

(m, 2H); elemental analysis (%) calcd for $C_{14}H_{23}N_3CuCl_2O_8$: C 33.9, H 4.7, N 8.5; found: C 34.1, H 4.6, N 8.4.

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- [16] Parameters for the cyclic voltammetric measurements of **1**-(ClO₄)₂-**3**-(ClO₄)₂: scan rate of 100 mV s⁻¹, tetrabutylammonium hexafluoro-phosphate 0.2 M, CH₃CN, RT, potential reported relative to SSCE. Ferrocene was used as internal reference at $E_{1/2} = 370$ mV. **1**-(ClO₄)₂: irreversible reduction with a small returning wave, $E_{1/2} = -380$ mV, $E_{\text{pc}} = -445$ mV, $E_{\text{pa}} = -315$ mV, $\Delta E = 130$ mV. **2**-(ClO₄)₂: reversible wave at $E_{1/2} = -105$ mV, $E_{\text{pc}} = -145$ mV, $E_{\text{pa}} = -60$ mV, $\Delta E = 85$ mV. **3**-(ClO₄)₂: reversible wave at $E_{1/2} = -180$ mV, $E_{\text{pc}} = -240$ mV, $E_{\text{pa}} = -125$ mV, $\Delta E = 120$ mV.
- [17] At 298 K, $[\text{Cu}^{\text{II}}\text{L}^1]_i = 1.25$ mM; $[\text{L}^1]/[\text{Cu}^{\text{II}}]_i = 1.28$; $[\text{Cu}^{\text{II}}\text{L}^2]_i = 1.21$ mM, $[\text{L}^2]/[\text{Cu}^{\text{II}}]_i = 1.28$.
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Migration of a Phosphane Ligand between the Two Metal Centers in Diruthenium Hydrido Complexes**

Yasuhiro Ohki and Hiroharu Suzuki*

In the coordination sphere of a metal cluster complex, the substrate can often interact with multiple metal centers simultaneously. The bridging coordination of hydride or carbon monoxide is a typical example of such interaction, and the multiple coordination of the ligand seems to be closely related to the dynamic behavior and reactivity of the ligand. Indeed, a carbonyl ligand in a cluster complex often undergoes intramolecular migration between the metal centers by way of an intermediary species with the bridging carbonyl.^[1] For a better understanding of the nature of *multi-metallic activation*, it is important to elucidate the interaction between the ligand and the multiple metal centers through the

- [*] Prof. H. Suzuki, Y. Ohki⁺
Department of Applied Chemistry
Graduate School of Science and Engineering
Tokyo Institute of Technology and
CREST, Japan Science and Technology Corporation (JST)
O-okayama, Meguro-ku, Tokyo 152-8552 (Japan)
Fax: (+81) 3-5734-3913
E-mail: hiroharu@n.cc.titech.ac.jp
- [⁺] Present address: Department of Chemistry
Graduate School of Science
Nagoya University

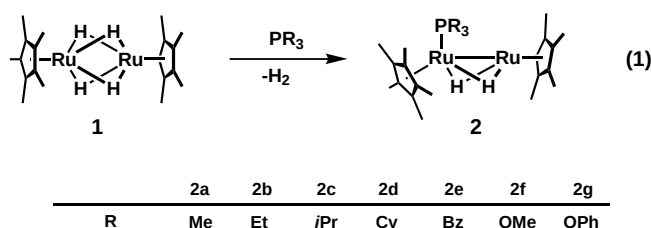
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analysis of the molecular structure and the dynamic processes of the cluster complex. Previously, we reported that a bridging phosphido complex $[(\eta^5\text{-C}_5\text{Me}_5\text{Ru})_2(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$ was formed in the reaction of $[(\eta^5\text{-C}_5\text{Me}_5\text{Ru})_2(\mu\text{-H})_4]$ (**1**)^[2] with triphenylphosphane as a result of P–C(aromatic) bond cleavage induced by synergy of the adjacent metal centers.^[3] We report herein the formation of novel dinuclear dihydrido complexes $[(\eta^5\text{-C}_5\text{Me}_5\text{Ru})_2(\text{PR}_3)(\mu\text{-H})_2]$ (**2**) in the reaction of $[(\eta^5\text{-C}_5\text{Me}_5\text{Ru})_2(\mu\text{-H})_4]$ (**1**) with a phosphorus ligand containing no aryl substituents. We also discuss the intramolecular migration of the phosphorus ligand between the two ruthenium atoms.

