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Synthesis of Group 8−Group 6 Heterotrimetallic Polyhydrido Complexes Having Only a C_5Me_5 Group as Auxiliary Ligand

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Summary: Novel heterotrimetallic polyhydrido complexes containing ruthenium and group 6 metals, $(Cp'Ru)_2(Cp'M)(\mu\text{-}H)_5$ *(**4**, M = Mo; **5**, M = W) and* $(Cp'Ru)(Cp'W)_2(H)_7$ *(**6**), have been synthesized by the reaction of dimeric ruthenium methoxo complex* $(Cp'RuOMe)_2$ *(**3**) with dinuclear polyhydrido complexes* $Cp'Ru(\mu\text{-}H)_3MH_3Cp'$ *(**1**, M = Mo; **2**, M = W) and* $(Cp'WH_4)_2$*, respectively. The* ^1H *NMR spectra of **6** exhibit fluxionality stemming from the dynamic motion of the* RuW_2 *core associated with exchange of the coordination sites among the hydrido ligands.*

A transition metal cluster shows fascinating reactivities stemming from cooperativity of the metal centers.[1] Reactivity of a cluster would primarily depend on the combination of the metals constructing the cluster. A heterometallic cluster containing different kinds of metal would induce electronic anisotropy in the reaction field as a result of polarization of the metal−metal bond. We have reported the synthesis and reactions of a series of heterobimetallic polyhydrido complexes, $Cp'Ru(\mu\text{-}H)_3IrCp'$, $Cp'Ru(\mu\text{-}H)_4OsCp'$, $Cp'Ru(\mu\text{-}H)_3ReH_2Cp'$, $Cp'Ru(\mu\text{-}H)_3MoH_3Cp'$ (**1**), and $Cp'Ru(\mu\text{-}H)_3WH_3Cp'$ (**2**), having only Cp' groups as the ancillary ligand and demonstrated the site-selective coordination of substrates, such as ethylene, amine, and phosphines.[2]

Although a number of heterobimetallic polyhydrido complexes have thus far been prepared,[3] only little is known about heteropolymetallic polyhydrido complexes.[2c,4] As observed for the ruthenium polyhydrido clusters $(Cp'Ru)_2(\mu\text{-}H)_4$, $(Cp'Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2$, and $(Cp'Ru)_4(H)_6$, an increase in the nuclearity of the cluster would enhance the electron transfer between the cluster and the coordinated substrate, and as a result, the reactivity of the cluster would be raised.[5] Actually, heterotrimetallic polyhydrido complexes $(Cp'Ru)_2(Cp'Re)(H)_4$ and

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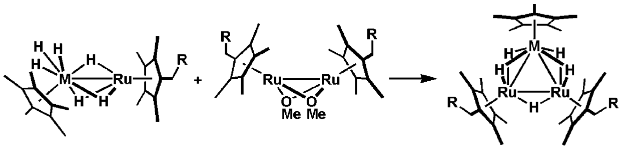
$(Cp'Ru)(Cp'Re)_2(H)_5$ undergo H/D-exchange between the hydrido ligands and D_2 much faster than the heterobimetallic complex $Cp'Ru(\mu\text{-}H)_3ReH_2Cp'$.[2c] As far as polyhydrido complexes are concerned, there are no examples of a cluster containing ruthenium and group 6 metals. We report herein the synthesis of novel heterotrimetallic polyhydrido complexes containing ruthenium and oxophilic group 6 metals and the dynamic processes of these compounds in solution.

The reaction of a metal alkoxide with a metal polyhydrido complex is a versatile method for the preparation of a polyhydrido cluster.[2a,3b,c] We applied this method for the preparation of Ru_2M (M = Mo, W) polyhydrido complexes by using a dimeric methoxo complex, $(Cp'RuOMe)_2$ (**3**),[6] and polyhydrido complexes $Cp'Ru(\mu\text{-}H)_3MH_3Cp'$ (**1**, M = Mo; **2**, M = W).

