



Note

Reaction of multifunctional molecule $(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ with triosmium carbonyl clusters

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ABSTRACT

Reaction of $(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ with 3 equiv. of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ at ambient temperature affords the triple cluster $[\text{Os}_3(\text{CO})_{10}\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ (**1**) through coordination of the phosphine and imine groups. Thermolysis of **1** in benzene leads to decarbonylation and C–H/C–N bond activation of the ligand to generate $(\mu\text{-H})\text{Os}_3(\text{CO})_8(\mu_3\text{-Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NC}=\text{CH}_2)$ (**2**). The molecular structure of **2** has been determined by an X-ray diffraction study.

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1. Introduction

Recently, the ability of a metal cluster to organize a flexible polyfunctional ligand around its coordination sphere has led to design of intramolecularly organized recognition sites [1–4]. In addition, since the cluster-bonded ligand is capable of interacting with several metal centers, it frequently displays a reactivity different from that found in the monometallic systems [5–9]. We have prepared the heptafunctional molecule $(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ [10] and shown its coordination chemistry with tungsten carbonyls to generate a novel cryptand-like metallacycle complex. Arising from our continuous interest in the activation of organic substrates by metal clusters [11], this paper reports the reaction of $(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ with triosmium carbonyl clusters to produce a tripodal macromolecule and its thermal reactivity leading to C–H and C–N bond activation of the ligand.

2. Results and discussion

Treatment of $(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ with 3 equiv. of $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ in dichloromethane at ambient temperature for 3 h results in facile substitution of the labile acetonitrile ligands by imine–phosphine groups to afford the tripodal triple cluster $[\text{Os}_3(\text{CO})_{10}\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ (**1**) in 77% yield (Scheme 1) after purification by column chromatography. Compound **1** forms an air-stable, orange solid which is soluble in common organic solvents. The ^1H NMR spectrum of free $(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)$

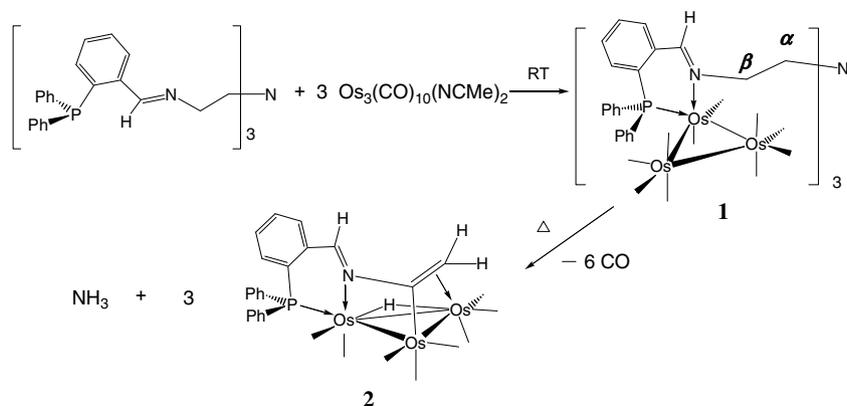
$\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ in CD_2Cl_2 presents a doublet resonance at 8.84 ppm for the CH–N proton and two triplets at 3.39 and 2.45 ppm for the ethylene protons, while its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a singlet at –13.02 ppm for the phosphine groups [10]. Upon coordination to the Os_3 clusters, the imine CH–N proton resonance is shifted upfield to 8.19 ppm, and the phosphine ^{31}P resonance is shifted downfield to 15.83 ppm. The ethylene proton resonances are split into four signals in the range 4.42–2.38 ppm, indicating asymmetric coordination of the imine–phosphine ligand to result in diastereotopic CH_2 groups. The spectral data suggest equivalence of the three $[\text{Os}_3(\text{CO})_{10}\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2]$ units in solution likely through C_3 rotations. The IR absorptions in the carbonyl region for **1** are shifted to lower energy compared with $\text{Os}_3(\text{CO})_{12}$, consistent with the stronger net donor capability of imine–phosphine ligands compared with CO [12].

We have previously prepared the complex $\text{Os}_3(\text{CO})_{10}\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2(o\text{-C}_5\text{H}_4\text{N})$ [13], which contains an imine–phosphine linkage analogous to **1**, and the structure of which shows that the P–N group chelates one Os atom with the bulky Ph_2P ligand in the more opened equatorial position, while the imine group takes up an axial position. It is probable that the imine–phosphine species in **1** adopt a similar axial–equatorial chelating fashion. The energy-minimized configuration constructed for **1** (Fig. 1) suggests a triangular arrangement for the Os_3 clusters.