The reaction of **1** with an equimolar amount of a series of phosphorus ligands such as phosphanes and phosphites in toluene resulted in the quantitative formation of novel complexes $[(\eta^5\text{-C}_5\text{Me}_5\text{Ru})_2(\text{PR}_3)(\mu\text{-H})_2]$ (**2**) which bear the phosphorus ligand on one of the two ruthenium atoms [Eq. (1)]. Treatment of **2** with additional amounts of the



phosphorus ligand does not yield the corresponding bisphosphane complexes, probably due to the steric hindrance to the incoming phosphorus ligand. Complexes **2a–2g** are highly unsaturated (30e) and sensitive to moisture and air. Selected spectral data of **2** are listed in Table 1. The ratio of integral

intensities among the ^1H NMR signals for C_5Me_5 , PR_3 , and Ru–H of **2a–2g** indicated the formation of the dinuclear ruthenium dihydrido complexes containing a terminal phosphorus ligand. The ^{31}P NMR signals of **2a–2g** were observed in the range of $\delta = -7$ to 180 ppm. For example, the chemical shifts are $\delta = -6.9$, 77.9, 26.9, and 175.3 ppm for **2a**, **2c**, **2e**, and **2f**, respectively. These shifts are consistent with the coordination of the phosphorus ligands in the terminal mode.

The molecular structures of **2a–2g** were determined by X-ray diffraction studies.^[4] The perspective views of the structures are shown in Figure 1, and the selected geometric parameters are listed in Table 1. The ORTEP drawings clearly show the unsymmetrical structure of **2** in each, with PR_3 terminally coordinated to one of the two ruthenium atoms. The Ru–Ru vector is almost perpendicular to the C_5Me_5 ligand coordinated to the Ru2. The Ru1 atom adopts an approximate piano-stool geometry. The Cp–Ru1–P1 angles are around 130° irrespective of the cone angle of the phosphorus ligands.^[5] It is noteworthy that there is a significant correlation among the $\Sigma\chi_i$ values of PR_3 ,^[5] the Ru1–P distances, and the Ru2–Ru1–P1 angle; with the increase of the electron-withdrawing character of the substituents on the phosphorus, the Ru1–P distance becomes shorter and the Ru2–Ru1–P1 angle narrows. Another notable feature of the structures is a short Ru–Ru distance (2.5084(4)–2.5502(7) Å) in agreement with the highly unsaturated (30e) character of **2**. A preliminary result of the DFT (B3LYP) calculation using a Gaussian98 A9 program package indicated that there was a direct bonding interaction between the two ruthenium atoms, which was less than that for a single bond;^[6] however, the metal–metal bond is never a triple bond in accord with the EAN rule. The shortening the Ru–Ru bond is, therefore, probably due to the presence of bridging hydride.

