthy that the reaction of **2** with dialkylzinc proceeds stepwise. Treatment of the mono-μ_3-alkylzinc complex **3** with an additional equimolar amount of dialkylzinc leads to the quantitative formation of a bis-μ_3-alkylzinc complex, $(Cp'Ru)_3(\mu_3\text{-}ZnR)_2(\mu\text{-}H)_3$ (**4**), which has triply bridging alkylzinc groups on both faces of the Ru_3 plane. The reaction of **3a** with dimethylzinc quantitatively yielded $(Cp'Ru)_3(\mu_3\text{-}ZnMe)_2(\mu\text{-}H)_3$ (**4a**), and the ethylzinc analogue $(Cp'Ru)_3(\mu_3\text{-}ZnEt)_2(\mu\text{-}H)_3$ (**4b**) was obtained in a similar manner (eq 3). These di-μ_3-alkylzinc complexes are, of course, directly synthesized by the reaction of **2** with more than two molar amount of the corresponding dialkylzinc reagent. Treatment of **2** with 5 equiv of dimethylzinc exclusively yielded the bicapped complex **4a**.



(3)

Bis-μ_3-ZnMe complex **4a** was identified on the basis of the observation of three singlet signals for the methyl protons of the methyl zinc ligands, the Cp′ group, and the hydrides at δ −1.32 (s, 6 H), 1.97 (s, 45 H), and 7.96 (s, 3 H) ppm, respectively, in the ^{1}H NMR spectrum. The validity of the assignment of the signal at δ 7.96 was proved by the labeling experiment using triruthenium pentadeuteride **2-d_5** instead of pentahydride **2**. The reaction of **2-d_5** with 2 equiv of diethylzinc smoothly proceeded to result in the formation of an isotopomer, $(Cp'Ru)_3(\mu_3\text{-}ZnEt)_2(\mu\text{-}D)_3$ (**4b-d_3**). The signal observed at δ 7.96 assignable to the hydrido ligands of **4b** disappeared in the ^{1}H NMR spectrum of the product. The intensity ratio of 2:15 between the methylzinc group and the C_5Me_5 groups unambiguously showed the introduction of the two μ_3-methylzinc groups into the Ru_3 core.

In the ^{13}C NMR spectrum of **4a**, a signal assignable to the methylzinc groups appeared at δ 6.0 with a coupling constant of $J_{CH} = 119.4$ Hz. As mentioned above, the J_{CH} value of 119.4 Hz is slightly smaller than that usually observed for the

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[18] Bergamo, M.; Beringhelli, T.; D'Alfonso, G.; Mercandelli, P.; Sironi, A. *J. Am. Chem. Soc.* **2002**, *124*, 5117.

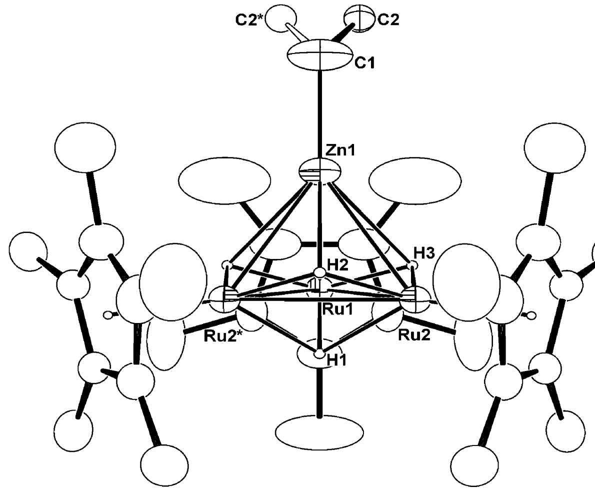

Figure 2. Molecular structure of $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}ZnEt)(\mu_3\text{-}H)$ (**3b**), with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms C2*: *x*, −*y*, *z*.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}ZnEt)(\mu_3\text{-}H)$, 3b

bond lengths		bond angles	
Ru1−Ru2	2.7451(6)	Ru2−Ru1−Ru2*	59.81(2)
Ru2−Ru2*	2.7372(8)	Ru2*−Ru2−Ru1	60.095(10)
Ru1−Zn1	2.6749(10)	Ru1−Zn1−Ru2	61.98(2)
Ru2−Zn1	2.6562(8)	Ru2−Zn1−Ru2*	62.03(3)
Zn1−C1	1.984(8)	Zn1−Ru1−Ru2	58.67(2)
C1−C2	1.400(17)	Zn1−Ru2−Ru1	59.34(2)
		Zn1−Ru2−Ru2*	58.986(13)

methylene group of an organic compound and is characteristic of the methyl or methylene group directly attached to an electropositive metal such as Mg and Zn.

The chemical shift of δ 7.96 ppm for the hydrido ligand is much lower than that of the mono-μ_3-alkylzinc complex **3a** (δ 2.95) and is comparable to that of the proton signal in the 1:2 adduct of sodium hydride and dimethylzinc, $NaH[Zn(CH_3)_2]_2$ (δ 5.44), in which the hydride is considered to have a bonding interaction with zinc.[15] These results strongly indicate that the hydrido ligands have a bonding interaction with the zinc atom.

X-ray Crystal Structure of μ_3-Ethylzinc Complex 3b and Bis-μ_3-methylzinc Complex 4a. The molecular structure of μ_3-ethylzinc complex **3b** was definitely determined by means of an X-ray diffraction study using a reddish-brown single crystal obtained from dioxane at room temperature. The X-ray crystallography of **3b** clearly demonstrated a trinuclear structure triply bridged by the ethylzinc group (Figure 2). The crystal data for **3b** are given in the Experimental Section (Table 4), and relevant bond lengths and angles are listed in Table 1.

