Manuscript

Title:

Coordination studies of 1,2-bis(diphenylphosphino)ethane with di-μ-hydroxo dinuclear complexes of tungsten(IV) and molybdenum(IV) †

Authors:

MAKOTO MINATO[1]*, TAKASHI ITO[1], and JIAN-GUO REN[2]

M. Minato, T. Ito, J.-G. Ren

[1]*Department of Materials Chemistry, Graduate School of Engineering,*
Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan
[2]*Department of Chemistry, Shanxi University, Taiyuan, 030006, China*

*Author to whom correspondence should be addressed. E-mail: minato@ynu.ac.jp

† The authors are pleased to dedicate this paper to Professor Rastko D. Vukicevic in the year of his 65th birthday with continued best wishes for his retirement.

***Abstract*:**

The new trifluoroethoxo phosphine complexes $[Cp_2M(\eta^1\text{-dppe})(CF_3CH_2O)]^+$ and $[Cp_2(CF_3CH_2O)M(\mu\text{-dppe})MCp_2(CF_3CH_2O)]^{2+}$ (M = Mo or W, Cp = η-C_5H_5 and dppe = $Ph_2PCH_2CH_2PPh_2$) have been prepared by reaction of cationic di-μ-hydroxo dinuclear complex of molybdenocene or tungstenocene $[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}$ with dppe. It was ascertained that the amount of dppe added to the reaction mixture could influence the product distribution. A mechanism involving initial replacement of the hydroxo ligand by the alkoxo group followed by nucleophilic attack of the phosphine is proposed on the basis of the reaction profile.

Keywords:

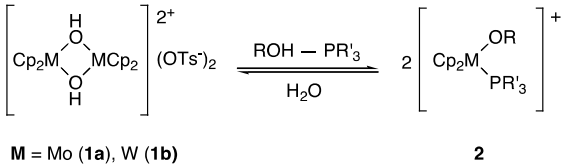
molybdenocene; tungstenocene; dinuclear complexes; dppe

RUNNUNG TITLE: THE NEW ALKOXO DPPE COMPLEXES

INTRODUCTION

We have previously showed that cationic di-μ-hydroxo dinuclear complexes of molybdenocene and tungstenocene $[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}$ (Cp = η-C_5H_5; M = Mo (**1a**) or W (**1b**)) are conveniently prepared by reactions of Cp_2MH_2 and $Cp_2M(OTs)_2$ (OTs = *p*-$CH_3C_6H_4SO_3$) in aqueous acetone[1]. These novel dinuclear complexes have attracted much attention due to their ability to catalyze intra- and inter-molecular H/D exchange reactions[2], and reduction of ketones[3] and nitriles[4].

The hydroxo groups in the complexes **1** were sufficiently labile to undergo displacement by a wide variety of substrates, affording molybdenocene and tungstenocene derivatives; hence, they are useful as precursors of these types of compounds[1,5,6]. We found that reactions between complexes **1** and monodentate tertiary phosphines always proceeded with concomitant incorporation of coexisting alcohols to yield novel alkoxo phosphine complexes $[Cp_2M(PR'_3)(RO)]^+(OTs^-)$ (**2**, R' = Et, Bu^n, and Ph; R = Me, Et, Pr^i, CF_3CH_2, and Ph) (Scheme 1)[1c]. It was proved that these reactions took place spontaneously under mild conditions (20~50 °C). Furthermore, the resulting complexes **2** were readily and quantitatively reverted to the original complexes **1** on dissolving the former in benzene containing a small quantity of water with liberation of the phosphine ligands, which suggests the reversibility of the reactions.



M = Mo (**1a**), W (**1b**) **2**

Scheme 1. The reactions between complexes **1** and monodentate tertiary phosphines.