Polyhydrido complex **1** reacted with dimeric methoxo complex **3** at 50 °C to form the heterotrimetallic complex $(Cp'Ru)_2(Cp'Mo)(\mu\text{-}H)_5$ (**4**) in 41% yield with liberation of methanol (eq 1). A tungsten analogue of **4**, $(Cp'Ru)_2(Cp'W)(\mu\text{-}H)_5$ (**5**), was prepared in a similar manner.[7] The relatively low yield of **4** is probably due to thermal instability of the starting complex **1**. Complex **5** was alternatively synthesized in high yield by the treatment of $[(Cp'Ru)(Cp'W)H_5Li]_3$ with the cubane-type tetranuclear ruthenium chloro complex $(Cp'RuCl)_4$ (eq 2).[7] Both



(1)

1 : M = Mo, R = H
1' : M = Mo, R = Me
2 : M = W, R = H
2' : M = W, R = Me

3 (R = H)
3' (R = Me)

4 : M = Mo, R = H (41 %)
4' : M = Mo, R = Me (17 %)
5 : M = W, R = H (69 %)
5' : M = W, R = Me (87%)

$$[(Cp'Ru)(Cp'W)H_5Li]_3 + (Cp'RuCl)_4 \xrightarrow[(86\%)]{} \mathbf{5} \qquad (2)$$

4 and **5** are air- and moisture-sensitive and soluble in pentane, toluene, and THF. To the best of our knowledge, complexes **4** and **5** are the first example of a heterotrimetallic polyhydrido complex with a triangular Ru_2M (M = Mo, W) structure that has no carbonyl ligands.

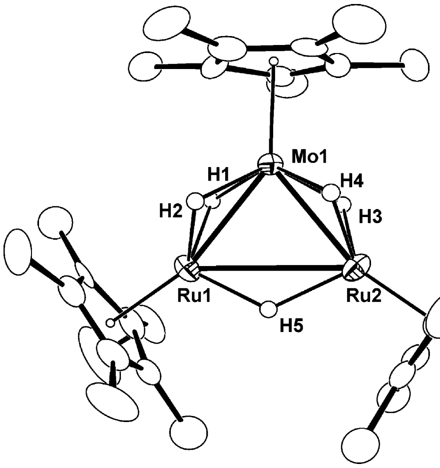


Figure 1. ORTEP drawing of **4′**. Selected bond lengths (Å) and angles (deg): Ru1−Mo1 = 2.5422(15), Ru2−Mo1 = 2.5406(11), Ru1−Ru2 = 3.1475(18), Mo1−Ru1−Ru2 = 51.72(4), Mo1−Ru2−Ru1 = 51.76(3), Ru2−Mo1−Ru1 = 76.52(4).

In the ^1H NMR spectrum of **4** recorded at room temperature, two Cp′ signals were observed at δ 1.98 (30H) and 1.96 (15H). From the integral intensities of these signals, they are assigned to the Cp′ group bound to the ruthenium and the molybdenum, respectively. To establish the assignment of the Cp′ signals, the C_5EtMe_4 analogue of **4**, $[(C_5EtMe_4)Ru]_2(Cp'Mo)(\mu\text{-}H)_5$ (**4′**), was prepared by the reaction of $(C_5EtMe_4)Ru(\mu\text{-}H)_3MoH_3Cp'$ (**1′**) with $[(C_5EtMe_4)RuOMe]_2$ (**3′**). The ^1H NMR spectrum of **4′** at room temperature reveals the signal of the Cp′ group bound to the molybdenum atom at δ 1.96 (15H) and those of the C_5EtMe_4 group bound to the ruthenium atom at δ 1.98 (12H) and 1.96 (12H). Similarly, the ^1H NMR spectrum of **5** reveals two Cp′ signals at δ 2.23 and 1.89 in the intensity ratio of 15H:30H.