The Ru_3 core consists of an approximately equilateral triangle, and one face of the Ru_3 core is bridged by an ethylzinc group. Complex **3b** is a 44*e* complex as well as the parent triruthenium pentahydride **2**, and the formal Ru−Ru bond order should be 5/3 according to the EAN rule. The average Ru−Ru distance of 2.7424 Å in **3b** is very similar to that of **2** (ca. 2.75 Å).[19] Not only electron density at the ruthenium centers but also the size of the reaction site are likely affected by the introduced triply bridging ligand. Complex **3b** provides a reaction site, which is a triangular space surrounded by the three Cp′ groups, on the opposite side of the μ_3-ZnEt group with respect to the Ru_3 plane. The three Ru-Cp′(centroid) vectors tilt away from the μ_3-ZnEt group by 4.6° (av) with respect to the Ru_3 plane, and the size of the reaction site of **3b** is, therefore, slightly reduced in comparison with that of **2**. The triply bridging zinc atom is located above the center of the Ru_3 triangle, and the average Ru−Zn distance is 2.662 Å. This is significantly longer than the sum of the covalent radii of ruthenium and zinc (ca. 2.50 Å).

A search of the Cambridge structural database found only one precedent, $\{Pt_3(\mu\text{-}CO)_3(PPh^iPr_2)_3\}\{\mu_3\text{-}ZnI_2\}$,[7b] for the trinuclear transition metal complex having a triply bridging zinc ligand. Complex **3b** is the second example of a structurally well-defined trinuclear cluster capped by zinc.

Hydrogen atoms bound to the metal atom were located in the difference Fourier maps and were refined isotropically. Three of the four hydrogen atoms are located above the Ru_2Zn plane and bridge these three metals. The rest lies above the center of the Ru_3 plane and triply bridges the ruthenium centers. The result that the three hydrido ligands have a bonding interaction with the zinc atom is well consistent with the downfield shift of their resonance signal in the ^1H NMR spectrum.

As mentioned above, the Ru−Zn distance of ca. 2.66 Å is significantly longer than the sum of the covalent radii, ca. 2.50 Å, of Ru and Zn. The interatomic distances between the transition metal and the zinc in several metal hydrido complexes are listed in Table 2. The existence of a bridging hydride demonstrates a tendency to elongate the transition metal−zinc bond. In the case of having no bridging hydrido ligand, the transition metal−zinc distance is almost equal to the sum of the ionic radii or less. The Ru−Zn distance of 2.66 Å in **3b** probably reflects the bridging coordination of the hydrido ligand between the ruthenium and the zinc.

The structure of bis-μ_3-alkylzinc complex **4** obtained by the reaction of **3** with dialkylzinc was also confirmed by means of an X-ray diffraction study. A single crystal of **4a** suitable for X-ray diffraction study was available from a THF solution at −5 °C. The pentametallic Ru_3Zn_2 cluster **4a** crystallized in the centrosymmetric space group *P*6₃/*m*. An ORTEP drawing is illustrated in Figure 3. Crystallographic data for **4a** are summarized in the Experimental Section (Table 4), and selected bond lengths and bond angles are listed in Table 3.

Two zinc atoms are located at the axial positions in approximate trigonal bipyramidal geometry. Bis-μ_3-ZnMe complex **4a** is also a 44*e* complex as well as parent complex **2** and mono-μ_3-ZnEt-capped complex **3b**, and the Ru−Ru bond length of 2.7581(9) Å of **4a** is almost equal to those of **2** and **3b**. Although the positions of the three hydrido ligands are not definitely determined due to the disordered structure of **4a** related by S_3 symmetry, the interatomic distance of 2.6414(10) Å between the ruthenium and the zinc atoms strongly implies that the hydrido ligand bridges the ruthenium and the zinc atoms. The hydrides likely lie above three of the six Ru_2Zn planes or on three of the six Ru−Zn edges. On the basis of the ^1H NMR spectrum, it can be concluded that the three hydrides in **4a** rapidly exchange their coordination sites in solution.

Reaction of $(Cp'Ru)_2(\mu\text{-}H)_4$ (1) with Dialkylzinc: Formation of Novel Dinuclear Complexes Containing Bridging Alkylzinc Ligands. The reaction of a transition metal polyhydride with dialkylzinc is a versatile method for the formation of a transition metal−zinc bond, and this method is applicable to the dinuclear ruthenium polyhydride. The reaction of dinuclear ruthenium tetrahydride **1** with 1 equiv of dimethylzinc

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[19] Suzuki, H.; Kakigano, T.; Tada, K.; Igarashi, M.; Matsubara, K.; Inagaki, A.; Oshima, M.; Takao, T. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 67.

[20] Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 6163.

Table 2. Bond Type of the Hydrides and Bond Lengths between Transition Metal (M) and Zinc (Zn) for Hydrido Complexes Having M−Zn Bonds

complex	bond type[a]	bond length (Å)	r (Å)[b]	Δ (Å)[c]	ref
$Cp_2MoH_2(ZnBr_2)$	M−(μ-H)−Zn	2.793(3)	2.54	0.25	6a
$Mn_2Zn(\mu\text{-}H)_2(CO)_6(tmeda)(\mu\text{-}tedip)$	M−(μ-H)−Zn	2.544(4)	2.42	0.12	5
$V_2Zn_2H_4(BH_4)_2(PMePh_2)_4$	M−(μ-H)−Zn	2.656(1)	2.47	0.19	20
$[(dippp)Rh]_2(\mu\text{-}H)_2(\mu\text{-}ZnCp)_2$	M−(μ-H)−Zn	2.5854(7)	2.50	0.09	9h
Cp_2NbH_2ZnCp	H−M−Zn	2.5407(7)	2.59	−0.05	9e
$Cp_2TaH(ZnCp)_2$	H−M−Zn	2.590(2)	2.59	0.00	9f
$[MeC(CH_2PPh_2)_3]RhH_2ZnN(SiMe_3)_2$	H−M−Zn	2.3550(13)	2.50	−0.14	7a

[a] M is a corresponding transition metal. [b] r is the sum of the two covalent radii (M, Zn). [c] Δ is the difference between an actual measurement and r.