It is of interest to investigate if the Os_3 units can mediate rearrangement of the organic ligand under severe conditions. Thus, a benzene solution of **1** was heated to reflux under dinitrogen, and the reaction was monitored by IR until no absorptions due to the starting compound. After purification of the products by column chromatography, $(\mu\text{-H})\text{Os}_3(\text{CO})_8(\mu_3\text{-Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NC}=\text{CH}_2)$ (**2**) was obtained in 68% yield (based on the Os atoms) as an air-stable,

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Scheme 1.

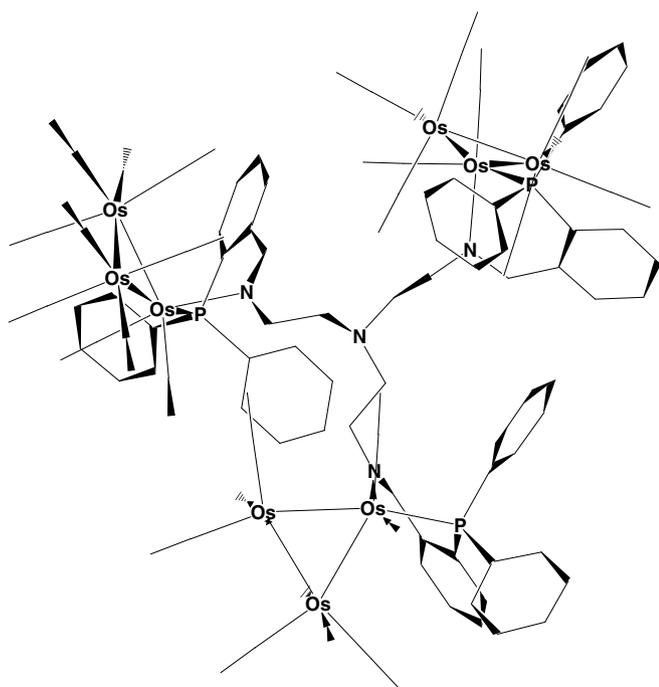


Fig. 1. Proposed configuration of **1**, showing a triangular arrangement for the three Os_3 clusters.

red crystalline solid. The FAB mass spectrum of **2** displays the molecular ion peak at m/z 1115 for ^{192}Os . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum presents a sharp singlet at -4.64 ppm for the phosphine group. The ^1H NMR spectrum shows a 15H multiplet in the range 7.81–6.90 ppm for the imine and phenyl proton resonances, two 1H singlets at 3.64 and 1.93 ppm for the methylene protons, and a 1H doublet ($J_{\text{P-H}} = 10$ Hz) at -14.54 ppm for the bridging hydride resonance, indicating activation of the tripodal ligand by the clusters upon heating. A single crystal of **2** was thus subjected to an X-ray diffraction analysis to reveal the structure.

The molecular structure of **2** is displayed in Fig. 2. The $(\text{Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ ligand has undergone a degradation reaction through N–C and C–H bond activation to generate the species $\text{Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{CH}=\text{NC}=\text{CH}_2$, which can be considered as a seven-electron donor to result in a total of 48 valence electrons for the cluster. The metal parts are based upon a triangular array of osmium atoms in which the osmium–osmium bonds show substantial variation, with Os1–Os2 2.8531(5) Å, Os1–Os3 2.9688(5) Å, and Os2–Os3 2.7502(5) Å. Lengthening of the Os1–Os3 edge is

likely caused by the bridging hydride ligand which was not located directly [14]. The Os1, Os2, and Os3 atoms are each associated with two, three, and three terminal carbonyl ligands, respectively, with the Os–C–O angles ranging from $174.3(9)^\circ$ to $179(1)^\circ$. The phosphine–imine group chelates the Os1 atom with the bite angle P1–Os1–N1 $84.1(2)^\circ$. The phosphine group takes up an equatorial site trans to the Os1–Os2 bond with P1–Os1 2.321(2) Å and P1–Os1–Os2 $157.00(7)^\circ$, while the imine N1 atom is in the axial position with N1–Os1 2.082(8) Å and N1–Os1–C1 $169.9(4)^\circ$. The C11–N1 distance of 1.28(1) Å retains a C–N double bond character, while the C10–N1 single bond distance is 1.46(1) Å. The C10–N1–C11 and N1–C11–C12 angles are $123.9(8)^\circ$ and $122.6(9)^\circ$, respectively, in agreement with an sp^2 hybridization for the N1 and C11 atoms. The vinyl carbon C10 is σ -bonded to the Os3 atom with C10–Os3 2.105(9) Å, and the C10–C9 double bond (1.38(1) Å) is π -bonded to the Os2 atom with the distances C10–Os2 2.268(9) Å and C9–Os2 2.36(1) Å. The C9–C10–N1–C11 torsional angle is $54.6(2)^\circ$.