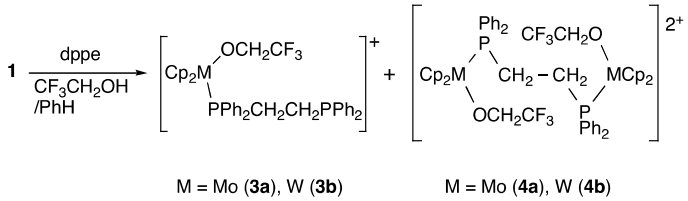
The syntheses of complexes **2** showed the following intriguing trends. In methanol, ethanol, or 2-propanol, only basic phosphines such as triethylphosphine or tributylphosphine reacted with **1**; no substitution of the hydroxo bridging groups by triphenylphosphine were observed in these solvents. However, in moderately acidic alcohol such as trifluoroethanol or in the presence of phenol, the reaction of less reactive triphenylphosphine took place smoothly to afford **2** in good yields. Therefore, the outcome of the reactions appears to be dependent on the nucleophilicity of tertiary phosphines and the acidity of coexisting alcohols. In addition, it was of particular interest in the reactions that no compounds resulting from incorporation of two phosphine ligands were formed; the labile alkoxo ligand bound to the central metals of **2** was not displaced by a second phosphine ligand even in the presence of the excess tertiary phosphine. These results are somewhat puzzling and questions have remained regarding the reasonable reaction mechanism.

As a natural extension of this study, we were interested to explore the reaction of the dinuclear complexes **1** with a chelating ligand. In the present paper, we concentrated on the reactions between **1** and dppe (where dppe represents

1,2-bis(diphenylphosphino)etane) since Green et al. reported that the reactions of analogous halogeno complexes [Cp_2MI_2] (M = Mo, W) with dppe resulted in formation of complexes [$Cp_2M(dppe)]^{2+}$ where the dppe ligand coordinates to the metals in a bidentate mode[7]. Thus, if we consider chelate effect of dppe ligand, we would anticipate formation of a similar bidentate-type complex in our case. Reported herein are results of such experiments. In addition, the purpose of this study is to propose a reasonable reaction mechanism pertained to all reactions between **1** and tertiary phosphines.

RESULTS AND DISCUSSION

The reactions of **1** with dppe were run in CF_3CH_2OH/C_6H_6 at room temperature. Our preliminary results demonstrated that the reaction afforded two organometallic species that were assigned as a mononuclear product **3** containing a monodentate dppe ligand and a bridged dimeric product **4** (Scheme 2). The reaction of dppe did not proceed in methanol or in ethanol at all, which is similar to the reaction of triphenylphosphine. It was further ascertained that the amount of dppe added to the reaction mixture could influence the product distribution. We then decided to search for conditions of the reaction in order to gain a better understanding of the factors controlling the selectivity of the products. The results are summarized in Table I.



Scheme 2. The reactions between complexes **1** and dppe.

Table I. Preparation of complexes **3** and **4**

Compound	Complex/mmol	dppe (mmol)	CF_3CH_2OH/C_6H_6 (mL)	Yield (%)
3a	**1a**/0.294	1.300	1.5/5.0	81
3b	**1b**/0.135	0.880	1.5/5.0	82
4a	**1a**/0.341	0.339	1.5/1.5	50
4b	**1b**/0.159	0.158	2.0/2.0	43

As shown in Table I, the good yields of **3** could be obtained if a large excess of dppe was added to **1** in solution at room temperature. On the other hand, the reactions of **1** with dppe in a molar ratio of 1:1 gave **4** as major product. It is worth pointing out that complexes containing chelating dppe ligand are not observed in the reactions of complexes **1**. Thus, dppe does not yield the expected chelated complexes.

Complexes **3** are soluble in methanol, ethanol, trifluoroethanol, and acetone, while **4** are soluble in the foregoing alcohols and essentially insoluble in acetone. We found that complexes **3**,**4** were stable to air in the solid state. Complexes **3**,**4** were characterized by standard methods, in particular NMR spectroscopy, as well as by an X-ray structural determination of **4a**. In addition, the combustion analyses for **3b** and **4a** were consistent with their spectroscopic properties (see Experimental section)[8]. Selected NMR data are collected in Table II.

