



# Syntheses of new Mo(II) and W(II) mono(hydrosulfido) complexes and their conversion into di- and tetranuclear sulfido-bridged heterobimetallic complexes

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## ABSTRACT

Treatment of  $[\text{Cp}'\text{MH}(\text{CO})_3]$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$  ( $\text{Cp}$ ),  $\eta^5\text{-C}_5\text{Me}_5$  ( $\text{Cp}^*$ )) with 1/8 equiv of  $\text{S}_8$  in THF, followed by the reaction with dppe under UV irradiation, gave new mono(hydrosulfido) complexes  $[\text{Cp}'\text{M}(\text{SH})(\text{CO})(\text{dppe})]$  ( $\text{Cp}' = \text{Cp}$ :  $\text{M} = \text{Mo}$  (**5**),  $\text{W}$  (**6**);  $\text{Cp}' = \text{Cp}^*$ :  $\text{M} = \text{Mo}$  (**7**),  $\text{W}$  (**8**);  $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{-CH}_2\text{PPh}_2$ ). When **5** and **6** dissolved in THF were allowed to react with  $[\text{RhCl}(\text{PPh}_3)_3]$  in the presence of base, heterodinuclear complexes with bridging S and dppe ligands  $[\text{CpM}(\text{CO})(\mu\text{-S})-(\mu\text{-dppe})\text{Rh}(\text{PPh}_3)]$  ( $\text{M} = \text{Mo}$  (**9**),  $\text{W}$  (**10**)) were obtained. Semi-bridging feature of the CO ligands were also demonstrated. Upon standing in  $\text{CH}_2\text{Cl}_2$  solutions, **9** and **10** were converted further to the dimerization products  $[(\text{CpM})_2\{\text{Rh}(\text{dppe})\}_2(\mu_2\text{-CO})_2(\mu_3\text{-S})_2]$  ( $\text{M} = \text{Mo}$  (**13**),  $\text{W}$ ). Detailed structures of mononuclear **7** and **8**, dinuclear **9** and tetranuclear **13** have been determined by the X-ray diffraction.

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## 1. Introduction

Sulfido-bridged multinuclear complexes are of much interest because of their relation to the active sites of certain biological and industrial catalysts [1]. Recent studies in this group have focused on the development of the rational methods to construct the desired di- and polynuclear cores with bridging sulfur ligands [2]. In the course of these studies, it has been shown by us and others that the employment of bis(hydrosulfido) complexes containing  $\text{M}(\mu\text{-SH})_2\text{M}$  or  $\text{M}(\text{SH})_2$  centers are quite potential methods to prepare a variety of homo- and heterometallic complexes with bridging sulfido ligands [2,3]. However, the complexes with only one hydrosulfido ligand are less precedented and their transformations into the multimetallic sites bridged by only one sulfido ligand have been investigated barely except for those derived from  $[\text{Cp}^*\text{IrH}(\text{SH})(\text{PMe}_3)]$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) [4].

Now we have found that the Mo(II) and W(II) mono(hydrosulfido) complexes newly prepared in this study can serve as precursors to heterodinuclear complexes having the Mo–Rh and W–Rh cores bridged by only one sulfide together with one dppe ligand. Interestingly, successive dimerization reactions converting these dinuclear complexes into sulfido-bridged tetranuclear clusters have also been observed. In this paper, we wish to describe the details of these reactions, demonstrating the new route to sulfido-bridged multinuclear complexes starting from mono(hydrosulfido) complexes. Choice of group 9 metals as the counter part in the

bimetallic complexes in this research group [3d,5] arises, at least in part, from the relation of the sulfido-bridged groups 6 and 9 metal complexes with the active sites of hydrodesulfurization catalysts, although no intriguing reactivities towards organo-sulfur compounds including thiophenes have been clarified yet for the heterobimetallic complexes reported in this paper.