The ^1H NMR signal of two Cp′ groups coordinated to the ruthenium atoms is a sharp singlet irrespective of temperature. This indicates that both compounds **4** and **5** have symmetry planes and belong to the C_s symmetry group. The shape and the chemical shift of the signal of the hydrido ligands depended on the temperature due to a fluxional behavior, namely, site-exchange of the hydrido ligands. At room temperature, a signal of the hydrido ligands was observed to be equivalent at δ −10.99 (5H). At −80 °C, the signal split into two peaks at δ −9.25 (1H) and −11.19 (4H). They are assigned to the bridging hydrido ligands on the Ru−Ru edge and the Ru−Mo edge, respectively. The assignment of the hydrido ligands was consistent with the result of the X-ray diffraction study (vide infra). The hydrido ligands of **5** are fluxional like those of **4**. In the ^1H NMR spectrum recorded at −60 °C in toluene-d_8, two hydrido signals were observed at δ −10.79 (4H) and −11.48 (1H). The signal observed at δ −10.79 has satellite peaks (J_{HW} = 108 Hz) due to spin coupling with the ^{183}W nucleus. This clearly indicates that the four hydrido ligands bridge two Ru−W bonds, and the rest is located on the Ru−Ru edge. The hydrido ligands in **5** mutually exchange the coordination sites, and the signals at δ −10.79 and −11.48 coalesced at around −25 °C. The free energy of activation for the dynamic process was estimated at $\Delta G^{\ddagger}_{298K} = 12.2$ kcal mol^{-1} and $\Delta G^{\ddagger}_{298K} = 11.2$ kcal mol^{-1}, for **4** and **5**, respectively, based on the line-shape analysis of the VT-^1H NMR spectra.

The molecular structures of **4′** and **5′** are shown in Figures 1 and 2, respectively, with the relevant bond lengths and angles.[8]

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[7] Synthesis of **5**. To a mixture of **2** (112.4 mg, 0.237 mmol) and $(Cp'RuOMe)_2$ (56.3 mg, 0.105 mmol) was added toluene (5 mL) at room temperature. After being stirred for 12 h at 50 °C, the solvent was removed under reduced pressure and the residue was purified by a column chromatography on alumina. A brown fraction eluted with toluene/diethyl ether (5:1) was evaporated to dryness to afford complex **5** (131.0 mg, 0.164 mmol, 69%). The C_5EtMe_4 analogue of **5**, $(C_5EtMe_4Ru)_2(Cp'W)(\mu\text{-}H)_5$ (**5′**), was prepared in a similar manner in 87% yield. Complex **5** was alternatively synthesized by the reaction of $[(Cp'Ru)(Cp'W)(H)_5Li]_3$ with $(Cp'RuCl)_4$. To a THF solution (10 mL) of **2** (508.2 mg, 0.905 mmol) was added a hexane solution of *n*-BuLi (1.6 M, 1.1 mL, 1.76 mmol). Then a THF solution of $(Cp'RuCl)_4$ (327 mg, 0.302 mmol) was added, and the mixture was stirred at room temperature. After 10 min, the solvent was removed under reduced pressure. The residue was extracted with toluene and purified by column chromatography on alumina with toluene/diethyl ether (5:1) to give complex **5** (623 mg, 0.782 mmol, 86%). **5**: ^1H NMR (400 MHz, benzene-d_6, rt, δ/ppm): 2.23 (s, 15H, *Cp′*W), 1.89 (s, 30H, *Cp′*Ru), −11.01 (s, J_{HW} = 86.0 Hz, 5H, *μ-H*). ^{13}C NMR (100 MHz, benzene-d_6, rt, δ/ppm): 97.1 (s, C_5Me_5W), 84.7 (s, C_5Me_5Ru), 14.1 (q, J_{CH} = 126.3 Hz, C_5Me_5W), 12.8 (q, J_{CH} = 125.6 Hz, C_5Me_5Ru). IR (ATR, cm^{-1}): 2976, 2953, 2899, 1449, 1370, 1026, 898, 842. Anal. Calcd for $C_{30}H_{50}Ru_2W$: C, 45.23; H, 6.33. Found: C, 45.04; H, 6.31. **5′**: ^1H NMR (400 MHz, benzene-d_6, rt, δ/ppm): 2.46 (q, J_{HH} = 7.3 Hz, 4H, CH_2CH_3), 2.23 (s, 15H, *Cp′*W), 1.92 (s, 12H, C_5EtMe_4Ru), 1.89 (s, 12H, C_5EtMe_4Ru), 1.04 (t, J_{HH} = 7.3 Hz, 6H, CH_2CH_3), −11.00 (s, J_{HW} = 86.0 Hz, 5H, *μ-H*). ^{13}C NMR (100 MHz, benzene-d_6, rt, δ/ppm): 97.1 (s, C_5Me_5W), 90.3 (s, C_5EtMe_4Ru), 84.9 (s, C_5EtMe_4Ru), 84.3 (s, C_5EtMe_4Ru), 21.3 (t, J_{CH} = 127.0 Hz, CH_2CH_3), 15.3 (q, J_{CH} = 124.3 Hz, CH_2CH_3), 14.1 (q, J_{CH} = 125.8 Hz, C_5Me_5W), 12.8 (q, J_{CH} = 125.9 Hz, C_5EtMe_4Ru), 12.6 (q, J_{CH} = 125.9 Hz, C_5EtMe_4-Ru). IR (ATR, cm^{-1}): 2963, 2898, 1455, 1373, 1263, 1027, 961, 899, 815. Anal. Calcd for $C_{32}H_{54}Ru_2W$: C, 46.60; H, 6.60. Found: C, 46.45; H, 6.84.