Table II. Selected NMR data (J in Hz) for **3** and **4**

Compound	^{1}H NMR[a]	^{31}P NMR[b]
	δ	δ
3a	7.2-7.6 (m, Ph, 20H), 5.46 (d, Cp, J_{PH} = 1.83, 10H), 3.20 (q, $CF_3C\underline{H}_2O$, J_{FH} = 9.56, 2H), 2.6-2.9 (br, $MoPC\underline{H}_2CH_2$, 2H), 1.6-1.9 (br, $MoPCH_2C\underline{H}_2$, 2H)	29.9 (s) −12.0 (br)
3b	7.2-7.6 (m, Ph, 20H), 5.42 (d, Cp, J_{PH} = 1.22, 10H), 3.45 (q, $CF_3C\underline{H}_2O$, J_{FH} = 9.56, 2H), 2.6-2.8 (br, $WPC\underline{H}_2CH_2$, 2H), 1.7-1.9 (br, $WPCH_2C\underline{H}_2$, 2H)	Not measured
4a	7.2-7.6 (m, Ph, 20H), 5.38 (d, Cp, J_{PH} = 1.83, 20H), 3.20 (q, $CF_3C\underline{H}_2O$, J_{FH} = 9.56, 4H), 2.2-2.4 (br, $MoPC\underline{H}_2$, 4H)	28.0 (s)
4b	7.2-7.6 (m, Ph, 20H), 5.35 (d, Cp, J_{PH} = 1.22, 20H), 3.40 (q, $CF_3C\underline{H}_2O$, J_{FH} = 9.56, 4H), 2.1-2.3 (br, $WPC\underline{H}_2$, 4H)	Not measured

[a] 270 MHz, CD_3OD, 293 K. [b] 202 MHz, CD_3OD, 293 K.

The ^{1}H-NMR spectra of complexes **3a**,**b** are similar, showing four different resonances besides the resonances due to TsO protons, and resemble those of **2** in the preceding paper[1c]. As shown in the Table II, resonances for the cyclopentadienyl ring protons of **3** appear at around δ 5.5 ppm as a doublet coupled to phosphorus; this represents significant shielding of these protons compared with chemical shifts in the parent dinuclear complexes **1** (δ 6.0 ppm) but is compatible with the observed chemical shifts of **2**. As expected, the spectra of **3** show two separate signals for the CH_2CH_2 fragment of the dppe ligand at around δ 2.7 and 1.8 ppm. The CF_3CH_2O units in **3a**,**b** show a quartet at δ 3.20 (**3a**, J_{FH} = 9.56 Hz) and at δ 3.45 (**3b**, J_{FH} = 9.56 Hz), respectively.

Assignment of the monodentate coordination mode of the dppe ligand is based on the observation of two discrete equal intensity resonances at around δ 29 and -12 ppm in the ^{31}P{^{1}H}-NMR spectrum of **3a**. The downfield resonance is assignable to a metal-bonded phosphorus atom, while the high-field resonance can readily be assigned

to an uncoordinated phosphorus atom since this chemical shift is very close to that of the free dppe.

In the ^{1}H-NMR spectrum of complex **4a**, the Cp protons occur at δ 5.4 ppm as a doublet with a P—H coupling constant of 1.83 Hz, while the CF_3CH_2 protons appear as a quartet with a F—H coupling constant of 9.56 Hz at δ 3.2 ppm. Unlike complex **3a**, the spectrum of **4a** shows only one multiplet for the CH_2CH_2 fragment at around δ 2.3 ppm. Furthermore, the ^{31}P{^{1}H}-NMR spectrum of **4a** contains only one resonance at around δ 28 ppm, which is assigned to the phosphorus atom on molybdenum. Evidently these results indicate that **4a** contains Mo(μ-dppe)Mo group. The spectrum of complex **4b** is almost identical to that of **4a**, supporting the analogous structure as **4a**.

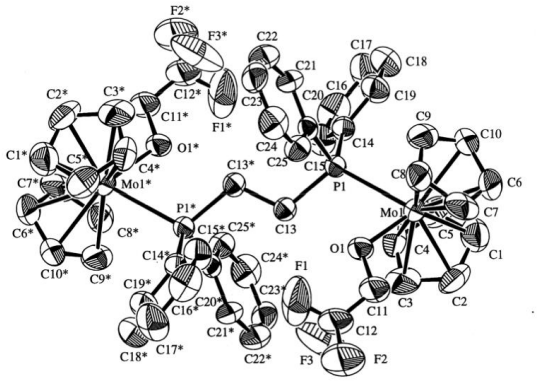


Fig. 1. Molecular structure of Complex **4a**.

