Angewandte Chemie

Heterometallic Complexes

DOI: 10.1002/anie.200804482

Drastic Acceleration of Phosphine/Phosphite Incorporation into a Tetrahydrido Ruthenium/Osmium Complex, and One-way Ruthenium to Osmium Migration of a Phosphorus Ligand**

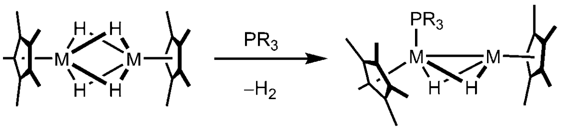
*Hajime Kameo, Yumiko Nakajima, and Hiroharu Suzuki**

Cluster complexes form an attractive class in the reactions of transition metal complexes, owing to their capability of activating substrates effectively through the cooperative effects of multiple metal centers.[1] To date, we have demonstrated several examples of cooperative activation by treating various substrates, including unsaturated hydrocarbons, with $[Cp^*Ru(\mu\text{-}H)_4RuCp^*]$ (**1**, $Cp^* = \eta^5\text{-}C_5Me_5$) and $[(Cp^*Ru)_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$.[2]

Heterometallic cluster complexes that contain different metals may exhibit electronic anisotropic characters stemming from polarized metal–metal bonds.[3] Therefore, significant heterometallic effects, such as marked regioselectivity and remarkable acceleration, could occur in the reaction in addition to the typical effects of cluster complexes resulting from multiple coordination and multielectron transfer.

We synthesized a series of heterometallic dinuclear polyhydrido complexes, such as $[Cp^*Ru(\mu\text{-}H)_4OsCp^*]$ (**2**),[4a] $[Cp^*Ru(\mu\text{-}H)_3IrCp^*]$,[4b] $[Cp^*Ru(\mu\text{-}H)_3ReH_2Cp^*]$,[4c] $[Cp^*Ru(\mu\text{-}H)_3MoH_3Cp^*]$,[4d] and $[Cp^*Ru(\mu\text{-}H)_3WH_3Cp^*]$[4d] and demonstrated their heterometallic effects through reactions with unsaturated hydrocarbons, phosphines, amines, and acetylacetone. For example, the reaction of heterometallic Ru–Os complex $[Cp^*Ru(\mu\text{-}H)_4OsCp^*]$ (**2**) with ethylene exclusively afforded $[Cp^*Os(CH_2{=}CH_2)(\mu\text{-}\eta^1,\eta^2\text{-}CH{=}CH_2)_2RuCp^*]$ in which the vinyl groups are η^1-bonded to Os.[4a] In this reaction, C–H bond activation selectively occurred at the Os center because Os and Ru atoms served as activation and binding sites, respectively, indicating sharing of functions between the two metal atoms in the reactions of the heterometallic dinuclear polyhydrido clusters. However, the aforementioned reactions, particularly reactions with unsaturated hydrocarbons, involved multiple elementary steps, and the complexity of the reaction often obscured the heterometallic effect in each elementary step. To evaluate the heterometallic effect, this study focused on the addition of a phosphorus ligand to the dinuclear tetrahydrido complex $[Cp^*M(\mu\text{-}H)_4M'Cp^*]$ (**2**: M = Ru, M′ = Os; **3**: M = M′ = Os[5]) to produce a dihydrido–phosphine or dihydrido–phosphite complex $[Cp^*(X_3P)M(\mu\text{-}H)_2M'Cp^*]$ (X = OMe, Me). Through these reactions, we obtained positive evidence for a kinetic heterometallic effect (KHE) and a thermodynamic heterometallic effect (THE), namely, remarkable acceleration of the incorporation of phosphine or phosphite groups into the heterodinuclear tetrahydride **2** and intramolecular migration of $P(OMe)_3$ from the ruthenium center to the osmium center in one direction in $[Cp^*\{(MeO)_3P\}Ru(\mu\text{-}H)_2OsH_2Cp^*]$ (**4**), respectively.