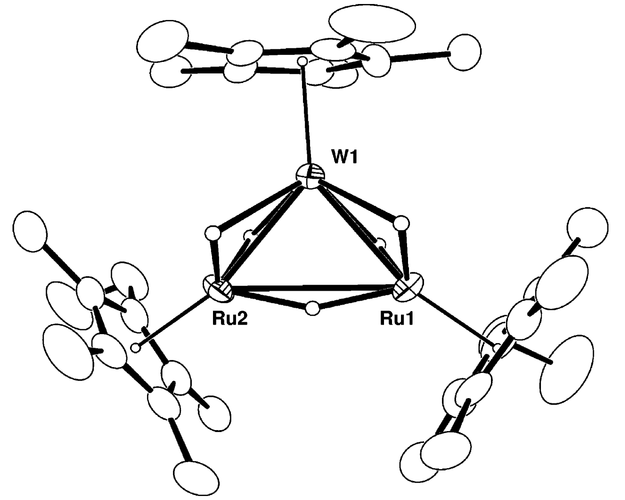
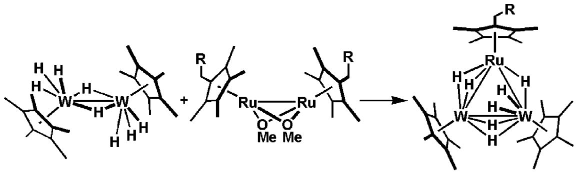


Figure 2. ORTEP drawing of **5′**. Selected bond lengths (Å) and angles (deg): Ru1−Ru2 = 3.1963(21), Ru1−W1 = 2.5285(18), Ru2−W1 = 2.5267(18), Ru2−W1−Ru1 = 78.44(4), W1−Ru1−Ru2 = 50.76(2), W1−Ru2−Ru1 = 50.81(2).

The structures of **4′** and **5′** are almost identical. One of the hydrido ligands bridges the two ruthenium atoms, and the rest bridge the ruthenium and the molybdenum or the tungsten atom. The planes consisting of five ring carbons of the Cp′ or C_5-$EtMe_4$ groups are almost perpendicular to the Ru_2M plane. Complex **4′** consists of an approximately isosceles triangle with a long Ru−Ru bond, 3.1475(18) Å, and short Ru−Mo bonds, 2.5422(15) and 2.5406(11) Å, respectively. The Ru−M bonds are comparable to that of Cp′Ru(μ-H)$_3$MH$_3$Cp′ (**1**, Ru−Mo = 2.5255(7) Å; **2**, Ru−W = 2.5176 (8)), but considerably shorter than those of the Ru_2M carbonyl cluster, of which the metal−metal distances are in the range 2.82−3.01 Å.[9] This is probably due to the presence of the two hydrido ligands on the Ru−M edge. The structural features of **4′** and **5′** resemble those of the isoelectronic complexes $(C_5EtMe_4Ru)_2(Cp'Re)(H)_4$ and $[(C_5EtM_4Ru)_2(Cp'Re)(H)_5][BPh_4]$, which have a long Ru−Ru bond and a short Ru−Re bond.[2c]

A different type of heterotrimetallic polyhydrido complex with a RuW_2 framework was synthesized. The reaction of ditungsten polyhydrido complex $(Cp'WH_4)_2$[10] with methoxo complex **3** at room temperature afforded the heterotrimetallic polyhydrido cluster $(Cp'Ru)(Cp'W)_2(H)_7$ (**6**) in 63% yield (eq 3). Labeled complex $[(C_5EtMe_4)Ru](Cp'W)_2(H)_7$ (**6′**) was prepared by the reaction of $[(C_5EtMe_4)RuOMe]_2$ (**3′**) with $(Cp'WH_4)_2$.