Table III. Selected bond distances (Å) and angles (°) for **4a**

Distances			
Mo1—P1	2.541(4)	Mo1—O1	2.070(10)
Mo1—C1	2.29(2)	Mo1—C2	2.33(2)
Mo1—C3	2.37(3)	Mo1—C4	2.33(2)
Mo1—C5	2.31(3)	Mo1—C6	2.31(2)
Mo1—C7	2.27(2)	Mo1—C8	2.35(2)
Mo1—C9	2.37(2)	Mo1—C10	2.34(2)
O1—C11	1.45(2)	C11—C12	1.37(4)
Angles			
P1—Mo1—O1	75.5(3)	Mo1—P1—C13	113.0(5)
Mo1—P1—C14	111.1(5)	Mo1—P1—C20	116.9(5)
Mo1—O1—C11	119.4(10)	P1—Mo1—C2	132.2(6)

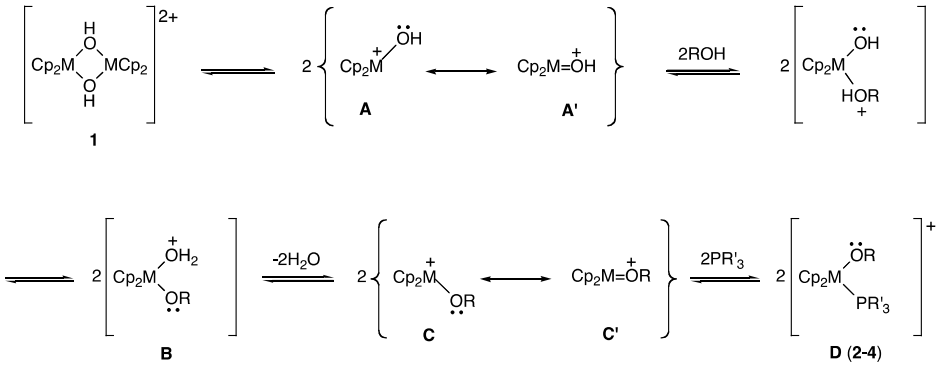
Complex **4a** was fully characterized by an X-ray crystal structure determination. Dark red crystals suitable for the X-ray analysis were obtained by recrystallization from CF_3CH_2OH/Et_2O. The more important bond lengths and bond angles are given in Table III. A summary of the crystallographic data is given in Table IV (see Experimental section). As is to be anticipated from the NMR consideration, the analysis indicates that the molecule is symmetric structure in the solid state with a formulation $[Cp_2(CF_3CH_2O)Mo(\mu\text{-dppe})Mo(OCH_2CF_3)Cp_2](OTs)_2(CF_3CH_2OH)_2$ in which two molecules of trifluoroethanol are included as a crystallization solvent. Fig. 1 shows an ORTEP drawing of the cation of **4a**. TsO molecules were found to be disordered and were omitted for clarity. From this picture it is clear that the two molybdenum centers are held together by dppe ligand. The coordination sphere around the metal center is completed by bridging dppe ligand, CF_3CH_2O group, and two cyclopentadienyl rings, which are arranged in the form of a distorted tetrahedron. The cyclopentadienyl rings are bound to molybdenum in an η^5 fashion and each of the ring

157 carbon atoms are coplanar. Thus, complex **4a** has geometry typical of bent
158 metallocene.

159 The structure can be compared with that of the related alkoxo phosphine complex
160 $[Cp_2Mo(PBu^n_3)(CF_3CH_2O)]^+$ (**2a**)[1c]. The Mo—P bond distance (2.541(4) Å) is
161 remarkably similar to that exhibited by **2a** (2.540(4) Å). On the other hand, the
162 Mo—O bond distance of 2.070(10) Å is significantly longer than that found in **2a**
163 (2.019(8) Å). Furthermore, the O—Mo—P angle of 75.5(3)° is slightly greater than
164 the corresponding angle of 74.4(3)° found in **2a**. The most interesting feature of the
165 structure is the observation of the long O—C bond distance of 1.45(2) Å, which is
166 considerably longer than the *ca*. 1.39 Å found in **2a**.

167 .