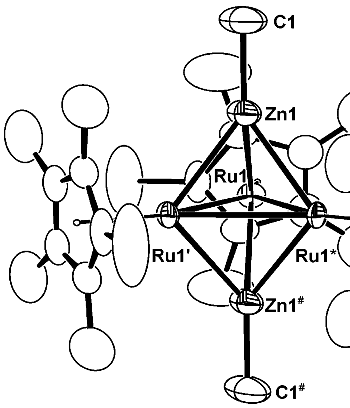
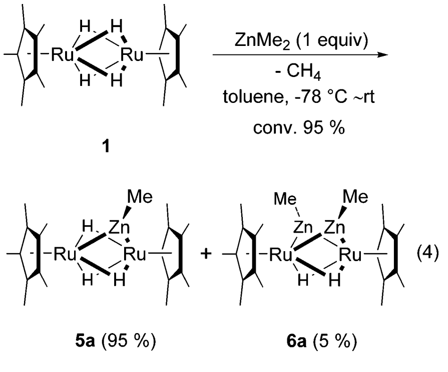


Figure 3. Molecular structure of $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}ZnMe)_2$ (**4a**), with thermal ellipsoids at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms Ru1*: $1-y, x-y+1, z$; Ru1′: $y-x, 1-x, z$; Zn1#: $x, y, -z+0.5$.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for $\{Cp'Ru(\mu\text{-}H)\}_3(\mu_3\text{-}ZnMe)_2$, 4a

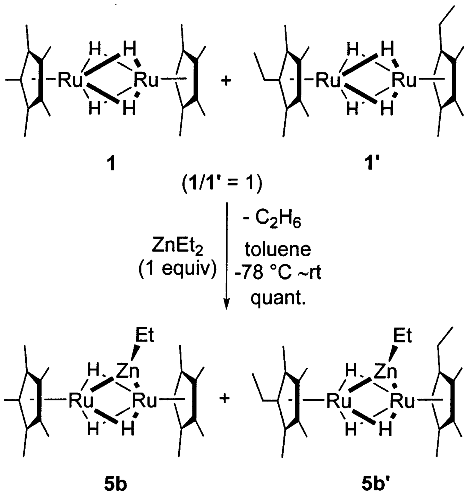
bond lengths		bond angles	
Ru1−Ru1*	2.7581(9)	Ru1*−Ru1−Ru1′	60.00(0)
Ru1−Zn1	2.6414(10)	Ru1−Zn1−Ru1*	62.95(3)
Zn1−C1	1.992(12)	Zn1−Ru1−Zn1#	105.85(4)

resulted in the formation of a 95:5 mixture of the mono-μ-ZnMe complex $(Cp'Ru)_2(\mu\text{-}ZnMe)(\mu\text{-}H)_3$ (**5a**) and the bis-μ-ZnMe complex $(Cp'Ru)_2(\mu\text{-}ZnMe)_2(\mu\text{-}H)_2$ (**6a**) (eq 4). The reaction was accompanied with liberation of methane, which was detected by means of ^1H NMR spectroscopy.



The ethylzinc analogue $(Cp'Ru)_2(\mu\text{-}ZnEt)(\mu\text{-}H)_3$ (**5b**) was synthesized in a similar manner by using 1 equiv of diethylzinc instead of dimethylzinc. While the mono-μ-ZnEt complex **5b** is selectively obtained in the 1:1 reaction of **1** with diethylzinc, formation of **5a** is always accompanied with a small amount of bis-μ-ZnMe complex **6a** even in the reaction of **1** with slightly less dimethylzinc, as mentioned above. This result clearly indicates that a ratio $k(\mathbf{5}-ZnR_2)/k(\mathbf{1}-ZnR_2)$, where $k(\mathbf{5}-ZnR_2)$ and $k(\mathbf{1}-ZnR_2)$ are the rate constant of the reaction of ZnR_2 with **1** and that of ZnR_2 with **5**, respectively, is smaller in the case of R = Et than the case of R = Me. This is probably due to the bulkiness of the dialkylzinc reagent.

Scheme 3. Crossover Experiment among 1, 1′, and $ZnEt_2$

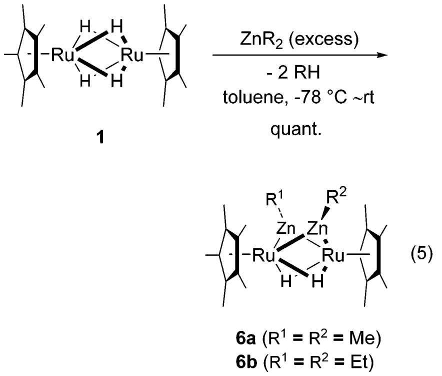


The reaction path involving fragmentation to a mononuclear species and subsequent recombination to dinuclear complex **5** was ruled out on the basis of the following crossover experiment. Treatment of a 1:1 mixture of **1** and $\{(C_5Me_4Et)Ru\}_2(\mu\text{-}H)_4$ (**1′**) with diethylzinc led to the formation of a 1:1 mixture of **5b** and $\{(C_5Me_4Et)Ru\}_2(\mu\text{-}ZnEt)(\mu\text{-}H)_3$ (**5b′**), and the crossover product $\{(C_5Me_5)Ru\}\{(C_5Me_4Et)Ru\}(\mu\text{-}ZnEt)(\mu\text{-}H)_3$ (**5b″**) was not detected at all (Scheme 3).

The mono-μ-ZnR complex **5** was identified by means of NMR spectroscopy. The ^1H NMR spectrum of **5a** recorded at room temperature exhibited three singlet signals with the intensity ratio of 30:3:3, assignable to C_5Me_5, μ-ZnMe, and the hydrido ligands, respectively, at δ 1.82, 0.25, and −15.06 ppm. The ^1H NMR spectrum of **5b** is very similar to that of **5a** except for the signal of the alkyl group bound to the zinc atom. This proved the structural similarity between **5a** and **5b**. In the ^1H NMR spectra of both **5a** and **5b**, the signal of the three hydrido ligands was observed to be equivalent at room temperature despite the coordination of the hydrides at the different sites, namely, *cis* and *trans* to the μ-ZnR group. With a decrease in the temperature, the signal broadened and then split into two singlets with the intensity ratio of 1:2. This implies the site-exchange of the hydrido ligands between the *cis* and the *trans* sites (vide infra).