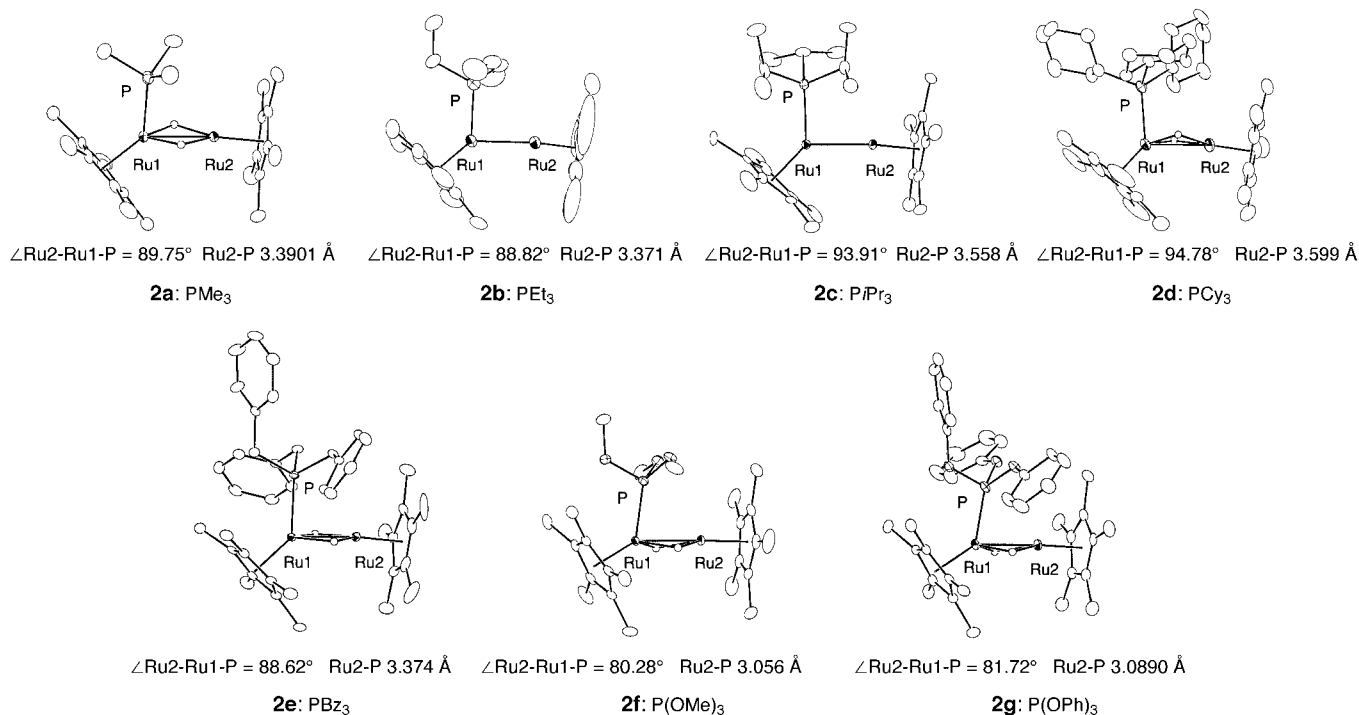
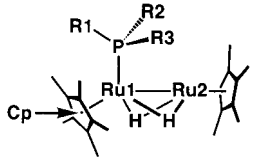


Figure 1. Molecular structures of **2a–2g**, with thermal ellipsoids at 30% probability level.

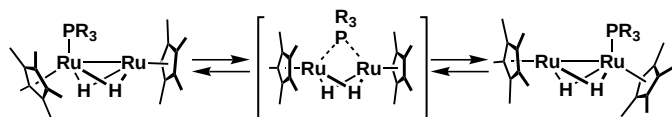
Table 1. Structural parameters and spectral data for complexes **2**.^[a]