168



169 Scheme 3. Possible mechanism for complexes **2-4** formation.

170

171 A mechanism accounting for the reaction pathways is proposed in Scheme 3 on
172 the basis of literature precedents and the reaction profile. In addition, certain general
173 observations pertained to all reactions between **1** and tertiary phosphines included in

this study. As mentioned in the Introduction, each step in Scheme 3 is likely to be reversible. It is well known that most 18-electron complexes undergo ligand substitution reactions via dissociative pathways[9]. Hence, it is conceivable that the first step in the sequence leading to formation of **2**-**4** (**D**) is dissociation of **1** into the monomeric 16-electron complexes **A**. In this case it is possible that a resonance limiting form **A'**, which may be formally viewed as a protonated oxo-complex[10]. Taking into account the fact that the reaction between **1** and a tertiary phosphine is very susceptible to a coexisting alcohol as noted in the Introduction, it seems likely that the next step consists of nucleophilic attack of an alcohol on the metal center. Then proton transfer to the hydroxy group occurs to give alkoxo complex **B**; this process is quite similar to the reported hydrolysis of **1**[2]. Subsequent elimination of water from **B** produces an unsaturated species **C**. This dehydration step seems to be a facile process since π-donation by an alkoxo ligand is well established toward early transition metals[11] and so the canonical form **C'** would make a greater contribution to the hybrid. Inevitably the final step in the mechanism is nucleophilic attack of a tertiary phosphine on the central metal to afford the product **D**.

CONCLUSION

The new trifluoroethoxo phosphine complexes $[Cp_2M(\eta^1\text{-dppe})(CF_3CH_2O)]^+$ (**3**) and $[Cp_2(CF_3CH_2O)M(\mu\text{-dppe})MCp_2(CF_3CH_2O)]^{2+}$ (**4**) have been prepared by reactions of cationic di-μ-hydroxo dinuclear complex of molybdenocene and tungstenocene $[Cp_2M(\mu\text{-OH})_2MCp_2]^{2+}$ (**1**) with dppe. It was ascertained that the amount of dppe added to the reaction mixture could influence the product distribution. Thus, the

196 reaction of **1** with dppe in a molar ratio of 1:1 gives **4** as major product, while the good
197 yield of **3** can be obtained if a large excess of dppe is added to **1**.

198 EXPERIMENTAL SECTION

199 *General procedures*

200 All manipulations were performed under an inert atmosphere of nitrogen or argon
201 using standard Schlenk techniques. Commercially available reagent grade chemicals
202 (Wako Chemical) were used as such without any further purification. Solvents were
203 purified according to standard procedures. All NMR spectra were recorded on a JEOL
204 JNMEX-270 spectrometer or a JEOL JNMGX-500 spectrometer ($^{31}P\{^1H\}$ NMR).
205 $^{31}P\{^1H\}$ NMR peak positions were referenced to external H_3PO_4. Di-μ-hydroxo
206 dinuclear complexes $[Cp_2M(\mu\text{-}OH)_2MCp_2]^{2+}$ (Cp = η-C_5H_5; M = Mo (**1a**) or W (**1b**))
207 were prepared by literature procedures[1c].

208 *Reaction of **1** with excess dppe*

209 A solution containing **1a** (0.244 g, 0.294 mmol) and dppe (0.500 g, 1.260 mmol) in
210 CF_3CH_2OH/C_6H_6 (1.5 mL/5 mL) was stirred at room temperature for 140 h. During
211 the stirring, the solution changed from green to red. From the resulting solution, the
212 solvent was evaporated to dryness under reduced pressure. The residue was washed
213 successively with hexane and ether and then extracted with acetone. The extract was
214 reduced to dryness and the residue was washed with hexane and ether to yield **3a** (0.430
215 g, 81%) as an orange-red powder. This procedure is also applicable to the synthesis of
216 the tungsten analogue **3b** (yield = 82%). **3b**: Anal. Calcd for $C_{45}H_{43}F_3O_4SP_2W$: C,
217 55.00; H, 4.41. Found: C, 54.28; H, 4.53.

*Reaction of **1** with 1 equiv of dppe*

A solution containing **1a** (0.289 g, 0.341 mmol) and dppe (0.135 g, 0.339 mmol) in CF_3CH_2OH/C_6H_6 (1.5 mL/1.5 mL) was stirred at room temperature for 15 h. During the stirring, the solution changed from green to red. From the resulting solution, the solvent was evaporated to dryness under reduced pressure. The residue was washed successively with hexane, ether, and acetone, and then extracted with ethanol. The extract was reduced to dryness and the residue was washed with hexane and ether to yield **4a** (0.237 g, 50%) as an orange-red powder. Purification of the product by recrystallization from CF_3CH_2OH/Et_2O afforded dark red crystals in the form of flat plates. This procedure is also applicable to the synthesis of the tungsten analogue **4b** (yield = 43%). **4a**: Anal. Calcd for $C_{64}H_{62}F_6O_8S_2P_2Mo_2$: C, 55.26; H, 4.49. Found: C, 55.03; H, 4.53.