## 2. Results and discussion

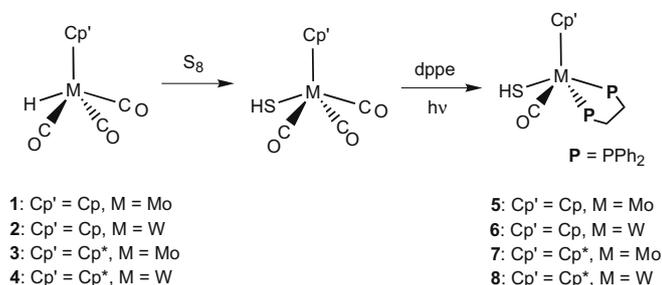
### 2.1. Preparation of new mono(hydrosulfido) complexes

When Mo and W mono(hydrosulfido) complexes  $[\text{Cp}'\text{M}(\text{SH})(\text{CO})_3]$ , which were generated *in situ* from hydrido-carbonyl complexes  $[\text{Cp}'\text{MH}(\text{CO})_3]$  ( $\text{Cp}' = \text{Cp}$ :  $\text{M} = \text{Mo}$  (**1**),  $\text{W}$  (**2**);  $\text{Cp}' = \text{Cp}^*$ :  $\text{M} = \text{Mo}$  (**3**),  $\text{W}$  (**4**);  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ;  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) and  $\text{S}_8$  according to the literature [6], were treated with dppe under UV irradiation in THF at 0 °C, new mono(hydrosulfido) complexes  $[\text{Cp}'\text{M}(\text{SH})(\text{CO})(\text{dppe})]$  ( $\text{Cp}' = \text{Cp}$ :  $\text{M} = \text{Mo}$  (**5**),  $\text{W}$  (**6**);  $\text{Cp}' = \text{Cp}^*$ :  $\text{M} = \text{Mo}$  (**7**),  $\text{W}$  (**8**);  $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) were obtained by replacement of two CO ligands with dppe (Scheme 1). Due to the instability of  $[\text{Cp}'\text{M}(\text{SH})(\text{CO})_3]$ , preparation of **5–8** by thermal substitution at higher temperatures without UV irradiation was unsuccessful. Complexes **5–8** were characterized by spectroscopic and analytical data. For **7** and **8**, an X-ray analysis was also undertaken.

In the IR spectra, the weak bands characteristic to  $\nu(\text{SH})$  at 2542, 2528, 2530, and 2512  $\text{cm}^{-1}$  together with the strong  $\nu(\text{CO})$  bands at 1829, 1810, 1821, and 1814  $\text{cm}^{-1}$  were observed for **5**, **6**, **7**, and **8**, respectively. It is noteworthy that the  $\nu(\text{CO})$  value of 1829  $\text{cm}^{-1}$  observed for **5**, viz.  $[\text{CpMo}(\text{SH})(\text{CO})(\text{dppe})]$ , is

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Scheme 1.

somewhat lower than those of the Cl and H analogues, [CpMoCl(CO)(dppe)] (1845 cm<sup>-1</sup>) [7] and [CpMoH(CO)(dppe)] (1840 cm<sup>-1</sup>) [8]. The <sup>1</sup>H NMR spectra exhibited the high-field resonances assignable to SH protons coupled to two inequivalent P atoms (**5**: -3.17; **6**: -2.41; **7**: -2.17; **8**: -1.62 ppm). The <sup>31</sup>P{<sup>1</sup>H} NMR spectra displayed two signals due to these P atoms of dppe ligands, where the *J*<sub>P-P</sub> values are much larger for Mo complexes **5** (35 Hz) and **7** (31 Hz) than for W complexes **6** (6 Hz) and **8** (unobservable).

The structures of **5–8** have been confirmed by the single-crystal X-ray analysis for **7** and **8**. Selected bond distances and angles in **7** and **8** are listed in Table 1, while the ORTEP drawing for **7**, which is essentially identical with that of **8**, is depicted in Fig. 1.

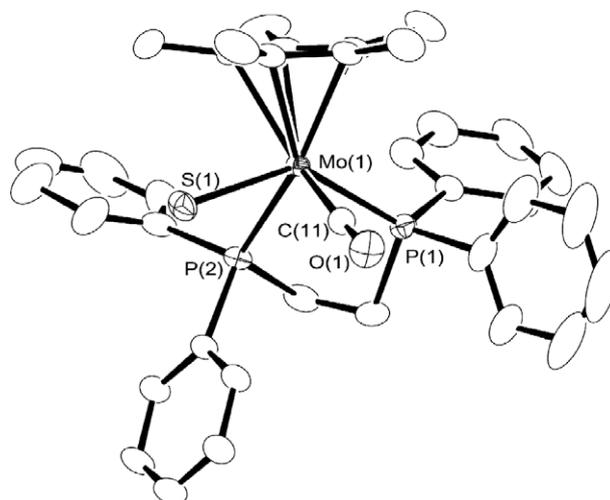
Complex **7** has an expected four-legged piano-stool structure, although it is distorted considerably. Thus, with respect to the pseudo-*trans* bond angles around the metal centers, the S(1)–M–P(1) angles at 136.84(2)° for **7** (M = Mo) and 137.05(5)° for **8** (M = W) are much larger than the P(2)–M–C(11) angles at 105.25(7)° in **7** and 106.1(2)° in **8**. Analogous distortion was observed previously for the related complexes [Cp\*W(SH)(CO)<sub>3</sub>] [9] and [CpMoBr(CO)(dppe)] [10], where the pseudo-*trans* bond angles associated with the SH and Br ligands are significantly larger: S–W–C (*trans*) at 134.9(4)° versus C–W–C (*trans*) at 108.2(2)° in the former and Br–Mo–P (*trans*) at 143.07(3)° versus P–Mo–C (*trans*) at 113.3(2)° in the latter.