We have reported the formation of dinuclear dihydrido–phosphine and dihydrido–phosphite complexes $[Cp^*(R_3P)Ru(\mu\text{-}H)_2RuCp^*]$ (R = Me (**5a**), Et (**5b**), *i*Pr (**5c**), Bn (**5d**), OMe (**5e**), and OPh (**5f**)) in the reaction of diruthenium tetrahydrido complex **1** with various phosphorus ligands [Eq. (1)]. We also demonstrated that the phosphorus ligand reversibly migrated between the two ruthenium atoms.[6]



(1)

1: M = Ru
3: M = Os

5: M = Ru
6: M = Os

Similarly, diosmium tetrahydrido complex **3** reacted with $P(OMe)_3$ to generate a dinuclear phosphite complex $[Cp^*Os(\mu\text{-}H)_2Os\{P(OMe)_3\}Cp^*]$ (**6**) [Eq. (1)]. As anticipated from the vertical trend within the periodic table, **3** is less reactive than the Ru analog **1**. Whereas the reaction of **1** with 1.2 equivalents of $P(OMe)_3$ at room temperature went to completion after 10 min, producing **5e** selectively, the reaction of **3** with 10 equivalents of $P(OMe_3)_3$ at room temperature required nearly 10 days for completion.

In contrast, the reaction of heterometallic Ru–Os complex **2** with $P(OMe)_3$ was faster than that of the homometallic complexes. The reaction of **2** with 1.0 equivalents of $P(OMe)_3$ in tetrahydrofuran was completed within 10 min, resulting in the exclusive formation of $[Cp^*Ru(\mu\text{-}H)_2Os\{P(OMe)_3\}Cp^*]$ (**7**), in which trimethylphosphite was coordinated to the Os atom [Eq. (2)].

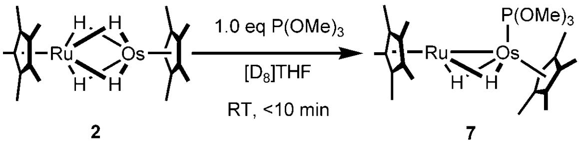
The newly synthesized compounds **6** and **7** were unambiguously characterized on the basis of ^1H, ^{13}C, and ^{31}P NMR spectroscopic data as well as elemental analysis.[7] The solid-

---

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

[**] The present research is supported by the grants No.18105002 (Scientific Research (S)) from Japan Society of the Promotion of Science and No. 18064007 (Priority Area "Synergy of Elements") from the Ministry of Education, Culture, Sports, Science, and Technology (Japan). H. Kameo acknowledges financial support from Grant-in-Aid for JSPS Fellows.

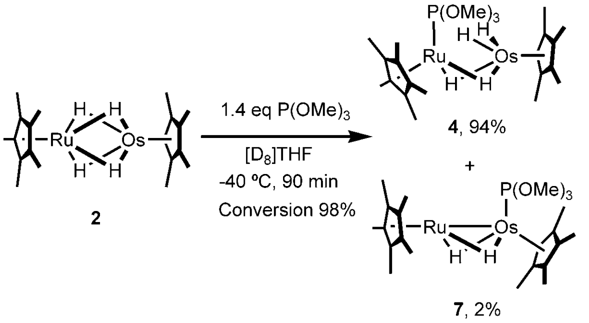
Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200804482.



(2)

state structures of **6** and **7** were confirmed by X-ray diffraction studies.[8]

Monitoring of the reaction by ^{1}H NMR spectroscopy at −40 °C clearly revealed the formation of an intermediate tetrahydrido complex [Cp*{(MeO)$_3$P}Ru(μ-H)$_2$OsH$_2$Cp*] (**4**),[9] which was converted into **7** as a result of reductive elimination of dihydrogen, and subsequent migration of P(OMe)$_3$ from the Ru center to the Os center [Eq. (3)].