(3)

3 (R = H)
3′ (R = Me)

6 : R = H (63 %)
6′ : R = Me (66 %)

The structure of **6′** illustrated in Figure 3 established the triangular RuW_2 core.[8] A notable feature of the structure is the inequality of the two Ru−W distances. While the Ru1−W1 distance is 2.585(3) Å, the Ru1−W2 distance is 3.120(3) Å.

Complexes **4**, **5**, and **6′** have similar triangular metal cores, namely, two short M−M bonds (2.5−2.6 Å) and one long M−M bond (3.0−3.1 Å). In the structure of **4**, we were able to determine the location of the hydrido ligands. The short M−M bond is bridged by the two hydrido ligands, and the long M−M bond is singly bridged by a hydrido ligand. This would be the case for complex **5**, which is a homologue of **4**. According to these results, we concluded that two hydrogen atoms located the bridging position of the short metal−metal bond and one hydrogen atom bridged the long metal−metal bond in **6′**. It is also noteworthy that the W2−CT2 vector tilts from the plane with the Ru and the two W atoms. A space provided over the W2 as a result of tilt of the Cp′ ring is likely sufficient for the coordination of the two terminal hydrides. The stretching vibration observed at 1898 cm^{-1} also supports the presence of the terminal hydride ligands.

The ^1H NMR spectrum of **6** recorded at room temperature revealed two Cp′ signals at δ 2.29 (30H) and 1.99 (15H). These were unequivocally assigned to the Cp′ ligands bound to the tungsten and the ruthenium, respectively, in comparison with the NMR data of **6′**. A sharp singlet of the hydrido ligands was observed at δ −4.49, with the satellite coupling with ^{183}W (J_{HW} = 57.3 Hz). This value is the average of the coupling constants for the seven hydrido ligands with the ^{183}W nucleus, since the hydrido ligands mutually exchange the coordination sites as mentioned below.

The signal at δ −4.49 broadened and then split into four peaks with a decrease in the temperature. At −120 °C, four relatively sharp signals were observed at δ −0.20 (1H), −1.31 (2H), −5.11 (2H), and −11.17 (2H). The ^1H NMR signals of the C_5-Me_5 groups were also temperature-dependent. While the signals of the C_5Me_5 groups bound to the tungsten centers were observed to be equivalent at δ 2.29 at room temperature, they split into two broad singlet peaks at δ 2.25 and 2.18 at −120 °C. The ^1H NMR data recorded at −120 °C and the X-ray structure are fully consistent with the structure depicted in eq 3, and the temperature-dependence of the NMR data strongly indicates a dynamic process of the RuW_2 core. This process involves oscillation of the ruthenium center between the two tungsten atoms associated with the site-exchange of the hydrido ligands, as illustrated in Scheme 1. Such an intramolecular dynamic process of a metal core is rare, and there has, thus far, been only one precedent, reported by Caulton et al.[4] This is the second example.