## 2.2. Preparation of sulfido-bridged dinuclear heterometallic complexes from **5** and **6**

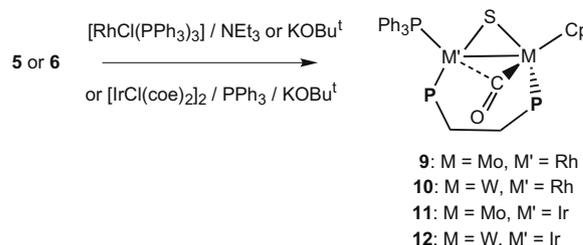
Reaction of **5** with [RhCl(PPh<sub>3</sub>)<sub>3</sub>] in THF in the presence of excess NEt<sub>3</sub> afforded the heterobimetallic complex [CpMo(CO)(μ-S)(μ-dppe)Rh(PPh<sub>3</sub>)] (**9**) having one sulfide and one dppe as bridging ligands. The W analogue [CpW(CO)(μ-S)(μ-dppe)Rh(PPh<sub>3</sub>)] (**10**) was obtained from **6** but by the use of the stronger base KOBu<sup>t</sup> in place of NEt<sub>3</sub> (Scheme 2). Reaction of **5** and [RhCl(PPh<sub>3</sub>)<sub>3</sub>] in the presence of KOBu<sup>t</sup> did not proceed cleanly,

**Table 1**  
Selected interatomic distances (Å) and angles (°) in **7** and **8**.

|                 | <b>7</b> (M = Mo) | <b>8</b> (M = W) |
|-----------------|-------------------|------------------|
| M(1)–S(1)       | 2.5355(7)         | 2.511(2)         |
| M(1)–P(1)       | 2.4913(6)         | 2.468(2)         |
| M(1)–P(2)       | 2.4758(6)         | 2.467(1)         |
| M(1)–C(11)      | 1.924(2)          | 1.927(5)         |
| C(11)–O(1)      | 1.169(3)          | 1.166(7)         |
| S(1)–M(1)–P(1)  | 136.84(2)         | 137.05(5)        |
| S(1)–M(1)–P(2)  | 74.26(2)          | 77.55(4)         |
| S(1)–M(1)–C(11) | 79.70(7)          | 79.2(2)          |
| P(1)–M(1)–P(2)  | 76.07(2)          | 76.09(4)         |
| P(1)–M(1)–C(11) | 78.70(6)          | 76.4(2)          |
| P(2)–M(1)–C(11) | 105.25(7)         | 106.1(2)         |
| M(1)–C(11)–O(1) | 173.3(2)          | 174.6(5)         |



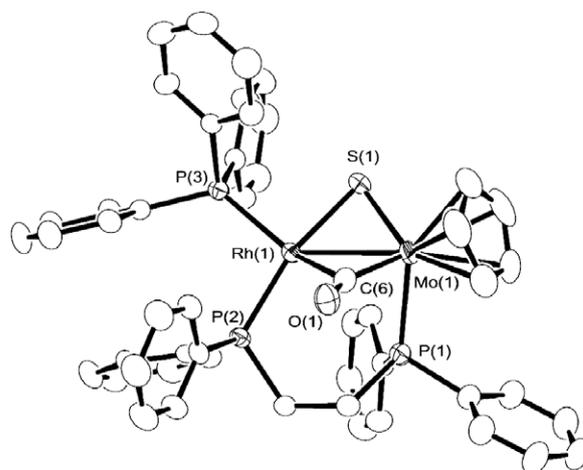
**Fig. 1.** An ORTEP drawing for **7** (30% probability level). Hydrogen atoms are omitted for clarity.