Addition of a large excess amount of dialkylzinc to **1** causes overreaction to generate a bis-μ-ZnR-bridged complex, $(Cp'Ru)_2(\mu\text{-}ZnR)_2(\mu\text{-}H)_2$ (**6a**: R = Me; **6b**: R = Et) (eq 5). However, the third μ-ZnR group cannot be introduced into the molecule.

Strict control of the ratio between complex **1** and dialkylzinc is, therefore, necessary to obtain the mono-μ-ZnR complex **5** selectively.



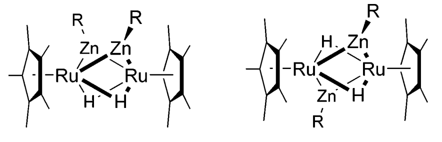
1

(5)

6a ($R^1 = R^2 =$ Me)
6b ($R^1 = R^2 =$ Et)

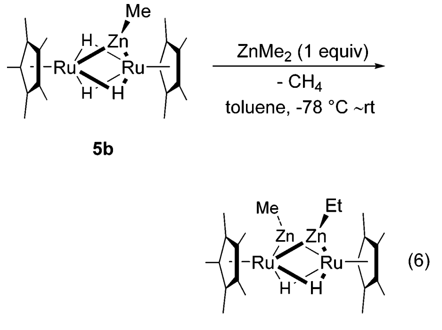
Although there are two possible structures, namely, *cis*- and *trans*-geometries, for the bis-μ-ZnR complex **6** (Chart 2), they are readily distinguishable by analyzing the ^{1}H NMR spectrum of the mixed-ligand complex obtained by the reaction of **5b** and dimethylzinc.

Chart 2



6-*cis* **6-*trans***

The reaction of **5b** with 1 equiv of dimethylzinc in toluene exclusively afforded the mixed-ligand complex $(Cp'Ru)_2(\mu\text{-}ZnMe)(\mu\text{-}ZnEt)(\mu\text{-}H)_2$ (**6c**) (eq 6). In the ^{1}H NMR spectrum of **6c**, the signals of the hydrido ligands appeared at δ −13.95 and −14.64 ppm with equal intensity. This spectrum unequivocally demonstrates that bis-μ-ZnR complex **6c** is in the *cis*-geometry. Therefore, we concluded that the bis-μ-ZnR complexes **6a** and **6b** also have *cis*-geometries as well as **6c**.



5b

(6)

6c

The bridging alkylzinc group readily undergoes protonolysis to regenerate **1** upon treatment with an excess amount of methanol or ethanol.

The variable-temperature ^{1}H NMR spectra of **5** demonstrated fluxionality of the signals of the hydrido signals. The hydride region of the VT-^{1}H NMR spectra of **5b** are illustrated in Figure 4. While the signal of the hydrides was observed as a broad signal at room temperature and it decoalesced and split into two signals with the intensity ratio of 2:1 below ca. −20 °C, the signal of the C_5Me_5 group remained unchanged. A site-exchange process of the three hydrides among the two *cis*- and a *trans*-site reasonably explains the fluxionality of the spectra.

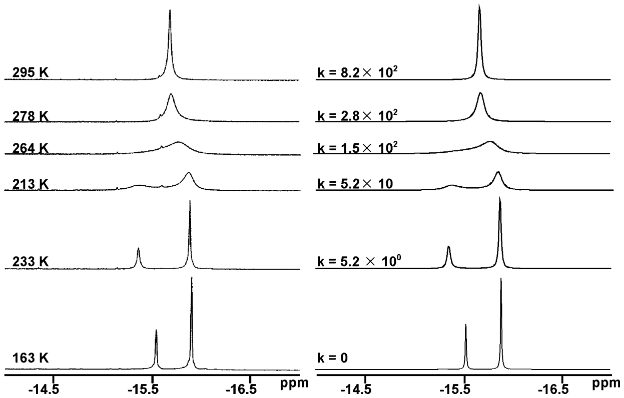
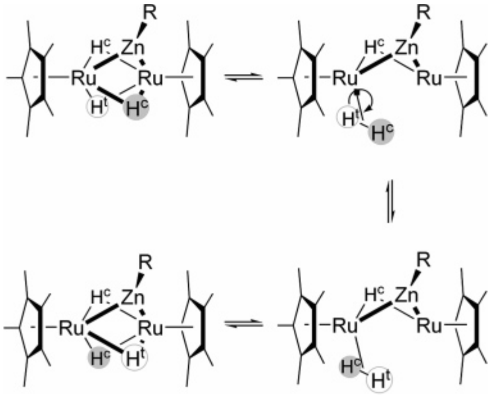


Figure 4. Variable-temperature ^{1}H NMR spectra of $(Cp'\text{-}Ru)_2(\mu\text{-}ZnEt)(\mu\text{-}H)_3$ (**5b**) showing hydrido signals (left) and results of simulation (right).

Scheme 4. Plausible Mechanism for the Site-Exchange of the Hydrido Ligands in 5b



The activation parameters were estimated at $\Delta S^\ddagger = -5.8 \pm 2.0$ cal mol^{-1} K^{-1} and $\Delta H^\ddagger = 11.0 \pm 0.5$ kcal mol^{-1} for **5a** and $\Delta S^\ddagger = -12.4 \pm 1.8$ cal mol^{-1} K^{-1} and $\Delta H^\ddagger = 9.6 \pm 0.5$ kcal mol^{-1} for **5b** by the line-shape analysis of the VT-^{1}H NMR spectra. Small absolute values of the enthalpy of activation imply that the site-exchange of the hydrides is an intramolecular process and proposes a possible reaction path involving an intermediary η^2-H_2 species (Scheme 4). The enthalpies of activation of 11 and 9.6 kcal mol^{-1} for **5a** and **5b**, respectively, are close to that calculated for the site-exchange of the hydrides in $Re_2H_2(CO)_9$ via an η^2-H_2 intermediate.[18]

