Capped Metal Polyhydride Clusters

Trinuclear Ruthenium Polyhydride Complexes with a Triply Bridging Ligand: [{(η^5-C_5Me_5)Ru}$_3$(μ_3-M)(μ-H)$_3$(μ_3-H)] (M = Li, Mg*i*Pr, and ZnEt) and [{(η^5-C_5Me_5)Ru}$_3$(μ_3-M)(μ-H)$_3$] (M = AlEt and GaMe)**

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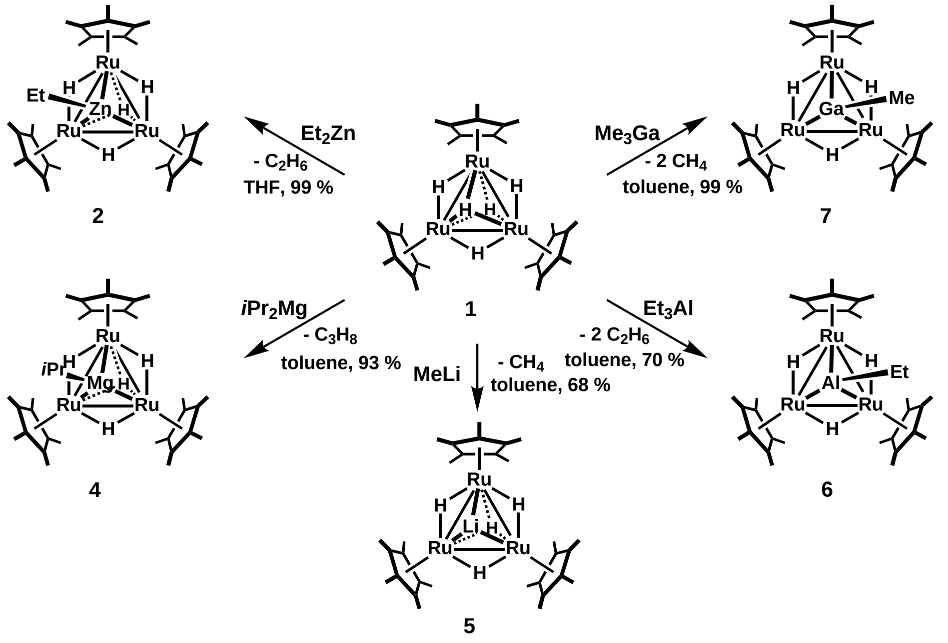
We have shown that metal polyhydride clusters, especially those that have C_5Me_5 groups, have remarkable reactivity, such as an unprecedented mode of C–C bond cleavage, C=C double bond cleavage of terminal alkenes, and alkane C–H bond cleavage.[1] The reactivity of the cluster complex depends on the steric and electronic environment of the reaction site. Our effort has, therefore, been focused on developing a versatile method for changing the electron density at the metal center, and we reported the syntheses and reactions of di- and trinuclear clusters with μ-C=NHR, μ-PR_2, or μ_3-BR groups.[2] As an extension of this idea, we have investigated the synthesis of a series of trinuclear Ru clusters that have a variety of bridging ligands containing a metal atom. The introduction of a Lewis basic or acidic metal atom into the framework of the cluster would directly affect the electronic environment of the reaction site and, as a result, would give us control over the reactivity and selectivity of the cluster. Although there have been several studies on the reaction of a transition-metal hydride complex with metal alkyls such as RLi, R_2Mg, R_2Zn, R_3Al, and R_3Ga,[3] no attempts to control electron density at the metal center of the trimetallic cluster have been reported. Herein, we report the synthesis of a novel class of trinuclear polyhydride complexes of ruthenium that have a triply bridging metal alkyl ligand, and evaluate their influences on the reactivity of the clusters by means of cyclic voltammetry.