R	Me	Et	<i>i</i> Pr	Cy	Bz		OMe	OPh
					no. 1	no. 2		
Ru1–P distance	2.281(2)	2.285(2)	2.340(2)	2.336(2)	2.292(1)	2.299(1)	2.2175(9)	2.200(1)
P–Ru1–Cp angle	131.1	132.8	134.9	133.7	133.1	133.9	128.7	131.3
Ru2–Ru1–P angle	89.75(5)	88.82(6)	93.91(6)	94.78(4)	88.62(3)	86.16(3)	80.28(3)	81.72(3)
P–R1 distance	1.831(7)	1.845(8)	1.854(10) ^[b]	1.899(7)	1.880(4)	1.864(4)	1.625(2)	1.641(2)
P–R2, P–R3 distances	1.807(7)	1.81(1)	1.857(9) ^[b]	1.874(5)	1.860(4)	1.869(4)	1.616(2)	1.636(3)
	1.812(7)	1.846(9)	1.881(9) ^[b]	1.875(6)	1.847(4)	1.870(4)	1.611(2)	1.638(3)
Ru1–Ru2 distance	2.520(1)	2.5262(9)	2.5361(9)	2.5502(7)	2.5326(4)	2.5356(5)	2.5102(4)	2.5084(4)
$\Sigma\chi_i$ value ^[c]	7.8	5.6	3.1	0.3	10.3	10.3	23.4	29.2
Cone angle for PR3 ^[c]	118	132	160	170	165	165	107	128
¹ H NMR (C ₅ Me ₅ , δ , RT) ^[d]	1.88	1.87	1.71, 1.95	1.80, 2.00	1.75	1.75	1.90	1.77
¹ H NMR (Ru–H, δ , RT) ^[d]	–13.65	–13.89	–14.75	–14.70	–13.44	–13.44	–14.23	–14.14
³¹ P{ ¹ H} NMR (δ , RT) ^[d]	–6.89	36.3	77.9	64.9	26.9	26.9	175.3	147.1
$\Delta H^\ddagger_{\text{migration}}$ [kcal mol ^{–1}]	6.8	9.2	12.6	15.7	7.2	7.2	6.2	— ^[e]
$\Delta S^\ddagger_{\text{migration}}$ [eu]	–8.0	–5.6	–8.8	–3.5	–16.3	–16.3	–14.0	— ^[e]

[a] Labeling scheme as shown. [b] P–R1 in **2c** does not stretch toward Ru2. [c] These values are cited in reference [5]. [d] In C₆D₆. [e] The activation parameters for **2g** could not be determined because the signals for C₅Me₅ groups are observed to be equivalent in the range from –110 °C to 25 °C.

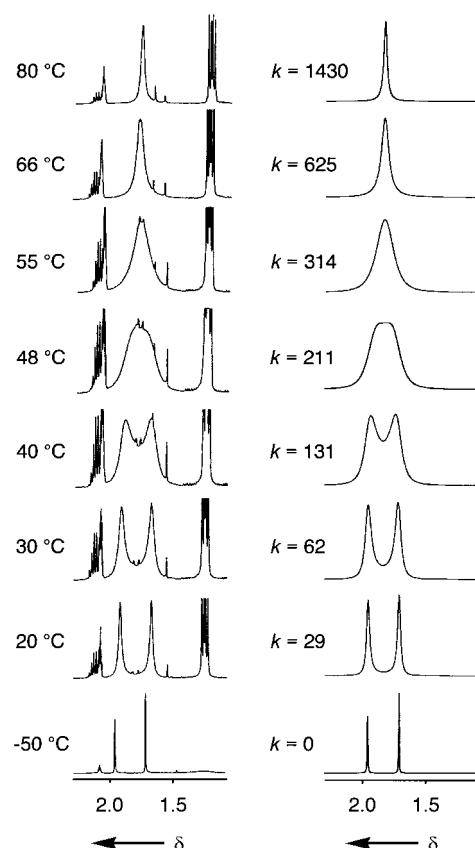
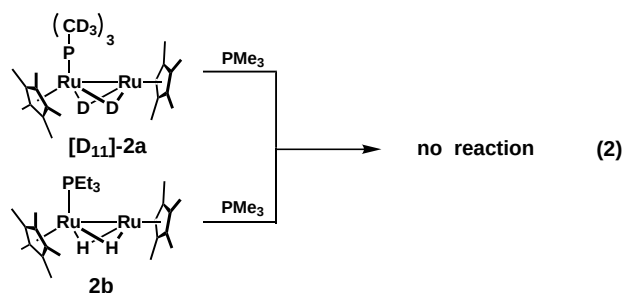
Although the two cyclopentadienyl ligands in **2** are each in a different steric environment in the solid state, their ¹H NMR signals were observed to be equivalent above room temperature. As the temperature was lowered, the signal for the C₅Me₅ group was remarkably broadened and split into two peaks below about –100 °C. The intramolecular migration of

the line-shape analysis of the variable-temperature ¹H NMR spectra (Figure 2) are also listed in Table 1. The small $\Delta S^\ddagger$ values rule out the possibility of an intermolecular process, and are consistent with the above-mentioned intramolecular process. The values are similar to those found in migration of a