Conclusion

A change in the electronic environment of the reaction field deeply affects the course of the reaction, and the development of a reasonable and efficient method to control electron density at the metal site of the polyhydrido cluster has, therefore, been one of the main research targets in our group. To increase the partial anionic charge at the ruthenium center of the cluster by forming a polarized Ru−metal bond, we have examined the reaction of the ruthenium cluster with a variety of metal alkyls that contain an electropositive metal. As a result, we have successfully synthesized trinuclear ruthenium hydrido complex **3**, which has a triply bridging alkylzinc group, by the reaction of triruthenium pentahydrido complex **2** with dialkylzinc ZnR_2 (R = Me and Et). Bis-μ_3-ZnR complex **4** was quantitatively obtained by the treatment of monocapped complex **3** with 1 equiv of ZnR_2. The ^{1}H NMR spectra of **3** and **4** revealed that the three hydrido ligands of each complex have bonding interactions with not only the ruthenium atoms but also the zinc atom. The weak bonding interaction between the three hydrido ligands and the zinc atom was clearly confirmed by the X-ray diffraction study of **3b**, while metal-bound hydrogen atoms were not located in the difference Fourier maps of **4**. In the variable-temperature ^{1}H NMR study of **3b**, activation parameters, $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$, for the coordination-site exchange process among the hydrido ligands were estimated at -1.5 ± 1.3 cal mol^{-1} K^{-1} and 15.0 ± 0.4 kcal mol^{-1}, respectively. These values strongly implied that the process was intramolecular and hydrido ligands exchanged via an η^2-H$_2$ intermediate.

Dinuclear ruthenium complex **5**, having a μ-ZnR group, was also synthesized by the reaction of diruthenium tetrahydrido complex **1** with dialkylzinc. Complex **5** further reacted with 1 equiv of ZnR$_2$ to yield bis-μ-ZR complex **6**, selectively. A crossover experiment, namely, the reaction of μ-ZnEt complex **5b** with ZnMe$_2$, confirmed the *cis*-geometry of the two μ-alkylzinc ligands in **6**. The variable-temperature ^{1}H NMR experiment of **5** demonstrated fluxionality of the hydrido ligands, and the activation parameters were estimated at $\Delta S^{\ddagger} = -5.8 \pm 2.0$ cal mol^{-1} K^{-1} and $\Delta H^{\ddagger} = 11.0 \pm 0.5$ kcal mol^{-1} for **5a** and $\Delta S^{\ddagger} = -12.4 \pm 1.8$ cal mol^{-1} K^{-1} and $\Delta H^{\ddagger} = 9.6 \pm 0.5$ kcal mol^{-1} for **5b** by the line-shape analysis. On the basis of these activation parameters, we proposed reaction paths that involved an η^2-H$_2$ intermediate for the site-exchange of the hydrido ligands in **5**.

Estimation of the electronic charge at the ruthenium sites of the resulting cluster complexes, **3**, **4**, **5**, and **6**, and examination of their reactivities would be the basic imperatives subsequent to the synthetic studies.

Experimental Section

General Procedures. All manipulations were undertaken utilizing standard Schlenk, high-vacuum line, and glovebox techniques under an atmosphere of argon. Solvents were distilled under an atmosphere of argon from sodium benzophenone ketyl (toluene, THF, and Et$_2$O) or P$_2$O$_5$ (pentane). Benzene-d_6, toluene-d_8, and THF-d_8 were distilled under an atmosphere of argon from sodium benzophenone ketyl and stored under an atmosphere of argon. Other reagents used in this study that were purchased from commercial sources were used without further purification. JEOL-GSX-500, Varian Gemini-300, and Varian INOVA 400 Fourier transform spectrometers were used for NMR spectroscopy. ^{1}H and ^{13}C NMR spectra were referenced to an internal solvent and corrected to TMS. Elemental analyses were recorded on a Perkin-Elmer 2400II. Dinuclear ruthenium complexes (Cp′Ru)$_2$(μ-H)$_4$ (**1**) and {(η^5-C$_5$Me$_4$Et)-Ru}$_2$(μ-H)$_4$ (**1′**) and trinuclear ruthenium complexes (Cp′Ru)$_3$(μ-H)$_3$(μ_3-H)$_2$ (**2**) were prepared according to a previously published method.[2a,b,e,h,4]

Preparation of {Cp′Ru(μ-H)}$_3$(μ_3-ZnMe)(μ_3-H) (3a). A 50 mL Schlenk tube was charged with **2** (143 mg, 0.201 mmol) and THF (10 mL). After cooling the solution to −78 °C, dimethylzinc (1.1 M solution in toluene, 180 μL, 0.198 mmol) was added dropwise with vigorous stirring. The cooling bath was removed and the reaction mixture was warmed to room temperature. The color of the solution turned reddish-brown. Removal of the solvent under reduced pressure gave 159 mg (0.199 mmol, 99%) of **3a** as a reddish-brown solid. ^{1}H NMR (300 MHz, rt, C$_6$D$_6$, δ/ppm): −26.82 (br s, $w_{1/2} = 25.2$ Hz, 1 H, Ru*H*), −1.21 (s, 3 H, Zn*Me*), 2.00 (s, 45 H, C$_5$*Me*$_5$), 2.95 (br s, $w_{1/2} = 25.2$ Hz, 3 H, Ru*H*). ^{13}C NMR (75.5 MHz, rt, C$_6$D$_6$, δ/ppm): 5.2 (q, $J_{\mathrm{CH}} = 119.0$ Hz, ZnMe), 13.0 (q, $J_{\mathrm{CH}} = 127.0$ Hz, C$_5$*Me*$_5$), 85.6 (s, *C*$_5$Me$_5$). Anal. Calcd for C$_{31}$H$_{52}$Ru$_3$Zn: C, 46.93; H, 6.61. Found: C, 47.16; H, 6.46.