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(8) X-ray crystal data for **4′**: $C_{32}H_{54}MoRu_2$, monoclinic, $P2_1$ (No. 4), a = 11.088(6) Å, b = 12.012(4) Å, c = 12.627(5) Å, β = 101.95(4)°, V = 1645.3(12) Å^3, Z = 2, ρ_{calcd} = 1.487 g cm^{-3}, T = −120 °C, $2\theta_{max}$ = 55°, μ(Mo Kα) = 1.298 mm^{-1}; 3827 reflections, 3426 observed ($I_o > 2\sigma(I_o)$), 351 parameters; R1 ($I_o > 2\sigma(I_o)$) = 0.0432, wR2 (all data) = 0.1026. X-ray crystal data for **5′**: $C_{32}H_{54}Ru_2W$, monoclinic, $P2_1$ (No. 4), a = 11.116(8) Å, b = 12.000(10) Å, c = 12.624(10) Å, β = 101.78(3)°, V = 1648(2) Å^3, Z = 2, ρ_{calcd} = 1.662 g cm^{-3}, T = −100 °C, $2\theta_{max}$ = 55°, μ(Mo Kα) = 4.402 mm^{-1}; 3941 reflections, 3840 observed ($I_o > 2\sigma(I_o)$), 348 parameters; R1 ($I_o > 2\sigma(I_o)$) = 0.0347, wR2 (all data) = 0.0879. X-ray crystal data for **6′**: $C_{31}H_{54}RuW_2$, triclinic, $P\bar{1}$ (No. 2), a = 8.039(8) Å, b = 11.224(16) Å, c = 19.51(3) Å, α = 94.46(3)°, β = 100.65(3)°, γ = 110.17(3)°, V = 1605(3) Å^3, Z = 2, ρ_{calcd} = 1.853 g cm^{-3}, T = −50 °C, $2\theta_{max}$ = 55°, μ(Mo Kα) = 7.630 mm^{-1}; 7430 reflections, 6519 observed ($I_o > 2\sigma(I_o)$), 323 parameters; R1 ($I_o > 2\sigma(I_o)$) = 0.0702, wR2 (all data) = 0.2018. CCDC 249312 (**4′**), CCDC 249313 (**5′**), and CCDC 249314 (**6′**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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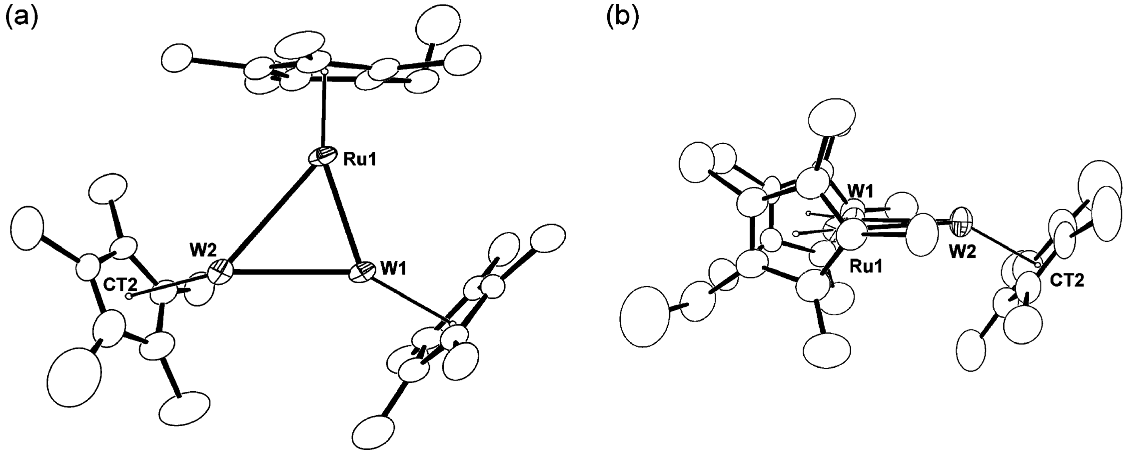
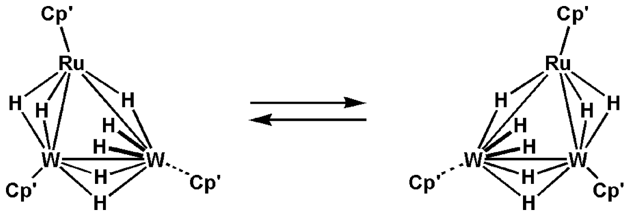


Figure 3. ORTEP drawing of **6′**. Selected bond lengths (Å) and angles (deg): Ru1−W1 = 2.585(3), Ru1−W2 = 3.120(3), W1−W2 = 2.605(4), Ru1−W1−W2 = 73.91(5), W1−W2−Ru1 = 52.75(7), W1−Ru1−W2 = 53.34(7). CT2 is the centroid of the five ring carbons of the Cp′ ligand.

Scheme 1. Intramolecular Dynamic Process of 6



In summary, we have described the synthesis and structure determination of an unprecedented type of heterotrimetallic polyhydrido complex containing ruthenium and group 6 metals. These compounds have triangular structures with an Ru_2M (M = Mo, W) or RuW_2 core. VT-^{1}H NMR studies revealed a site-exchange process of the hydrido ligand and oscillation of the ruthenium atom between the two tungsten atoms in **6**.

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Supporting Information Available: Experimental procedures, VT-^{1}H NMR experiments, and crystallographic information files (CIFs). This material is available free of charge via the Internet at http://pubs.acs.org.

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