Scheme 1. Fluxional behavior of the diruthenium hydrido complexes.

the phosphorus ligand between the two ruthenium centers likely accounts for this fluxional behavior (Scheme 1). Only a few examples are thus far known for the migration of a terminal phosphane ligand among metal centers,^[7] but the mechanistic details are still uncertain. The possibility of an intermolecular process, namely, liberation of the PR₃ group from one of the ruthenium centers and its recombination with another ruthenium atom, is ruled out because the coordinated PR₃ group in **2** is not exchanged with added phosphanes [Eq. (2)]. Kinetic parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, estimated from

Figure 2. Variable-temperature ¹H NMR spectra of **2c** (left) and calculated spectra (right; C₅Me₅ region).

silyl group on a diruthenium core.^[8] A dinuclear species with a bridging five-coordinate phosphane ligand in between the two ruthenium atoms is plausible for the transition state (Scheme 1). Such a dinuclear μ -PR₃ complex has been reported recently,^[9] and a dipalladium complex bridged by the pentacoordinate phosphane has also been reported.^[10] There is a close correlation between the $\Delta H^\ddagger$ values and the electronic parameters $\Sigma\chi_i$ defined by Tolman.^[5] The more electron-withdrawing the substituent on the phosphane ligand is, the smaller the $\Delta H^\ddagger$ value is. This result suggests that through-space interaction between the phosphorus and Ru2, $\sigma^*(\text{P}-\text{C})-\text{d}(\text{Ru}2)$ and/or $\text{p}(\text{P})-\text{d}(\text{Ru}2)$, possibly leads to the migration of the phosphorus ligand. Although we have not yet deduced which interaction is predominant, a linear relationship between the Ru2-Ru1-P angle and the $\Sigma\chi_i$ value for the phosphorus ligand (Figure 3) is consistent with such a backbonding interaction. The enhancement of the Ru2-P back-

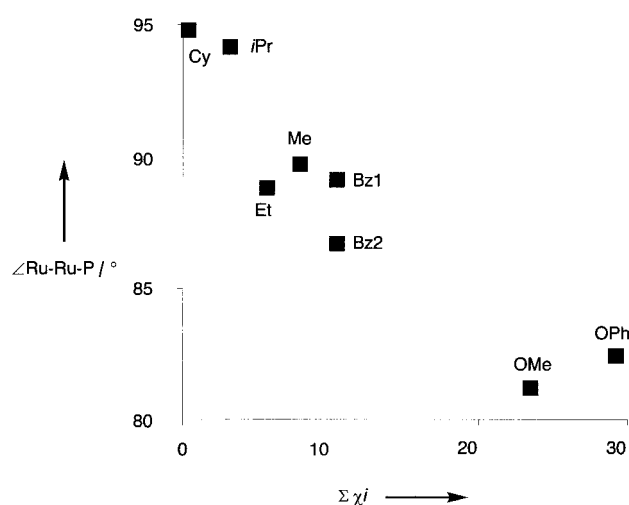


Figure 3. Relationship between Ru2-Ru1-P angles and electronic parameters $\Sigma\chi_i$.

bonding interaction due to introduction of electron-withdrawing substituents on the phosphorus atom likely leads to the decrease of the Ru2-Ru1-P angle. The $\sigma^*(\text{P}-\text{C})-\text{d}(\text{Ru}2)$ backbonding interaction may be rationalized by the coplanarity of the Ru2, Ru1, P, and R in **2a**, **2b**, **2f**, and **2g**, observed in the X-ray structure analyses.