Preparation of {Cp′Ru(μ-H)}$_3$(μ_3-ZnEt)(μ_3-H) (3b). A 50 mL Schlenk tube was charged with **2** (373 mg, 0.522 mmol) and THF (30 mL). After cooling the solution to −78 °C, diethylzinc (1.0 M solution in hexane, 525 μL, 0.525 mmol) was added dropwise with vigorous stirring. The cooling bath was removed and the reaction mixture was warmed to room temperature. The color of the solution turned reddish-brown. Removal of the solvent under reduced pressure gave 420 mg (0.520 mmol, 99%) of **3b** as a reddish-brown solid. ^{1}H NMR (300 MHz, rt, C$_6$D$_6$, δ/ppm): −26.97 (br s, $w_{1/2} = 11.0$ Hz, 1 H, Ru*H*), −0.50 (q, $J_{\mathrm{HH}} = 7.8$ Hz, 2 H, Zn*CH*$_2$CH$_3$), 1.11 (t, $J_{\mathrm{HH}} = 7.8$ Hz, 3 H, ZnCH$_2$*CH*$_3$), 2.00 (s, 45 H, C$_5$*Me*$_5$), 2.56 (br s, $w_{1/2} = 6.0$ Hz, 3 H, Ru*H*). ^{13}C NMR (125 MHz, rt, C$_6$D$_6$, δ/ppm): 11.8 (q, $J_{\mathrm{CH}} = 123.0$ Hz, ZnCH$_2$*CH*$_3$), 13.0 (q, $J_{\mathrm{CH}} = 125.4$ Hz, C$_5$*Me*$_5$), 20.3 (t, $J_{\mathrm{CH}} = 115.8$ Hz, Zn*CH*$_2$CH$_3$), 85.4 (s, *C*$_5$Me$_5$). Anal. Calcd for C$_{32}$H$_{54}$Ru$_3$Zn: C, 47.61; H, 6.74. Found: C, 47.42; H, 6.71.

Preparation of {Cp′Ru(μ-D)}$_3$(μ_3-ZnEt)(μ_3-D) (3b-*d*$_4$). A 50 mL Schlenk tube was charged with a trinuclear ruthenium penta-deuteride complex **2-*d*$_5$** (25 mg, 0.035 mmol) and THF (5 mL). After cooling the solution to −78 °C, diethylzinc (35 μL, 0.035 mmol) was added dropwise with vigorous stirring. The cooling bath was removed and the reaction mixture was warmed to room temperature. The color of the solution turned reddish-brown. Removal of the solvent under reduced pressure gave 28 mg (0.034 mmol, 98%) of **3b-*d*$_4$** as a reddish-brown solid. Measuring the ^{1}H NMR spectrum of **3b-*d*$_4$** in C$_6$D$_6$, two resonance signals attributable to the hydrides of **3b** (δ −26.97 and 2.56) disappeared.

Preparation of {Cp′Ru(μ-H)}$_3$(μ_3-ZnMe)$_2$ (4a). A 50 mL Schlenk tube was charged with **2** (76 mg, 0.106 mmol) and toluene (10 mL). After cooling the solution to −78 °C, dimethylzinc (200 μL, 0.220 mmol) was added dropwise with vigorous stirring. The cooling bath was removed and the reaction mixture was stirred at room temperature for 24 h. Removal of the solvent and the remaining reagent under reduced pressure gave 209 mg (0.099 mmol, 93%) of **4a** as a brown solid. ^{1}H NMR (300 MHz, rt, C$_6$D$_6$, δ/ppm): −1.32 (s, 6 H, Zn*Me*), 1.97 (s, 45 H, C$_5$*Me*$_5$), 7.96 (s, 3 H, Ru*H*). ^{13}C NMR (125 MHz, rt, C$_6$D$_6$, δ/ppm): 6.0 (q, $J_{\mathrm{CH}} = 119.4$ Hz, Zn*Me*), 12.8 (q, $J_{\mathrm{CH}} = 126.3$ Hz, C$_5$*Me*$_5$), 86.5 (s, *C*$_5$Me$_5$). Anal. Calcd for C$_{32}$H$_{54}$Ru$_3$Zn$_2$: C, 44.04; H, 6.24. Found: C, 43.99; H, 6.30.

Preparation of {Cp′Ru(μ-H)}$_3$(μ_3-ZnEt)$_2$ (4b). A 50 mL Schlenk tube was charged with **2** (166 mg, 0.233 mmol) and THF (10 mL). After cooling the solution to −78 °C, diethylzinc (1.0 M solution in hexane, 600 μL, 0.600 mmol) was added dropwise with vigorous stirring. The cooling bath was removed and the reaction mixture was stirred at room temperature for 24 h. Removal of the solvent and the remaining reagent under reduced pressure gave 209 mg (0.232 mmol, 99%) of **4b** as a brown solid. Complex **4b** was also obtained by the reaction of **3b** (25 mg, 0.031 mmol) with an equivalent of ZnEt$_2$ in toluene for 24 h. ^{1}H NMR (300 MHz, rt, C$_6$D$_6$, δ/ppm): −1.32 (s, 6 H, Zn*Me*), 1.97 (s, 45 H, C$_5$*Me*$_5$), 7.96 (s, 3 H, Ru*H*). ^{13}C NMR (125 MHz, rt, C$_6$D$_6$, δ/ppm): 6.0 (q, $J_{\mathrm{CH}} = 119.4$ Hz, Zn*Me*), 12.8 (q, $J_{\mathrm{CH}} = 126.3$ Hz, C$_5$*Me*$_5$), 86.5 (s, *C*$_5$Me$_5$). Anal. Calcd for C$_{34}$H$_{58}$Ru$_3$Zn$_2$: C, 45.33; H, 6.49. Found: C, 45.37; H, 6.11.

Preparation of {Cp′Ru(μ-D)}$_3$(μ_3-ZnEt)$_2$ (4b-*d*$_3$). A 50 mL Schlenk tube was charged with a trinuclear ruthenium penta-deuteride complex **2-*d*$_5$** (25 mg, 0.035 mmol) and THF (5 mL). After cooling the solution to −78 °C, diethylzinc (1.0 M solution in hexane, 70 μL, 0.070 mmol) was added dropwise with vigorous stirring. The cooling bath was removed and the reaction mixture was stirred at room temperature for 24 h. Removal of the solvent under reduced pressure gave 28 mg (0.034 mmol, 98%) of **4b-*d*$_3$** as a reddish-brown solid. Measuring the ^{1}H NMR spectrum of **4b-*d*$_3$** in C$_6$D$_6$, a resonance signal attributable to the hydrides of **4b** (δ 8.08) disappeared.