Scheme 2.

yielding the untractable products. The structure of **9** has been determined in detail by the X-ray analysis, while the preliminary X-ray results have confirmed the structure of **10** essentially identical with that of **9**.

The ORTEP drawing for **9** is shown in Fig. 2, while important interatomic distances and angles therein are listed in Table 2. Complex **9** has a dinuclear core bridged by one sulfide and one dppe. The CO molecule also bridges the Mo–Rh bond but the interaction with Rh is weak. Thus, the Mo–C(6) bond distance and the Mo–C(6)–O angle are 1.969(6) Å and 151.6(4)°, whereas the Rh–C(6) bond length and Rh–C(6)–O angle are 2.202(4) Å and 126.5(4)°. Such semi-bridging mode of CO bound to Mo–Rh core



**Fig. 2.** An ORTEP drawing for **9** (30% probability level). Hydrogen atoms are omitted for clarity.

**Table 2**  
Selected interatomic distances (Å) and angles (°) in **9**.

|                  |            |                  |            |
|------------------|------------|------------------|------------|
| Mo(1)–Rh(1)      | 2.7361(7)  | Mo(1)–S(1)       | 2.2599(12) |
| Mo(1)–P(1)       | 2.4515(15) | Mo(1)–C(6)       | 1.969(6)   |
| Rh(1)–S(1)       | 2.2916(17) | Rh(1)–P(2)       | 2.2540(15) |
| Rh(1)–P(3)       | 2.2911(12) | Rh(1)–C(6)       | 2.202(4)   |
| C(6)–O(1)        | 1.200(7)   |                  |            |
| Mo(1)–S(1)–Rh(1) | 73.90(4)   | Mo(1)–C(6)–Rh(1) | 81.79(18)  |
| Mo(1)–C(6)–O(1)  | 151.6(4)   | Rh(1)–C(6)–O(1)  | 126.5(4)   |
| S(1)–Mo(1)–P(1)  | 114.68(5)  | S(1)–Mo(1)–C(6)  | 99.4(1)    |
| P(1)–Mo(1)–C(6)  | 81.5 (2)   | S(1)–Rh(1)–P(2)  | 163.32(5)  |
| S(1)–Rh(1)–P(3)  | 88.95(5)   | S(1)–Rh(1)–C(6)  | 91.9(2)    |
| P(2)–Rh(1)–P(3)  | 100.85(5)  | P(2)–Rh(1)–C(6)  | 87.7(2)    |
| P(3)–Rh(1)–C(6)  | 145.4(1)   |                  |            |

was demonstrated previously for e.g.,  $[(Cp^*Rh(S_2C_2(B_{10}H_{10}))_2)M(CO)_2]$  ( $M = Mo$  [11],  $W$  [12]), where the Rh–CO distances are significantly longer (2.49–2.58 Å) than those in **9**. If the Mo–Rh bond is ignored, the geometry around Mo is a distorted three-legged piano-stool and that around Rh is a distorted T-shape with further weak interaction with CO. Around Rh, the Mo atom is almost coplanar with the Rh–P(2)–P(3) plane with the distance of 0.03 Å, while the separations of S(1) and C(6) from this plane are 0.54 and 1.22 Å, respectively, and the Rh–P(2)–P(3) and Rh–S(1)–C(6) planes are oriented with the dihedral angle of 36.6°. It is noteworthy that the Mo–Rh distance at 2.7361(7) Å is shorter than those of the sulfido-bridged Mo–Rh complexes reported previously. Thus, for nine Mo–Rh complexes with sulfido bridge(s) found by the SciFinder Scholar search, the precedented sulfido-bridged Mo–Rh distances are in the range 2.83–3.12 Å [3b,13], where the shortest distance at 2.833(1) Å was observed in the trinuclear cluster  $[(Mo(S_2CNEt_2)_2(\mu_2-Cl)\{Rh(PMe_2Ph)_2\}(\mu_3-S)(\mu_2-S)_3)]$  [14]. Short Mo–Rh bond lengths in **9** presumably results from the electron-deficient nature of its dinuclear core with only 30-electron count.