(3)

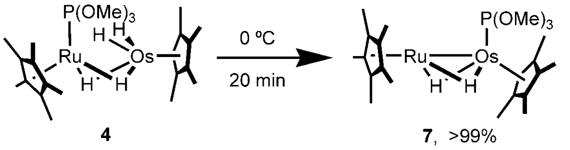
A preliminary kinetic experiment revealed that the treatment of **1** and **3** with P(OMe)$_3$ produced the dihydrido–phosphite complexes **5e** and **6**, respectively, without the formation of an intermediate species, whereas the formation of the intermediate tetrahydrido–phosphite complex **4** was detected in the reaction of **2**. The disappearance of **2** was monitored by ^{1}H NMR spectroscopy, and the reaction was demonstrated to be first-order in the tetrahydride. The acceleration of the reaction in the heterometallic system is remarkable in comparison to the homometallic system. The rate constant of the reaction with **2** is larger than those with **1** and **3** by factors of 65 and 1900, respectively. The electronic and steric biases induced in the Ru–Os core of **2** are responsible for the significant acceleration of the reaction. This effect is an appropriate example of the KHE. The activation parameters[10] indicate that the rate-determining step is associative (Table 1), and the enthalpy of activation is the dominant factor determining the origin of the KHE.

Above 0 °C, intermediate **4** was transformed into the complex [Cp*Ru(μ-H)$_2$Os{P(OMe)$_3$}Cp*] (**7**) as a result of phosphite migration from the Ru center to the Os center and concurrent elimination of dihydrogen [Eq. (4)].[11] The formation of the strong Os–P bond causes the migration of the phosphorus ligand.

Table 1: The entropy and the enthalpy of activation, and the reaction rate for reaction with P(OMe)$_3$ at −50 °C.

Complex (MM′)	$\Delta H^{\neq}$ [kcal mol^{-1}]	$\Delta S^{\neq}$ [cal mol^{-1} K^{-1}]	k_{223K} [s^{-1}]
1 (Ru$_2$)	13.8 (9)	−15.3 (43)	2.6×10^{-5}
2 (RuOs)	9.3 (10)	−27.7 (41)	1.7×10^{-3}
3 (Os$_2$)	10.1 (9)	−39.0 (43)	9.0×10^{-7}[a]

[a] Value calculated by extrapolation.



(4)

The molecular structures of **6** (Figure 1) and **7** (Figure 2) were determined by X-ray diffraction studies using single crystals obtained from a pentane solution at room temperature. The structures of **6** and **7** were similar to the structure of **5e**, and the difference in the metal centers had a negligible effect on the structure. The P–O bond lengths show the similarity of d_{metal}–σ^*_{P-O} backbonding interactions[12] in **6**, **7**, and **5e**.

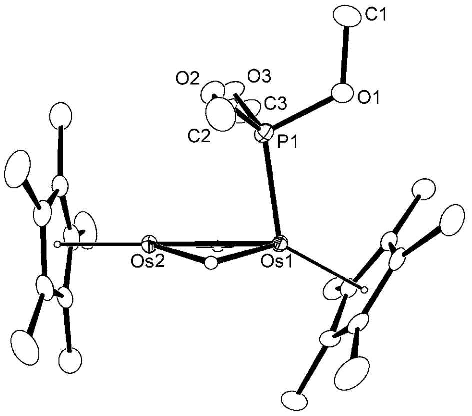


Figure 1. Molecular structure of **6** with thermal ellipsoids set at 30% probability. Selected bond lengths [Å] and angles [°]: Os1–Os2 2.4850(2), Os1–P1 2.2194(11), P1–O1 1.628(3), P1–O2 1.614(3), P1–O3 1.605(3); Os2-Os1-P1 82.71(3).

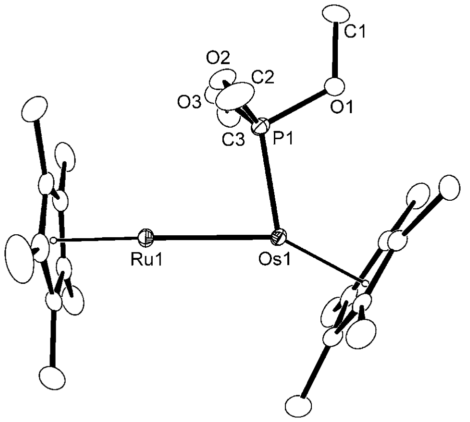


Figure 2. Molecular structure of **7** with thermal ellipsoids set at 30% probability. Selected bond lengths [Å] and angles [°]: Ru1–Os1 2.5166(3), Os1–P1 2.2152(9), P1–O1 1.624(3), P1–O2 1.608(3), P1–O3 1.614(3); Ru1-Os1-P1 81.49(3).