It is interesting that thermal decarbonylation of **1** leads to three molecules of **2** through cleavage of two β -C–H bonds and the amine N–C bond. One molecule of NH_3 should be produced concomitant with the reaction, though it was not confirmed experimentally. Co-thermolysis of $(\text{Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ and $\text{Os}_3(\text{CO})_{12}$ in methylcyclohexane solution (101°C) also produces **2** in lower yield (38%). The transformation from **1** to **2** apparently involves several bond breaking and H-atom migration steps, but the details remain unclear due to lack of reaction intermediates. Previous study showed that [13] heating the analogous complex $\text{Os}_3(\text{CO})_{10}\text{Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2(\text{o-C}_5\text{H}_4\text{N})$ in toluene results in an imine C–H bond activation to give $(\mu\text{-H})\text{Os}_3(\text{CO})_8\text{Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{C}=\text{NCH}_2\text{CH}_2(\text{o-C}_5\text{H}_4\text{N})$ and an α -C–H bond activation to give $(\mu\text{-H})\text{Os}_3(\text{CO})_8\text{Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}(\text{o-C}_5\text{H}_4\text{N})$. Since the pyridine moiety in $\text{Os}_3(\text{CO})_{10}\text{Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2(\text{o-C}_5\text{H}_4\text{N})$ is capable of binding to the Os_3 cluster, the geometrical factors likely control the structure of the products.

3. Experimental

3.1. General methods

All manipulations were carried out under an atmosphere of dinitrogen with standard Schlenk techniques. $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ [15] and $(\text{Ph}_2\text{P}(\text{o-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ [10] were prepared by literature method. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. ^1H and ^{31}P NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer. Fast-atom-bombardment (FAB) mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer. Elemental