An equimolar amount of diethylzinc was added to a solution of **1** in THF at −78 °C, and this mixture was warmed to room temperature resulting in the clean formation the new cluster **2** (Scheme 1).[4] The introduction of the triply bridging ethylzinc ligand into the Ru_3 core was confirmed by ^{1}H NMR spectroscopy; a single resonance signal (45 H) arising from three C_5Me_5 groups, and a resonance signal at $\delta = -0.50$ ppm (2 H) arising from a methylene group bound to the zinc atom was observed in the ^{1}H NMR spectrum. The signals from the hydrides appear at $\delta = -26.97$ (1 H) and 2.56 ppm (3 H), and assignment of these signals was confirmed with a labeling experiment by using [{(η^5-C_5Me_5)Ru}$_3$(μ-D)$_3$(μ_3-D)$_2$] ([D$_5$]-**1**) and diethylzinc. The dramatic downfield shift of the signals from the three hydride ligands is consistent with a bonding interaction between the hydride and the zinc atom, which is observed in the structure determined by an X-ray study (see below).



Scheme 1. Reactivity studies of **1** with metal alkyls.

[{(η^5-C_5Me_5)Ru}$_3$(μ-H)$_3$(μ_3-H)$_2$] **1**

[{(η^5-C_5Me_5)Ru}$_3$(μ-H)$_3$(μ_3-ZnEt)(μ_3-H)] **2**

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It is important to introduce one bridging ligand onto only one side of the Ru_3 core. If both faces of the Ru_3 plane are each covered with a bridging ligand, then there is no space for substrate activation on the Ru_3 plane. Strict control of the stoichiometry of the reaction is, therefore, necessary to obtain selectively the monocapped ethylzinc complex **2**, otherwise, addition of excess diethylzinc causes a further reaction to yield a bicapped ethylzinc complex **3**.

$[\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}ZnEt)_2]$ **3**

The reaction of **1** with a variety of metal-alkyl reagents such as $i$$Pr_2Mg$, MeLi, Et_3Al, and Me_3Ga in toluene led to the formation of the corresponding mono-μ_3-metal complexes **4**–**7** (Scheme 1). All of these complexes dissolve in nonpolar solvents such as pentane, toluene, and benzene. Most of the complexes are air- and moisture-sensitive, even in the solid state, and should be handled in an inert-gas atmosphere. Interestingly, in the reactions of **1** with metal–alkyl reagents, except for $ZnEt_2$, the corresponding bicapped complexes were not formed. These products were unambiguously identified on the basis of NMR spectroscopy (Table 1).

The structure of each complex has an approximate threefold axis, and the resonance signals for the three C_5Me_5 groups are observed to be equivalent both in the ^1H and ^{13}C NMR spectra. In the ^1H NMR spectra of **2, 4**, and **5**, a signal assigned to a triply bonded hydride ligand capping the three Ru atoms was observed around $\delta = -25$ ppm. Noteworthy, the resonance signals of the rest of the hydrides shifted significantly downfield because of their bonding interaction with the triply bridging metal atom. Evidence for this interaction was obtained by NMR spectroscopy, and by an X-ray diffraction study. In the ^1H NMR spectrum of **5** recorded at −60 °C, two hydride signals appear at $\delta = -24.17$ (1H) and −10.88 ppm (3H; −10.01 at room temperature). The latter was coupled with the ^7Li nucleus ($S = 2/3$, $J_{Li,H} = 11.2$ Hz). Additionally, the ^7Li NMR spectrum of **5** exhibits a quartet at $\delta = -1.4$ ppm with the same coupling constant ($J_{Li,H} = 11.2$ Hz). Similar bonding interactions between the triply bridging metal and the Ru-bound hydride were also observed in **2**, and **4**, and confirmed by X-ray diffraction studies (see below). The shifts of $\delta = -3.37$ and −3.84 ppm for the hydrides in the μ_3-AlEt complex **6** and the μ_3-GaMe complex **7**, respectively, are more downfield than that reported[7] for a hydride that directly bridges Al and Ru atoms ($\delta = -13.55$ ppm), and are more upfield than the chemical shift of a terminal hydride directly bound to an Al atom ($\delta = 4.5$ ppm).[7] Although these NMR data suggest of a weak bonding interaction between the hydride and the bridging Al or Ga atom, this possibility was ruled out on the basis of the X-ray structure analysis.