To study the heterometallic effect in detail, we carried out density functional calculations (DFT, B3LYP level)[13] on a series of tetrahydride complexes, in which the methyl groups of the Cp* ligand were replaced by H (**1′**, **2′**, and **3′**, Figure 3).[14] The calculation reproduced well the structures of **2** and **1**. Natural population analysis[15] indicated that the natural charge of the Ru atom in **2′** was almost neutral, and the Os atom had a negative charge (Ru +0.026, Os −0.209). In contrast, the natural charges of the two metal centers in **1′** were comparable (Ru^1 −0.116, Ru^2 −0.117), and the natural charges of the two metal centers in **3′** were similar to those of the metal centers in **1′** (see the Supporting Information). These results indicate that the different metal centers in **2** induced polarization, which was responsible for the acceleration of the reaction and site-selective addition. Moreover, elongation of the Ru−H bonds allowed the phosphorus ligand to approach the Ru atom more easily. These conclusions were also supported by the model calculation.[16]

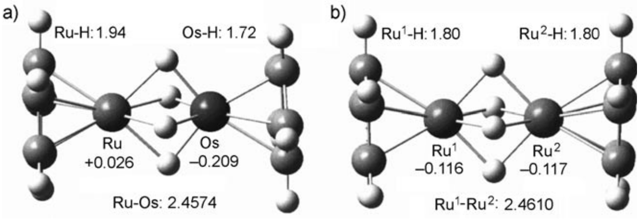


Figure 3. Optimized structures of a) CpRu(μ-H)$_4$OsCp (**2′**) and b) CpRu(μ-H)$_4$RuCp (**1′**). Bond lengths are given in Å. Average values are given for M−H bond lengths. Natural charges are underlined.

In summary, the heterometallic dinuclear complex **2** induced site-selective addition of phosphorus ligands (phosphine and phosphite) to the Ru atom, and the phosphorus ligand underwent unidirectional migration from Ru to Os. We demonstrated that the combination of Ru and Os within the heterometallic complex accelerated the incorporation of the phosphorus ligand. DFT calculations indicated that polarization between the metal centers in **2** played an important role in the site-selective addition and the acceleration of the reaction. In contrast, homometallic complexes **1** and **3** reacted with trimethylphosphite to afford the corresponding phosphite complexes **5e** and **6**, in which the phosphorus ligand migrated between the two metal atoms. The migration of the phosphorus ligand was probably governed by the binding enthalpy between the phosphorus and metal atoms. A detailed theoretical study is being conducted to gain a better understanding of heterometallic effects.

Received: September 11, 2008
Published online: November 21, 2008

Keywords: heterometallic complexes · hydride ligands · osmium · phosphanes · ruthenium

---

[1] a) R. D. Adams, F. A. Cotton, *Catalysis by Di- and Polynuclear Metal Cluster Complexes*, Wiley-VCH, New York, **1998**; b) B. C. Gates, L. Guzei, V. H. Knozinger, *Metal Clusters in Catalysis*, Elsevier, Amsterdam, **1986**.

[2] a) H. Suzuki, H. Omori, D. H. Lee, Y. Yoshida, M. Fukushima, M. Tanaka, Y. Moro-oka, *Organometallics* **1994**, *13*, 1129 – 1146; b) H. Suzuki, T. Kakigano, K. Tada, M. Igarashi, K. Matsubara, A. Inagaki, M. Oshima, T. Takao, *Bull. Chem. Jpn. Soc.* **2005**, *78*, 67 – 87; c) H. Suzuki, *Eur. J. Inorg. Chem.* **2002**, 1009 – 1023.