Preparation of (Cp′Ru)$_2$(μ-H)$_3$(μ-ZnMe) (5a). A 50 mL Schlenk tube was charged with **1** (80 mg, 0.168 mmol) and toluene (7 mL). After cooling the solution to −78 °C, dimethylzinc (160

μL, 0.168 mmol) was added dropwise with vigorous stirring. The color of the solution turned bright red immediately. The cooling bath was removed and the reaction mixture was warmed to room temperature. Removal of the solvent under reduced pressure gave the crude product **5a** as an orange solid (90 mg, ca. 90% purity based on ^{1}H NMR). The rest was a 1:1 mixture of the starting material **1** and a bis-μ-ZnMe complex **6a** (see below). ^{1}H NMR (300 MHz, rt, C_6D_6, δ/ppm): -15.06 (br s, $w_{1/2} = 20.4$ Hz, 3 H, Ru*H*), 0.25 (s, 3 H, Zn*Me*), 1.82 (s, 30 H, C_5*Me*$_5$). ^{13}C NMR (125 MHz, rt, C_6D_6, δ/ppm): 1.2 (q, $J_{CH} = 122.5$ Hz, Zn*Me*), 12.6 (q, $J_{CH} = 126.5$ Hz, C_5*Me*$_5$), 85.4 (s, *C*$_5$Me$_5$).

Preparation of (Cp′Ru)$_2$(μ-H)$_3$(μ-ZnEt) (5b). A 50 mL Schlenk tube was charged with **1** (118 mg, 0.248 mmol) and toluene (20 mL). After cooling the solution to −78 °C, diethylzinc (0.8 M solution in hexane, 310 μL, 0.248 mmol) was added dropwise with vigorous stirring. The color of the solution turned bright red immediately. The cooling bath was removed, and removal of the solvent under reduced pressure gave 141 mg (0.248 mmol, 100%) of **5b** as an orange solid. ^{1}H NMR (300 MHz, rt, C_6D_6, δ/ppm): -15.09 (br s, $w_{1/2} = 13.9$ Hz, 3 H, Ru*H*), 1.02 (q, $J_{HH} = 8.0$ Hz, 2 H, Zn*CH*$_2$CH$_3$), 1.84* (obscured by C_5Me_5, ZnCH$_2$*CH*$_3$), 1.84 (s, 30 H, C_5*Me*$_5$). *Determined by ^{1}H−^{1}H COSY spectrum. ^{13}C NMR (125 MHz, rt, C_6D_6, δ/ppm): 12.6 (q, $J_{CH} = 125.1$ Hz, C_5*Me*$_5$), 13.6 (q, $J_{CH} = 127.0$ Hz, ZnCH$_2$*CH*$_3$), 15.7 (t, $J_{CH} = 120.6$ Hz, Zn*CH*$_2$CH$_3$), 85.6 (s, *C*$_5$Me$_5$). Efforts for elemental analysis of the μ-ZnEt complexes **5b** and **6b** have been unrewarding due to their higher reactivities.

Reaction of a Mixture of the Dinuclear Complex (Cp′Ru)$_2$(μ-H)$_4$ (1) and {(η^5-C$_5$Me$_4$Et)Ru}$_2$(μ-H)$_4$ (1′) with 1 equiv of ZnEt$_2$. A 50 mL Schlenk tube was charged with **1** (11 mg, 0.023 mmol), **1′** (12 mg, 0.024 mmol), and toluene (10 mL). After cooling the solution to −78 °C, diethylzinc (48 μL, 0.048 mmol) was added dropwise with vigorous stirring. The color of the solution turned bright red immediately. The cooling bath was removed, and removal of the solvent under reduced pressure gave 24 mg (0.046 mmol, 99%) of a mixture of **5b** and {(η^5-C$_5$Me$_4$Et)Ru}$_2$-(μ-H)$_3$(μ-ZnEt) (**5b′**) as an orange solid. In this reaction, a mixed-ligand complex {(η^5-C$_5$Me$_5$)Ru}(μ-H)$_3$(μ-ZnEt){(η^5-C$_5$Me$_4$Et)Ru} was not formed. Spectral data for **5b′**: ^{1}H NMR (400 MHz, rt, C_6D_6, δ/ppm): -15.04 (br s, 3 H, Ru*H*), 0.90 (t, $J_{HH} = 8.0$ Hz, 6 H, C$_5$Me$_4$*Et*), 1.05 (q, $J_{HH} = 8.0$ Hz, 2 H, Zn*CH*$_2$CH$_3$), 1.84* (obscured by C$_5$Me$_5$, ZnCH$_2$*CH*$_3$), 1.84 (s, 24 H, C$_5$*Me*$_5$), 2.40 (q, $J_{HH} = 8.0$ Hz, 4 H, C$_5$Me$_4$*Et*). *Determined by ^{1}H−^{1}H COSY spectrum.

Preparation of (Cp′Ru)$_2$(μ-H)$_2$(μ-ZnMe)$_2$ (6a). A 50 mL Schlenk tube was charged with **1** (97 mg, 0.204 mmol) and toluene (10 mL). After cooling the solution to −78 °C, dimethylzinc (400 μL, 0.440 mmol) was added dropwise with vigorous stirring. The color of the solution turned bright orange immediately. The cooling bath was removed and the reaction mixture was stirred at room temperature for 1.5 h. Removal of the solvent and the remaining reagent under reduced pressure gave 136 mg (0.214 mmol, 105%) of **6a** as an orange-yellow solid. ^{1}H NMR (300 MHz, rt, C_6D_6, δ/ppm): -14.65 (s, 2 H, Ru*H*), 0.18 (s, 6 H, Zn*Me*), 1.81 (s, 30 H, C$_5$*Me*$_5$). ^{13}C NMR (125 MHz, rt, C_6D_6, δ/ppm): 3.9 (q, $J_{CH} = 120.2$ Hz, Zn*Me*), 12.5 (q, $J_{CH} = 126.5$ Hz, C$_5$*Me*$_5$), 85.3 (s, *C*$_5$Me$_5$). Anal. Calcd for $C_{22}H_{38}Ru_2Zn_2$: C, 41.58; H, 6.03. Found: C, 41.81; H, 5.92.