The X-ray studies of **2, 4, 5** (not shown), and **7** show that a metal–alkyl ligand bridges three Ru atoms on one of the Ru_3 faces, and the opposite face of the Ru_3 core is available as a reaction site (Figure 1).[8] The Ru_3 core of these complexes consist of an approximately equilateral triangle with edges of about 2.75 Å, and this value is similar to that of the parent complex **1** (≈ 2.75 Å). Although the Ru–Ru distances in these complexes are very similar to those observed in the parent compound **1**, the Ru–CENT vectors tilt with respect to the Ru_3 plane (Figure 1; Table 1). Notably, the tilt angles are classified into two groups. The tilt angles in **7** are negative (see Table 1, footnote [c]) while those observed in **2, 4**, and **5** are positive. Consequently, the reaction site of **7** is more exposed than that of **1**, which is in contrast to the cases of **2, 4**, and **5**. Thus, the introduction of the triply bridging metal ligand

Table 1: Selected spectral data and structural parameters of trinuclear polyhydride complexes **1, 2**, and **4**–**7**.[6]

Complex	**2**[a]	**4**[a]	**5**[a]	**6**[a]	**7**[a]		**1**[a]
					molecule 1	molecule 2	
^1H NMR (μ_3-H, 1 H, δ, RT)	−26.97	−24.70	−24.02	–	–		–
^1H NMR (μ-H, 3 H, δ, RT)	2.56	−5.25	−10.01	−3.37	−3.84		–
^1H NMR (hydride, δ, RT)	–	–	–	–	–		−7.23[b]
^1H NMR (μ_3-MR, δ, RT)	−0.50 (q)	−0.40 (sep)	–	−0.66(q)	−0.73 (s)		–
	1.11 (t)	1.34 (d)	–	0.81 (t)	–		–
^{13}C NMR (C_5Me_5, δ, RT)	85.4	84.4	79.9	87.1	84.4		85.7
^{13}C NMR ($C_5\mathit{Me}_5$, δ, RT)	13.0	13.1	13.8	13.2	12.9		13.1
Ru–Ru distance [Å]	2.7450(6)	2.7516(6)	2.735(5)	–	2.7309(13)	2.7311(11)	2.7503(8)
	2.7371(8)	2.7500(4)	2.737(4)	–	2.7348(12)	2.7353(13)	2.7534(8)
		2.7548(6)	2.723(5)	–	2.7381(13)	2.7336(12)	2.7453(6)
Ru–M distance [Å]	2.6747(10)	2.7487(13)	2.67(5)	–	2.480(2)	2.4934(18)	–
	2.6561(8)	2.8007(12)	2.84(9)	–	2.479(2)	2.4587(18)	–
		2.7715(13)	2.82(6)	–	2.458(2)	2.4780(18)	–
tilt angle [°][c]	4.6	8.1	9.7	–	−5.5	−5.2	0.0
	4.6	8.7	10.2	–	−6.2	−6.0	0.0
		7.8	12.7	–	−5.6	−5.3	0.0
first formal redox potential [mV]	−489	−1049	−1696	−521	−643		−510

[a] In C_6D_6. [b] A signal resonance signal was observed as a result of the site-exchange process between the μ-H and μ_3-H hydride ligands. [c] The angles between the Ru_3 plane and the Ru-CENT vector. When the Ru–CENT vector tilts away from the μ_3-M ligand with respect to the Ru_3 plane, the tilt angle is defined to be a positive value.