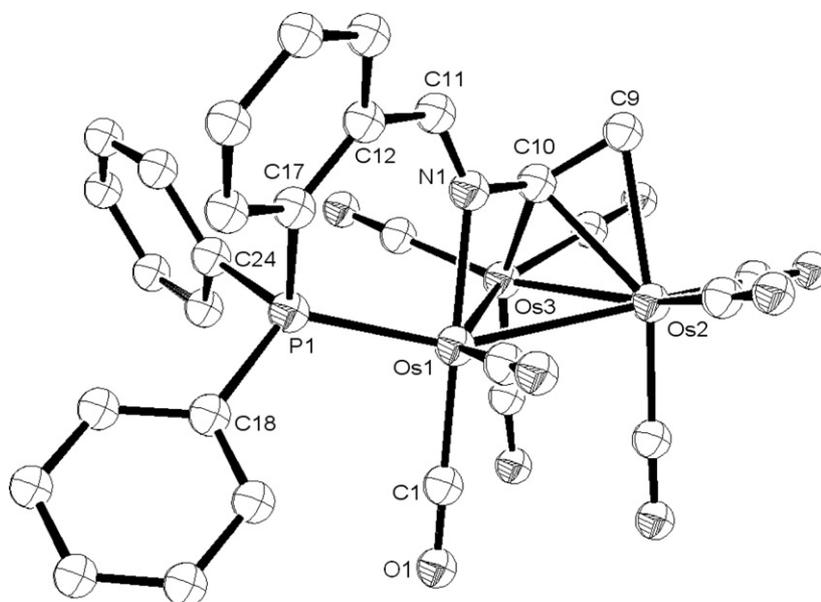


Fig. 2. Molecular structure of **2**. The hydrogen atoms have been artificially omitted for clarity. Selected bond lengths (Å) and bond angles (°): Os1–Os2 2.8531(5), Os1–Os3 2.9688(5), Os2–Os3 2.7502(5), Os1–P1 2.321(2), Os1–N1 2.082(8), Os2–C9 2.36(1), Os2–C10 2.268(9), Os3–C10 2.105(9), C9–C10 1.38(1), C10–N1 1.46(1), N1–C11 1.28(1), C11–C12 1.49(1), and Os1–Os2–Os3 63.96(1), Os1–Os3–Os2 59.71(1), Os2–Os1–Os3 56.34(1), Os1–P1–C17 105.8(3), Os1–P1–C18 119.0(3), Os1–P1–C24 117.5(3), P1–Os1–N1 84.1(2), P1–Os1–Os2 157.00(7), P1–Os1–Os3 115.30(6), N1–Os1–C1 169.9(4), N1–Os1–Os2 72.9(2), N1–Os1–Os3 69.8(2), Os2–C9–C10 69.1(5), Os2–C10–C9 76.3(6), C9–Os2–C10 34.7(3), Os2–C10–Os3 77.8(3), Os2–Os3–C10 53.7(2), Os3–Os2–C10 48.4(2), Os3–C10–C9 130.0(7), C9–C10–N1 115.6(8), C10–N1–C11 123.9(8), N1–C11–C12 122.6(9).

analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

3.2. Reaction of $(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ with $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$

$\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ (28 mg, 0.03 mmol) and $(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ (10 mg, 0.01 mmol) were placed in an oven-dried 50 ml Schlenk flask, equipped with a magnetic stir bar and a rubber serum stopper. Dichloromethane (20 ml) was introduced into the flask and the solution was stirred at room temperature for 3 h. The solution was concentrated to ca. 2 ml on a rotary evaporator and then subjected to column chromatography (alumina), eluting with ethyl acetate/*n*-hexane (1:3 v/v). The first orange band was collected, and the solvents were removed on a rotary evaporator. The residue was dissolved in dichloromethane and layered with *n*-pentane to afford air-stable, orange solid of $[\text{Os}_3(\text{CO})_{10}\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ (**1**; 27 mg, 77%). Anal. Calc. for $\text{C}_{93}\text{H}_{57}\text{N}_4\text{O}_{30}\text{Os}_9\text{P}_3$: C, 31.77; H, 1.63; N, 1.59. Found: C, 32.12; H, 1.70; N, 1.90%. IR (CH_2Cl_2 , ν_{CO}): 2088 m, 2037s, 2003vs, 1979m, 1958w, 1919vw cm^{-1} . ^1H NMR (CD_2Cl_2 , 23 °C): 8.19 (d, 3H, $J_{\text{P-H}} = 5$ Hz, CH–N), 7.72–6.51 (m, 42H, Ph), 4.42 (br, 3H), 4.11 (br, 3H), 2.96 (br, 3H), 2.38 (br, 3H, CH_2) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 23 °C): 15.83 (s) ppm.

3.3. Thermolysis of **1**

$[\text{Os}_3(\text{CO})_{10}\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ (**1**; 19 mg, 0.008 mmol) and benzene (20 ml) were placed in an oven-dried 50 ml Schlenk flask, equipped with a magnetic stir bar and a reflux condenser. The solution was heated to reflux under dinitrogen for 8 days, at which point the IR spectrum showed no absorption due to the starting compound. The solvent was removed under vacuum and the residue was subjected to column chromatography (alumina), eluting with ethyl acetate/*n*-hexane (1:15 v/v). The first red eluant was collected and dried on a rotary evaporator. Crystallization of

the residue from dichloromethane/methanol afforded air-stable, red crystals of $(\mu\text{-H})\text{Os}_3(\text{CO})_8(\mu_3\text{-Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NC}=\text{CH}_2)$ (**2**; 18 mg, 0.016 mmol, 68% based on the Os atom). Anal. Calc. for $\text{C}_{29}\text{H}_{18}\text{NO}_8\text{Os}_3\text{P}$: C, 31.38; H, 1.63; N, 1.26. Found: C, 31.75; H, 1.64; N, 1.75%. MS (FAB): m/z 1115 (M^+ , ^{192}Os). IR (CH_2Cl_2 , ν_{CO}): 2068s, 2034vs, 2008s, 1992s, 1979m, 1968m, 1975sh, 1947w cm^{-1} . ^1H NMR (CDCl_3 , 23 °C): 7.81–6.90 (m, 15H, CH–N, Ph), 3.64 (s, 1H), 1.93 (s, 1H, CH_2), –14.54 (d, $\mu\text{-H}$, $J_{\text{P-H}} = 10$ Hz) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 23 °C): –4.64 (s) ppm.