[3] a) D. W. Stephan, *Coord. Chem. Rev.* **1989**, *95*, 41 – 107; b) C. P. Casey, *J. Organomet. Chem.* **1990**, *400*, 205 – 221; c) N. Wheatley, P. Kalck, *Chem. Rev.* **1999**, *99*, 3379 – 3419; d) J. R. Fulton, T. A. Hanna, R. G. Bergman, *Organometallics* **2000**, *19*, 602 – 614.

[4] a) T. Shima, H. Suzuki, *Organometallics* **2005**, *24*, 3939 – 3945; b) T. Shima, H. Suzuki, *Organometallics* **2000**, *19*, 2420 – 2422; c) J. Ito, T. Shima, H. Suzuki, *Organometallics* **2004**, *23*, 2447 – 2460; d) T. Shima, J. Ito, H. Suzuki, *Organometallics* **2001**, *20*, 10 – 12.

[5] C. L. Gross, S. R. Wilson, G. S. Girolami, *J. Am. Chem. Soc.* **1994**, *116*, 10294 – 10295.

[6] Y. Ohki, H. Suzuki, *Angew. Chem.* **2002**, *114*, 3120 – 3123; *Angew. Chem. Int. Ed.* **2002**, *41*, 2994 – 2997.

[7] **6**: ^{1}H NMR (400 MHz, [D$_8$]THF, room temperature): $\delta = -13.53$ (d, J(P,H) = 13.6 Hz, 2H, Os−H), 1.94 (br s, $w_{1/2} = 4.4$ Hz, 30H, C$_5$Me$_5$), 3.41 ppm (d, J(P,H) = 13.6 Hz, 6H, P(OMe)$_3$). ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]THF, room temperature): 12.7 (s, C$_5$*Me*$_5$), 51.7 (s, P(OMe)$_3$), 78.2 (s, *C*$_5$Me$_5$). ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF, room temperature): $\delta = 119.7$ ppm. Elemental analysis calcd (%) for $C_{23}H_{41}O_3Os_2P_1$: C 35.45, H 5.01; found: C 35.55, H 5.32.**7**: ^{1}H NMR (400 MHz, [D$_8$]THF, room temperature): $\delta = -16.31$ (d, J(P,H) = 15.6 Hz, 2H, Os−H−Ru), 1.66 (s, 15H, RuC$_5$Me$_5$), 2.05 (d, J(P,H) = 0.8 Hz, 15H, OsC$_5$Me$_5$), 3.44 ppm (d, J(P,H) = 12.8 Hz, 9H, P(OMe)$_3$). ^{13}C{^{1}H} NMR (100 MHz, [D$_8$]THF, room temperature): $\delta =$ 12.2 (s, C$_5$*Me*$_5$), 12.6 (s, C$_5$*Me*$_5$), 51.4 (s, P(OMe)$_3$), 75.7 (s, *C*$_5$Me$_5$), 86.6 ppm (s, *C*$_5$Me$_5$). ^{31}P{^{1}H} NMR (162 MHz, [D$_8$]THF, room temperature): $\delta = 134.1$ ppm. Elemental analysis calcd (%) for $C_{23}H_{41}O_3Os_1P_1Ru_1$: C 40.16, H 6.01; found: C 40.04, H 6.03. The ^{1}H NMR signals for the two Cp*-groups in **6**, which are in different environments in the solid state, were equivalent above 0 °C, indicating that the intramolecular migration of the phosphorus ligand between the two osmium centers proceeded in the same way as that between the two ruthenium centers in **5**.[6]