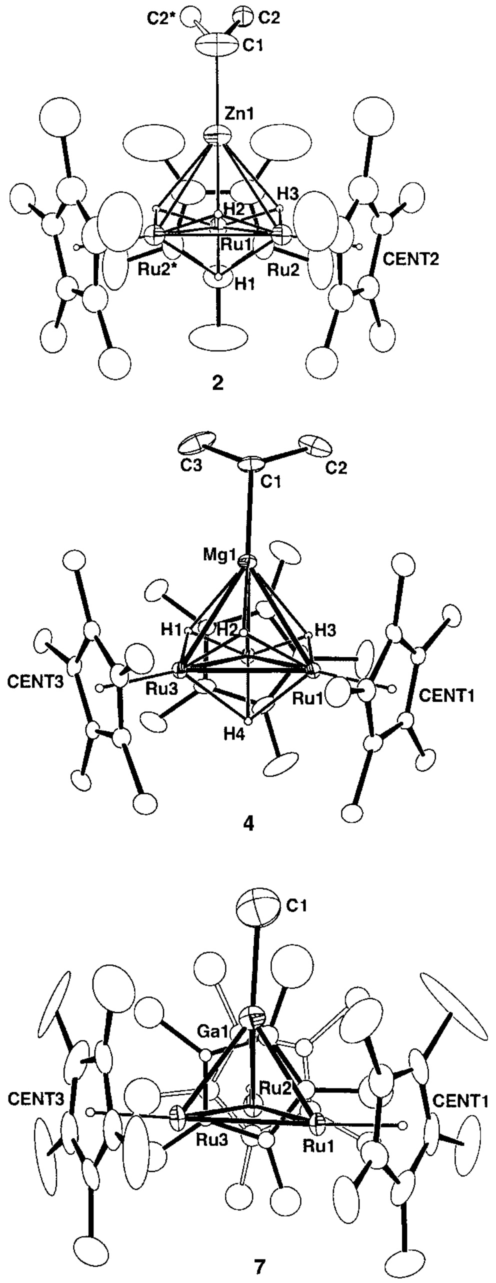

Figure 1. Molecular structures of **2**, **4**, and **7** with thermal ellipsoids drawn at the 30% probability level. One of the two independent molecules in a unit cell of **7** is depicted. Selected bond lengths [Å] and angles [°] are shown in Table 1.

above the Ru_3 core affects the size of the reaction site. In the structures of **2** and **4**, the three hydride ligands triply bridge the two ruthenium atoms and the μ_3-metal, and the positive tilt angles observed arise from the steric repulsion between these hydride ligands and the C_5Me_5 group. The average tilt angle of 10.8° for **5** strongly indicates that the hydrides locate above the Ru_2Li plane as in **2** and **4**. In contrast, the negative tilt angle for **7** implies that the hydride ligands are likely to be positioned on the opposite side of the μ_3-GaMe group with respect to the Ru_3 plane and they have little bonding interaction with the Ga atom. The triply bridging metal atoms (Zn, Mg, and Ga) are located almost equidistant from the three Ru atoms, and the average Ru–Zn, Ru–Mg, and Ru–Ga bond lengths are about 2.66, 2.77, and 2.47 Å, respectively. While the Ru–Ga distance is very close to the sum of the covalent radii of Ru and Ga (≈ 2.50 Å), the Ru–Zn and the Ru–Mg distances are significantly longer than the sum of the corresponding covalent radii, ≈ 2.50 and 2.61 Å, respectively.

A change in the electronic environment of the reaction site arising from the introduction of the μ_3-MR ligand to the Ru_3 core can be evaluated by cyclic voltammetry. The electron transfer between the Ru_3 core and the μ_3-MR ligand is certainly reflected in the redox potential, which is an important index of reactivity. In the cyclic voltammogram of the Ru_3Li cluster **5** recorded in THF, three one-electron oxidation waves are observed at −1696, −755 (E_{pa}), and −463 mV versus Ag/AgCl (Table 1, see also Supporting Information). The first and the third waves are reversible and the second wave is irreversible. The first anodic wave at −1696 mV corresponds to $\mathbf{5}^{0/+1}$. The oxidation potential of −1696 mV is much lower than that for the first oxidation wave of the parent triruthenium cluster **1** (−510 mV). This clearly shows an increase in electron density of the Ru_3 core of **5** because of polarization between the Ru atoms and the electropositive μ_3-Li ligand. The first oxidation wave for **4** was observed around −1050 mV. Therefore, the μ_3-MgR ligand similarly donates electrons to the Ru_3 core. As a result of the electron transfer from the μ_3-MR group to the Ru_3 core, the HOMO levels of **5** and **4** were significantly raised. In contrast, the first oxidation waves of the Ru_3M clusters containing Zn and Al appeared in the potential region similar to that of **1** but much higher than that of **4** and **5**. This is a consequence of the Lewis acidic character of these metals. Thus, the introduction of the triply bridging metal ligand is an effective method to change the redox potential, and therefore the reactivity of the trinuclear pentahydride cluster **1**.