*X-Ray crystallographic study of **4a***

A crystal suitable for X-ray crystallography was grown in CF_3CH_2OH-Et_2O. The dark red crystal thus obtained was mounted on a glass fiber. Measurement was made on a Rigaku AFC5R diffractometer by using Mo Kα radiation (λ = 0.71068 Å) for data collection. The unit-cell parameter was determined by least-squares fitting of 25 reflections with a range $21.39 < 2\theta < 25.95°$. The parameters used during the collection of diffraction data are given in Table IV. The structure was solved and refined by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

Crystallographic data for the structural analysis has been deposited with the

Cambridge Crystallographic Data Centre, as CCDC reference number 605332. Copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

Table IV. Summary of crystal structure data for **4a**•2CF_3CH_2OH

Formula	$C_{68}H_{68}F_{12}P_2O_{10}Mo_2S_2$
M	1591.21
Crystal system	monoclinic
Space group	$P2_1/c$ (#14)
a/Å	12.230(5)
b/Å	11.149(5)
c/Å	28.966(7)
β/°	101.07(3)
V/Å	3876(2)
Z	2
ρ_c/g cm^{-3}	1.363
μ/cm^{-1}	4.97
R/*wR*	0.102/0.143
GOF	2.28
T/°C	25

ACKNOWLEDGMENT

We are grateful to Dr. Mikio Yamasaki of Rigaku Corporation for an X-ray structure analysis. We also thank Dr. Masako Tanaka of Tokyo Institute of Technology for the elemental analysis.

REFERENCES

1 (a) J.-G. Ren, H. Tomita, M. Minato, K. Osakada, T. Ito, *Chem. Lett.,* (1994) 637.

(b) M. Minato, J. Ren, H. Tomita, T. Tokunaga, F. Suzuki, T. Igarashi, T. Ito, *J.*

Organomet. Chem., **473 (**1994**)** 149. (c) J.-G. Ren, H. Tomita, M. Minato, K. Osakada, M. Yamasaki, T. Ito, *Organometallics,* **15**, (1996) 852.

2 (a) C. Balzarek, D. R. Tyler, *Angew. Chem. Int. Ed*., **38** (1999) 2406. (b) C. Balzarek, T. J. R. Weakley, L. Y. Kuo, D. R. Tyler, *Organometallics*, **19** (2000) 2927. (c) K. L. Breno, D. R. Tyler, *Organometallics*, **20** (2001) 3864.

3 (a) L. Y. Kuo, T. J. R. Weakley, K. Awana, C. Hsia, *Organometallics*, **20** (2001) 4969. (b) L. Y. Kuo, D. M. Finigan, N. N. Tadros, *Organometallics*, **22** (2003) 2422.

4 K. L. Breno, M. D. Pluth, D. R. Tyler, *Organometallics*, **22** (2003) 1203.

5 J.-G. Ren, Z.-W. Wang, Z.-M. Zhang, D.-S. Liu, M. Minato, T. Ito, *Chinese J. Appl. Chem*., **17** (2000) 81.

6 M. Minato, J.-G. Ren, M. Kasai, K. Munakata, T. Ito, *J. Organomet. Chem*., **691 (**2006) 282.

7 T. Aviles, M. L. H. Green, A. R. Dias, C. Romao, *J. Chem. Soc., Dalton Trans.*, (1979) 1367.

8 For complexes **3a** and **4b**, no samples suitable for combustion analyses are available at present.

9 J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, p. 247-255.

10 (a) M. L. H. Green, A. H. Lynch, M. G. Swanwick, *J. Chem. Soc., Dalton Trans.*, (1972) 1445. (b) N. D. Silavwe, M. Y. Chiang, D. R. Tyler, *Inorg. Chem*., **24**

(1985) 4219.

11 J. C. Huffman, K. G. Moloy, J. A. Marsella, K. G. Caulton, *J. Am. Chem. Soc.,* **102** (1980) 3009.