In the IR spectra of **9** and **10**, the  $\nu(SH)$  bands of **5** and **6** disappeared. The strong  $\nu(CO)$  bands were observed at 1971 and 1970  $cm^{-1}$  for **9** and **10**, which are shifted to higher frequency region by ca. 140  $cm^{-1}$  from those of **5** and **6**. Change in the binding site of the CO ligands from the strongly  $\pi$ -back donating, 18-electron Mo and W centers with the chelating dppe ligand in **5** and **6** to the 16-electron Mo and W centers with only one coordinated P atom in **9** and **10** might result in the high-frequency shifts of  $\nu(CO)$  bands, even though they are adopting semi-bridging mode. The  $^1H$  NMR spectra show the Cp resonances as doublets of doublets, while the  $^{31}P\{^1H\}$  NMR spectra exhibit three signals each coupled with other two P and one Rh atoms. These spectral data for **9** and **10** are consistent with their X-ray structures.

Although syntheses of the Ir analogues by using  $[IrCl(PPh_3)_3]$  as the Ir source were unsuccessful, treatment of **5** and **6** with a mixture of 0.5 equiv of  $[IrCl(coe)_2]$  ( $coe = cyclooctene$ ) and one equiv of  $PPh_3$  afforded  $[CpM(CO)(\mu-S)(\mu-dppe)Ir(PPh_3)]$  (**11**:  $M = Mo$ , **12**:  $M = W$ ) in low yields (Scheme 2). However, since analytically pure crystals were not available, both **11** and **12** were characterized only spectroscopically. In the reaction mixtures of **7** and **8** with  $[RhCl(PPh_3)_3]$  or  $[IrCl(coe)_2]/PPh_3$  conducted under analogous conditions, formations of  $[Cp^*M(CO)(\mu-S)(\mu-dppe)M'(PPh_3)]$  ( $M = Mo, W; M' = Rh, Ir$ ) were shown by their NMR spectra. However, due to the high solubilities of these  $Cp^*$  analogues into THF, we could not obtain these products as crystals or solid by the procedure analogous to that to isolate the Cp complexes such as **9** and **10**. Attempts to isolate  $Cp^*$  analogues by crystallization from other solvents resulted in decomposition of the products. Complexes **9–12** are the rare examples of the dinuclear complexes having both sulfido and dppe bridges, although such fragments were observed as the partial cores in certain sulfido clusters [15].

### 2.3. Formation of tetranuclear clusters from **9** and **10**

When the  $CH_2Cl_2$  solutions of **9** and **10** were left standing at room temperature for a week, sulfido-bridged tetranuclear clusters  $[(CpM)_2\{Rh(dppe)\}_2(\mu_3-S)_2(\mu_2-CO)_2]$  ( $M = Mo$  (**13**),  $W$  (**14**)) precipitated as purple crystals in low yields (Scheme 3). Dimerization probably took place owing, at least in part, to the electron-deficient nature of **9** and **10**, which favors the transformation of the core structure into that with more metal–metal interactions. Clusters **13** and **14** are practically insoluble to common solvents and have been characterized by the X-ray analysis of **13**. Pertinent interatomic parameters are listed in Table 3.

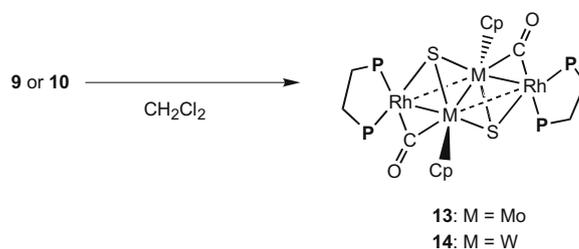
As shown in Fig. 3, **13** has a crystallographic inversion center at the midpoint of the raft-type tetranuclear  $Mo_2Rh_2$  core with two  $\mu_3-S$  ligands each bridging two Mo and one Rh atoms. As expected from the electron count of only 60 for the formal  $Mo(II)_2Rh(I)_2$  core, metal–metal single-bonds exist between two Mo atoms separated by 2.741(2) Å and at the two Mo–Rh edges with the distance at 2.772(2) Å. With respect to the remaining two Mo–Rh edges, the distance at 3.020(2) Å also suggests the presence of weak bonding interactions. The shorter Mo–Rh edges are each bridged further by CO almost symmetrically (see Table 3). Consistently, the IR spectrum of **13** shows strong  $\nu(CO)$  band at 1676  $cm^{-1}$ , which is characteristic to the symmetrically bridging CO ligand. Cluster **14** shows essentially the same IR spectrum, in which the  $\nu(CO)$  band is observed at 1656  $cm^{-1}$ . Ignoring the metal–metal interactions, the Mo center has a three-legged piano-stool structure, while the geometry around Rh is square planar. The S–Rh–C(6)–Mo torsion angle at almost 180° indicates that these four atoms are essentially coplanar.