In summary, we have synthesized and structurally characterized a series of trinuclear polyhydride clusters that contain triply bridging metal alkyls, and evaluated the change in the electronic environment of the reaction site by cyclic voltammetry.

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[4] A 50 mL Schlenk tube was charged with **1** (373 mg, 0.522 mmol) and THF (30 mL). After the solution had been cooled to −78 °C, diethylzinc (1.0 M solution in hexane: 520 μL, 0.520 mmol) was added dropwise while the solution was stirred vigorously. The cooling bath was removed, and the reaction mixture was warmed to room temperature to give a red-brown solution. Removal of solvent under reduced pressure gave **2** (420 mg, 0.520 mmol; 99 %) as a red-brown solid. **2**: ^{1}H NMR (300 MHz, [D$_6$]benzene, RT): $\delta = -26.97$ (br s, $w_{1/2} = 11.0$ Hz, 1 H, RuH), −0.50 (q, $J_{\rm H,H} = 7.8$ Hz, 2 H, Zn*CH$_2$*CH$_3$), 1.11 (t, $J_{\rm H,H} = 7.8$ Hz, 3 H, ZnCH$_2$*CH$_3$*), 2.00 (s, 45 H, C$_5$*Me$_5$*), 2.56 ppm (br s, $w_{1/2} = 6.0$ Hz, 3 H, RuH); ^{13}C NMR (125 MHz, [D$_6$]benzene, RT): $\delta = 11.8$ (q, $J_{\rm C,H} = 123.0$ Hz, ZnCH$_2$*CH$_3$*), 13.0 (q, $J_{\rm C,H} = 125.4$ Hz, C$_5$*Me$_5$*), 20.3 (t, $J_{\rm C,H} = 115.8$ Hz, Zn*CH$_2$*CH$_3$), 85.4 ppm (s, *C$_5$*Me$_5$); elemental analysis calcd (%) for $C_{32}H_{54}Ru_3Zn$: C, 47.61; H, 6.74; found: C, 47.42; H, 6.71.

[5] An X-ray study of [(Cp′Ru)$_3${μ$_3$-Li(thf)}(μ-H)$_3$(μ$_3$-H)] (**5**-thf) was carried out. The preliminary results ($R_1 = 0.200$) are shown in Table 1. The resulting data of this solution are insufficient to discuss in detail. However, it is sufficient to show the connectivity of the atoms of **5**-thf.