[8] X-ray crystallography: All data were collected on a Rigaku R-Axis RAPID imaging plate diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Crystal data for **6**: monoclinic; space group $P2_1/n$ (No. 14), $a = 8.3254(3)$, $b = 15.9634(4)$, $c = 19.9496(6)$ Å; $\beta = 98.9250(10)°$; $V = 2619.23(14)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.970$ Mg m^{-3}; $\mu(Mo_{K\alpha}) = 9.773$ mm^{-1}; 17727 reflections measured; 4944 unique reflections ($R_{int} = 0.0328$); $R_1 = 0.0220$ [$I > 2\sigma(I)$]; $wR_2 = 0.0515$ [$I > 2\sigma(I)$]. Crystal data for **7**: monoclinic; space group $P2_1/n$ (No. 14), $a = 8.3116(4)$, $b = 16.0047(7)$, $c = 19.8776(8)$ Å; $\beta = 99.0190(15)°$; $V = 2611.52(19)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.749$ Mg m^{-3}; $\mu(Mo_{K\alpha}) = 5.520$ mm^{-1}; 20997 reflections measured; 4957 unique reflections ($R_{int} = 0.0375$); $R_1 = 0.0222$ [$I > 2\sigma(I)$]; $wR_2 = 0.0503$ [$I > 2\sigma(I)$]. CCDC 701616 (**6**) and CCDC 701617 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

[9] **4**: ^{1}H NMR (400 MHz, [D$_8$]THF, −105 °C): $\delta = -21.28$ (br d, $w_{1/2} = 31.8$ Hz, 2H, Ru−H−Os), −13.95 (br s, $w_{1/2} = 29.7$ Hz, 2H, Os−H), 1.50 (s, 15H, Os−Cp*), 2.01 (d, J(P,H) = 2.0 Hz, 15H, Ru-Cp*), 3.37 ppm (d, J(P,H) = 10.4 Hz, 15H, P(OMe)$_3$). The two types of hydrido ligands mutually exchange coordination sites and the signal for the hydrides was decoalesced around −70 °C.

[10] A solution of **2** (4.6 mg, 0.0081 mmol) in [D$_8$]THF (2.0 mL), with cyclooctane (2 μL) as an internal standard, was divided up evenly into four NMR sample tubes. The NMR probe was cooled to the prescribed temperature (−80, −70, −60, or −50 °C) and 47–53 equivalents of trimethylphosphite was introduced into the tube at −78 °C. The sample was shaken and placed in the spectrometer. Data collection with an automated acquisition program began immediately after the sample was placed in the probe. The rate constants were calculated on the basis of the time conversion of [**2**]. The reaction conditions are shown in Table S1. The temperature dependence of the rate constants yielded the following activation parameters: $\Delta H^{\pm} = 9.3 \pm 0.9\ \mathrm{kcal\,mol^{-1}}$ and $\Delta S^{\pm} = -27.7 \pm 4.3\ \mathrm{cal\,mol^{-1}\,K^{-1}}$. The activation parameters of **1** and **3** were calculated in a similar manner.

[11] Some groups have reported phosphine migration between two metal atoms. For example; a) G. L. Geoffroy, *Acc. Chem. Res.* **1980**, *13*, 469–476; b) A. M. Bradford, G. Douglas, L. Manojiovic-Muir, K. W. Muir, R. J. Puddephatt, *Organometallics* **1990**, *9*, 409–416; c) R. D. Adams, B. Captain, W. Fu, P. J. Pellechia, *Inorg. Chem.* **2003**, *42*, 3111–3118; d) L. Pereira, W. K. Leong, S. Y. Wong, *J. Organomet. Chem.* **2000**, *609*, 104–109; e) S. Bouherour, P. Braunstein, J. Rosé, L. Toupet, *Organometallics* **1999**, *18*, 4908–4915; f) W. H. Watson, G. Wu, M. G. Richmond, *Organometallics* **2005**, *24*, 5431–5439.

[12] P. H. M. Budzelaar, P. W. N. M. Leeuwen, C. F. Roobeek, A. G. Orpen, *Organometallics* **1992**, *11*, 23–25.

[13] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[14] For Ru and Os, (541/541/211/1) basis sets[17] were used to represent valence electrons, where core electrons of Ru and Os were replaced with effective core potentials (ECPs). For C and H, 6-31G(d) and 6-311G(d,p) basis sets were employed, respectively.

[15] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746.

[16] Model calculations were carried out by using $\{\mathrm{CpM}(\mu\text{-H})_4\mathrm{M'Cp}\}$ (M, M′ = Ru or Os) and PH_3. For details see the Supporting Information.

[17] A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 111.