Dissociation of  $PPh_3$  from Rh site, followed by the migration of one P atom of  $\mu$ -dppe from Mo or W to Rh, might result in the dimerization of these species at the coordinatively unsaturated Mo or W site with potentially face-bridging S ligand, yielding **13** and **14**. Closely related core structures have been demonstrated previously, e.g. for the  $Mo_2Fe_2$  cluster  $[(Cp^*Mo)_2\{Fe(CO)_3\}_2(\mu_3-S)_2(\mu_2-CO)_2]$  ( $Cp^* = Cp$  (**15**),  $\eta^5-C_5H_4Me$ ) [16] and  $Mo_4$  cluster  $[(Cp^*Mo)_2Mo_2(\mu_3-S)_2(\mu_2-CO)_4]$  ( $Cp^* = \eta^5-C_5H_4COOR$ ;  $R = Me, Et$ ) [17]. However, synthesis of such clusters via the dimerization of well-defined heterobimetallic core is not precedented. It is also noteworthy that in a 62-electron cluster **15** all of the Mo–Mo, two Mo–Fe (with  $\mu$ -CO), and two Mo–Fe (without  $\mu$ -CO) bonds at 2.821(1), 2.776(1), and 2.805(1) Å, respectively, fall in the range of metal–metal single bond to provide the electron-precise core. In contrast, a 60-electron **13** somehow has only three single-bonds together with two much weaker bonds in spite of the less electron count.

## 3. Experimental

### 3.1. General considerations

All manipulations were carried out under  $N_2$  using standard Schlenk techniques. Solvents were dried by common methods



Scheme 3.

**Table 3**  
Selected interatomic distances (Å) and angles (°) in **13**.

|                     |          |                    |          |
|---------------------|----------|--------------------|----------|
| Mo(1)–Mo(1*)        | 2.741(2) | Mo(1)–Rh(1)        | 2.772(2) |
| Mo(1)–Rh(1*)        | 3.020(2) | Rh(1)–Rh(1*)       | 5.108(2) |
| Mo(1)–S(1)          | 2.324(4) | Mo(1)–S(1*)        | 2.378(4) |
| Rh(1)–S(1)          | 2.308(3) | Rh(1)–P(1)         | 2.251(3) |
| Rh(1)–P(2)          | 2.309(4) | Mo(1)–C(6)         | 2.05(2)  |
| Rh(1)–C(6)          | 2.05(2)  |                    |          |
| Mo(1*)–Mo(1)–Rh(1)  | 66.42(4) | Mo(1)–Rh(1)–Mo(1*) | 56.30(4) |
| Mo(1*)–Mo(1)–Rh(1*) | 57.28(4) | Mo(1)–S(1)–Mo(1*)  | 71.3(1)  |
| Mo(1)–S(1)–Rh(1)    | 73.5(1)  | Mo(1*)–S(1)–Rh(1)  | 80.2(1)  |
| Mo(1)–C(6)–Rh(1)    | 85.3(6)  | Mo(1)–C(6)–O(1)    | 138(1)   |
| Rh(1)–C(6)–O(1)     | 136(1)   | S(1)–Mo(1)–S(1*)   | 108.7(2) |
| S(1)–Rh(1)–P(1)     | 173.3(2) | S(1)–Rh(1)–P(2)    | 90.5(2)  |
| S(1)–Rh(1)–C(6)     | 100.8(4) | P(1)–Rh(1)–P(2)    | 84.0(2)  |
| P(1)–Rh(1)–C(6)     | 85.2(4)  | P(2)–Rh(1)–C(6)    | 165.2(4) |

and distilled under N<sub>2</sub> before use. Complexes **1**, **2** [18], **3** [19], **4** [20], [RhCl(PPh<sub>3</sub>)<sub>3</sub>] [21], and [IrCl(coe)<sub>2</sub>]<sub>2</sub> [22] were prepared according to the literature methods, while the chemicals were obtained commercially and used as received except for NEt<sub>3</sub>, which was dried over KOH and distilled under N<sub>2</sub> before use. UV irradiation was conducted by the use of a Ushio Optical Module X mercury lamp (250 W).