Preparation of (Cp′Ru)$_2$(μ-H)$_2$(μ-ZnEt)$_2$ (6b). A 50 mL Schlenk tube was charged with **1** (114 mg, 0.239 mmol) and toluene (8 mL). After cooling the solution to −78 °C, diethylzinc (480 μL, 0.480 mmol) was added dropwise with vigorous stirring. The color of the solution turned bright orange immediately. The cooling bath was removed, and the mixture was warmed to room temperature. Removal of the solvent and the remaining reagent under reduced pressure gave 165 mg (0.249 mmol, 104%) of **6b** as an orange-yellow solid. ^{1}H NMR (300 MHz, rt, C_6D_6, δ/ppm): -14.01 (s, 2 H, Ru*H*), 0.99 (q, $J_{HH} = 8.0$ Hz, 4 H, Zn*CH*$_2$CH$_3$), 1.80* (obscured by C$_5$Me$_5$, ZnCH$_2$*CH*$_3$), 1.80 (s, 30 H, C$_5$*Me*$_5$). *Determined by ^{1}H−^{1}H COSY spectrum. ^{13}C NMR (125 MHz, rt, C_6D_6, δ/ppm): 12.6 (q, $J_{CH} = 126.6$ Hz, C$_5$*Me*$_5$), 12.7 (q, $J_{CH} = 127.7$ Hz, ZnCH$_2$*CH*$_3$), 17.8 (t, $J_{CH} = 124.9$ Hz, Zn*CH*$_2$CH$_3$), 85.3 (s, *C*$_5$Me$_5$).

Table 4. Crystallographic Data of 3b and 4a[a,b]

	3b	4a
empirical formula	$C_{32}H_{54}Ru_3Zn$	$C_{32}H_{54}Ru_3Zn_2$
fw	807.33	872.70
temperature, K	223(2)	293(2)
cryst syst	monoclinic	hexagonal
space group	*C*2/*m* (#12)	*P*6$_3$/*m* (#176)
a, Å	17.237(4)	11.279(3)
b, Å	18.408(4)	
c, Å	11.175(3)	16.137(5)
α, deg		
β, deg	104.903(14)	
γ, deg		
volume, Å^3	3426.5(14)	1777.8(8)
Z	4	2
ρ_{calcd}, Mg m^{-3}	1.565	1.630
$2\theta_{max}$, deg	60.1	60.1
limiting indices	$0 \le h \le 24$ $0 \le k \le 25$ $-15 \le l \le 15$	$0 \le h \le 13$ $0 \le k \le 13$ $0 \le l \le 22$
μ(Mo Kα), mm^{-1}	2.010	2.592
F(000)	1632	876
cryst size, mm	0.50 × 0.50 × 0.30	0.50 × 0.40 × 0.20
GOF on F^2	1.079	1.118
no. of data collected/ unique	11 900/4449	2603/1722
no. of variables	193	73
R_1, wR_2 [$I > 2\sigma(I)$]	0.0430, 0.1188	0.0519, 0.0761
R_1, wR_2 (all data)	0.0455, 0.1212	0.0595, 0.0793
residual electron density, e Å^{-3}	0.722 (max) −0.779 (min)	1.045 (max) −1.141 (min)

[a] $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$. The function minimized: $w(F_o^2 - F_c^2)^2$.

Reaction of 5b with Dimethylzinc: Synthesis of (Cp′Ru)$_2$(μ-H)$_2$(μ-ZnMe)(μ-ZnEt) (6c). A 50 mL Schlenk tube was charged with **5b** (106 mg, 0.186 mmol) and toluene (20 mL). After cooling the solution to −78 °C, dimethylzinc (223 μL, 0.223 mmol) was added dropwise with vigorous stirring. The color of the solution turned bright orange immediately. The cooling bath was removed, and the mixture was warmed to room temperature. Removal of the solvent and the remaining reagent under reduced pressure gave 123 mg (0.189 mmol, 102%) of **6c** as an orange-yellow solid. ^{1}H NMR (400 MHz, rt, C_6D_6, δ/ppm): -14.64 (s, 1 H, Ru*H*), -13.95 (s, 1 H, Ru*H*), 0.19 (s, 3 H, Zn*Me*), 0.97 (q, $J_{HH} = 8.0$ Hz, 2 H, Zn*CH*$_2$CH$_3$), 1.76 (s, 30 H, C$_5$*Me*$_5$). *A signal attributable to the methyl proton was not observed probably due to the overlap with the C$_5$Me$_5$ signal.

Crystallographic Data Collection and Structure Determination. Suitable crystals of **3b** and **4a** were coated with silicon grease and sealed in glass capillaries. Data were collected by a Rigaku RAXIS-CS equipped with a sealed tube X-ray generator (50 kV, 100 mA) with monochromatized Mo Kα (0.71070 Å) radiation in a nitrogen stream at 223(2) (**3b**) and 293(2) K (**4a**). Each indexing was performed from three oscillations exposed for 90 s. The unit cell parameters and the orientation matrix for data collection were determined by the least-squares refinement with the setting angles listed in Table 4. Details of the data collection are summarized in Table 4.

Structure Determination and Refinement. The direct method on SHELXS-97[21] was applied to **3b** and **4a**. All structures were refined on F^2 by full-matrix least-squares methods, using SHELXL-97.[21] Collected nonequivalent reflections with $I > 2.0\sigma(I)$ were used

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(21) Sheldrick, G. M. *SHELX-97, Programs for Crystal Structure Analysis (Release 97-2)*; University of Göttingen: Göttingen, Germany, 1997.

for the structure determination. The C2 atom in **3b** is disordered with thermal parameters with 0.5:0.5 occupancy. The hydrogen atoms of methylene and methyl groups were included in the refinement on calculated positions riding on their carrier atoms. All calculations of least-squares refinements were performed with SHELXL-97 programs.

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Supporting Information Available: Tables of atomic coordinates and parameters, bond lengths and angles, torsion angles, and structure refinement details and ORTEP drawings of **3b** and **4a** with full numbering schemes; crystallographic data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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