We have synthesized novel diruthenium complexes containing a phosphorus ligand and demonstrated the migration of the phosphorus ligand between the two ruthenium centers. From a thermodynamic and structural standpoint, we propose a through-space backbonding interaction between the ruthenium and phosphorus atoms.

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[4] The diffraction data were measured on an AFC-7R four-circle diffractometer (**2a**, **2c**, **2f**) or RAXIS-2 imaging plate area detector (**2b**, **2d**, **2e**, **2g**). The structures were solved by the Patterson method (DIRDIF92 PATTY). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms except for Ru-H (refined isotropically) were fixed at the calculated positions. Crystal data for **2a**: monoclinic, $P2_1/n$, $a = 11.439(4)$, $b = 14.208(6)$, $c = 15.527(5)$ Å, $\beta = 90.79(3)^\circ$, $V = 2523(1)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.450$ g cm⁻³; 6316 reflections ($5^\circ \leq 2\theta \leq 55^\circ$), 4048 observed with $F > 3\sigma(F)$, 244 parameters; $R = 0.040$, $R_w = 0.037$. Crystal data for **2b**: monoclinic, $P2_1/c$, $a = 16.63(1)$, $b = 8.446(1)$, $c = 20.57(2)$ Å, $\beta = 95.00(7)^\circ$, $V = 2878(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.368$ g cm⁻³; 6646 reflections ($5^\circ \leq 2\theta \leq 60^\circ$), 4603 observed with $F > 3\sigma(F)$, 263 parameters; $R = 0.057$, $R_w = 0.054$. Crystal data for **2c**: monoclinic, Pn , $a = 11.168(4)$, $b = 11.170(4)$, $c = 11.902(4)$ Å, $\beta = 94.04(3)^\circ$, $V = 1481.0(9)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.424$ g cm⁻³; 3361 reflections ($5^\circ \leq 2\theta \leq 55^\circ$), 2859 observed with $F > 3\sigma(F)$, 290 parameters; $R = 0.038$, $R_w = 0.047$. Crystal data for **2d**: monoclinic, $P2_1/n$, $a = 30.8323(7)$, $b = 11.899(2)$, $c = 11.342(4)$ Å, $\beta = 91.27(2)^\circ$, $V = 4159(1)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.321$ g cm⁻³; 8667 reflections ($5^\circ \leq 2\theta \leq 60^\circ$), 5376 observed with $F > 3\sigma(F)$, 396 parameters; $R = 0.048$, $R_w = 0.060$. Crystal data for **2e**: triclinic, $P\bar{1}$, $a = 18.421(4)$, $b = 20.121(4)$, $c = 10.129(2)$ Å, $\alpha = 90.90(1)$, $\beta = 98.44(1)$, $\gamma = 88.19(2)^\circ$, $V = 3711(1)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.394$ g cm⁻³; 15623 reflections ($5^\circ \leq 2\theta \leq 60^\circ$), 11404 observed with $F > 3\sigma(F)$, 810 parameters; $R = 0.034$, $R_w = 0.033$. Crystal data for **2f**: monoclinic, $P2_1/n$, $a = 19.823(4)$, $b = 15.991(5)$, $c = 8.351(4)$ Å, $\beta = 98.86(3)^\circ$, $V = 2615(1)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.520$ g cm⁻³; 6638 reflections ($5^\circ \leq 2\theta \leq 55^\circ$), 4836 observed with $F > 3\sigma(F)$, 271 parameters; $R = 0.027$, $R_w = 0.025$. Crystal data for **2g**: monoclinic, $P2_1/a$, $a = 17.146(5)$, $b = 17.8115(9)$, $c = 11.599(2)$ Å, $\beta = 96.28(2)^\circ$, $V = 3521.0(10)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.481$ g cm⁻³; 7385 reflections ($5^\circ \leq 2\theta \leq 60^\circ$), 5970 observed with $F > 3\sigma(F)$, 406 parameters; $R = 0.037$, $R_w = 0.027$. CCDC-173306 to CCDC-173312 contains the supplementary crystallographic data (excluding structure factors) 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 CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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