3.4. Co-thermolysis of $(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ and $\text{Os}_3(\text{CO})_{12}$

$\text{Os}_3(\text{CO})_{12}$ (28 mg, 0.031 mmol), $(\text{Ph}_2\text{P}(o\text{-C}_6\text{H}_4)\text{CH}=\text{NCH}_2\text{CH}_2)_3\text{N}$ (36 mg, 0.037 mmol), and methylcyclohexane (20 ml) were placed in an oven-dried 50 ml Schlenk flask, equipped with a magnetic stir bar and a reflux condenser. The mixture was heated to reflux under dinitrogen for 96 h under dinitrogen. The solvent was removed under vacuum and the residue was subjected to column chromatography (alumina), eluting with ethyl acetate/*n*-hexane (1:15 v/v). Compound **2** (13 mg, 38%) was obtained from the second red band as the major product. The remaining several minor bands were not characterized.

3.5. Structure determination for **2**

The crystal of **2** found suitable for X-ray analysis was mounted in a thin-walled glass capillary and aligned on the Nonius Kappa CCD diffractometer, with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). The θ range for data collection is 2.13–25.36°. Of the 20256 reflections collected for **1**, 5368 reflections were independent. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by least-square cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package [16]. The data collection and refinement parameters are presented in Table 1.

Table 1
Crystallographic data for **2**

Formula	C ₂₉ H ₁₈ NO ₈ Os ₃ P
Crystal system	Monoclinic
Formula weight	1108.00
T (K)	200(2)
Space group	P2 ₁ /c
a (Å)	10.7074(3)
b (Å)	14.4341(3)
c (Å)	19.1529(5)
α (°)	90
β (°)	92.625(1)
γ (°)	90
V (Å ³)	2957.0(1)
Z	4
D _{calc} (Mg/m ³)	2.489
μ (mm ⁻¹)	12.964
R ₁ /wR ₂	0.0416/0.1070
Goodness-of-fit on F ²	1.117

4. Supplementary material

CCDC 678463 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

- [1] N. Fujita, Acc. Chem. Res. 32 (1999) 53.
- [2] P. Braunstein, L.A. Oro, P.R. Raithby, Metal Clusters in Chemistry, Wiley-VCH, Weinheim, Germany, 1999.
- [3] L. Que Jr., W.B. Tolman, Comprehensive Coordination Chemistry II, vol. 8, Elsevier, Oxford, UK, 2004, p. 1.
- [4] J.R. Aranzaes, C. Belin, D. Astruc, Angew. Chem. Int. Ed. 45 (2006) 132.
- [5] D.F. Shriver, H.D. Kaesz, R.D. Adams, The Chemistry of Metal Cluster Complexes, VCH, New York, 1990.
- [6] E. Sappa, Comprehensive Organometallic Chemistry III, vol. 6, Elsevier, Oxford, UK, 2006, p. 835.
- [7] M. Hidai, S. Kuwata, Y. Mizobe, Acc. Chem. Res. 33 (2000) 46.
- [8] C.E. Cooke, T. Ramnial, M.C. Jennings, R.K. Pomeroy, J.A.C. Clyburne, Dalton Trans. (2007) 1755.
- [9] (a) T.-W. Shiue, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, Organometallics 25 (2006) 4150;
(b) T.-W. Shiue, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, J. Organomet. Chem. 692 (2007) 3619;
(c) C.-C. Yang, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, J. Organomet. Chem. 598 (2000) 353.
- [10] W.-Y. Yeh, S.-C. Hsiao, S.-M. Peng, G.-H. Lee, Organometallics 24 (2005) 3365.
- [11] (a) Y.-C. Liu, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, J. Organomet. Chem. 689 (2004) 1944;
(b) Y.-C. Liu, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, J. Organomet. Chem. 690 (2005) 163.
- [12] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, 4th ed., Wiley, New Jersey, USA, 2005.
- [13] W.-Y. Yeh, C.-C. Yang, S.-M. Peng, G.-H. Lee, J. Chem. Soc., Dalton Trans. (2000) 1649.
- [14] (a) R.G. Teller, R. Bau, Struct. Bond. 41 (1981) 1;
(b) R.D. Adams, B. Captain, L. Zhu, Organometallics 25 (2006) 2049.
- [15] D. Braga, F. Grepioni, E. Parisini, B.F.G. Johnson, C.M. Martin, J.G.M. Nairn, J. Lewis, M. Martinelli, J. Chem. Soc., Dalton Trans. (1993) 1891.
- [16] G.M. Sheldrick, SHELXTL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.