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[8] a) Crystal data for **2**: $C_{32}H_{54}Ru_3Zn$, $M_r = 807.33$; red prismatic (0.50 × 0.50 × 0.30 mm); monoclinic, space group *C*2/*m* (No.12), $a = 17.237(4)$, $b = 18.408(4)$, $c = 11.175(3)$ Å, $\beta = 104.903(14)°$, $V = 3426.5(14)$ Å^3, $Z = 4$, $\rho_{\rm calcd} = 1.565$ g cm^{-3}, $T = 223(2)$ K, $\lambda({\rm Mo_{K\alpha}}) = 0.71070$ Å, $\mu({\rm Mo_{K\alpha}}) = 2.01$ mm^{-1}, $F(000) = 1632$, 11 900 reflections collected, 4449 were unique reflections, 188 parameters, $R_1 = 0.0429$ for 4253 reflections ($I_o > 2\sigma(I_o)$), $wR_2 = 0.1200$ for all data, GOF = 1.076, min./max. residual electron density −0.793/0.728 e Å^{-3}. Crystal data for **4**: $C_{33}H_{56}Ru_3Mg$, $M_r = 780.30$; black block (0.30 × 0.30 × 0.20 mm); monoclinic, space group *C*2/*c* (No.15), $a = 24.826(10)$, $b = 18.174(2)$, $c = 17.383(3)$ Å, $\beta = 118.232(18)°$, $V = 6910(3)$ Å^3, $Z = 8$, $\rho_{\rm calcd} = 1.500$ g cm^{-3}, $T = 123(2)$ K, $\lambda({\rm Mo_{K\alpha}}) = 0.71069$ Å, $\mu({\rm Mo_{K\alpha}}) = 1.331$ mm^{-1}, $F(000) = 3184$, 39 681 reflections collected, 9571 were unique reflections ($R_{\rm int} = 0.0682$), 372 parameters, $R_1 = 0.0388$ for 4133 reflections ($I_o > 2\sigma(I_o)$), $wR_2 = 0.0856$ for all data, GOF = 0.965, min./max. residual electron density −1.520/0.782 e Å^{-3}. Crystal data for **7**: $C_{31}H_{51}Ru_3Ga$, $M_r = 796.65$; red prismatic (0.50 × 0.50 × 0.30 mm); monoclinic, space group *Pn* (No.7), $a = 11.1306(3)$, $b = 18.8975(5)$, $c = 16.1142(5)$ Å, $\beta = 105.8670(10)°$, $V = 3260.33(16)$ Å^3, $Z = 4$, $\rho_{\rm calcd} = 1.623$ g cm^{-3}, $T = 223(2)$ K, $\lambda({\rm Mo_{K\alpha}}) = 0.71069$ Å, $\mu({\rm Mo_{K\alpha}}) = 2.197$ mm^{-1}, $F(000) = 1600$, 27 874 reflections collected, 7389 were unique reflections ($R_{\rm int} = 0.0643$), 496 parameters, $R_1 = 0.0561$ for 6516 reflections ($I_o > 2\sigma(I_o)$), $wR_2 = 0.1335$ for all data, GOF = 1.045, min./max. residual electron density −1.011/1.692 e Å^{-3}. Instruments: All data were collected on a Rigaku RAXIS-CS imaging plate area detector to a maximum 2θ value of 60.1° (**2**), 60.0° (**4**), and 54.9° (**7**). A numerical absorption correction program NUMABS[8b] was applied to the reflection data for **7**. The structure for **2** and **7** were solved by the Patterson method (DIRDIF 94[8c] PATTY[8d]). The structure of **4** was solved by the Patterson method (SHELXS-97[8e]). Non-hydrogen atoms were refined on F^2 by using SHELXL-97.[8f] The methyl carbon atom of the ethylzinc group in **2** is disordered with thermal parameters with 50.0 %:50.0 % occupancy. The unit cell of **7** contains two molecules, and one of the C_5Me_5 groups in each molecule is disordered with thermal parameters with 65.7 %:34.3 % (illustrated in Figure 1) and 53.1 %:46.9 % occupancy, respectively. All non-hydrogen atoms except a disordered carbon atom in **2** and **7** were refined anisotropically. The metal-bound hydride ligands were located by sequential difference Fourier synthesis and refined with isotropic thermal parameters. The remaining hydrogen atoms were placed in ideal positions and refined with a riding model. b) T. HIGASHI, NUMABS, Rigaku Corporation, Japan, **1999**; c) P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, DIRDIF94, University of Nijmegen, The Netherlands, **1994**; d) P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, PATTY, University of Nijmegen, The Netherlands, **1992**; e) G. M. Sheldrick, *Acta Crystallogr. Sect. D* **1993**, *49*, 18; f) G. M. Sheldrick, SHELXS-97, University of Göttingen, Göttingen (Germany), **1997**; g) CCDC-192701 (**2**), CCDC-192702 (**4**), and CCDC-192703 (**7**) contain 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).