IR spectra were recorded on a JASCO FT/IR-420 spectrometer, while <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were obtained from a JEOL alpha-400 spectrometer. Elemental analyses were done with a Perkin-Elmer 2400 series II CHN analyzer.

### 3.2. Preparation of **5**

Elemental sulfur (S<sub>8</sub>, 291 mg, 1.13 mmol) was added into a THF solution (60 mL) of **1** (2.25 g, 9.13 mmol) cooled to –5 °C, and the mixture was stirred for 1.5 h at this temperature in the dark. After adding dppe (3.99 g, 10.0 mmol), the mixture was subjected to UV irradiation at 0 °C with stirring. Monitoring the reaction by <sup>1</sup>H NMR spectroscopy indicated that it took ca. 32 h until the reaction completed. The resultant mixture was dried up in vacuo and the residue was stirred with benzene (20 mL) to give yellow suspension, which was filtered off. The yellow powder of **5**·C<sub>6</sub>H<sub>6</sub> was washed with benzene (20 mL × 4) and dried (3.74 g, 59% yield). IR (KBr): 2542w ν(SH); 1829vs cm<sup>-1</sup> ν(CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.7–7.2 (m, 26H, Ph and C<sub>6</sub>H<sub>6</sub>), 4.48 (d, J<sub>P-H</sub> = 2.4 Hz, 5H, Cp), 2.6–2.3 (m, 3H,

PCH<sub>2</sub>), 1.9 (m, 1H, PCH<sub>2</sub>), –3.17 (dd, J<sub>P-H</sub> = 8.8, 0.8 Hz, 1H, SH). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 89.6, 71.5 (d, J<sub>P-P</sub> = 35 Hz, 1P each). Anal. Calc. for C<sub>38</sub>H<sub>36</sub>OMoP<sub>2</sub>S: C, 65.33; H, 5.19. Found: C, 65.06; H, 5.27%.

### 3.3. Preparation of **6**

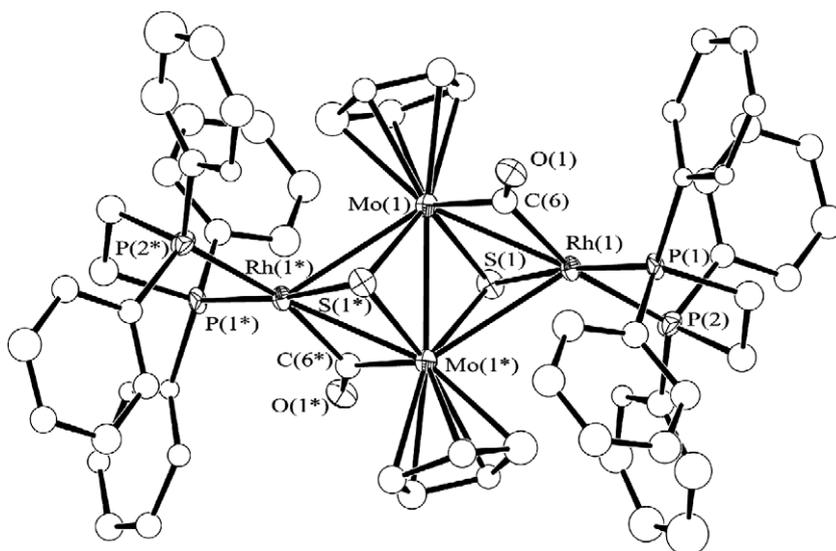
This complex was prepared similarly from **2** (1.00 g, 3.00 mmol), S<sub>8</sub> (96 mg, 0.37 mmol), and dppe (1.31 g, 3.30 mmol) under irradiation for 12 h, and isolated as a yellow–orange powder of **6**·C<sub>6</sub>H<sub>6</sub> (1.05 g, 44% yield). IR (KBr): 2528w ν(SH); 1810vs cm<sup>-1</sup> ν(CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.7–7.2 (m, 26H, Ph and C<sub>6</sub>H<sub>6</sub>), 4.56 (d, J<sub>P-H</sub> = 2.4 Hz, 5H, Cp), 2.6–2.3 (m, 3H, PCH<sub>2</sub>), 2.0 (m, 1H, PCH<sub>2</sub>), –2.41 (dd, J<sub>P-H</sub> = 9.0, 1.4 Hz, 1H, SH). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 60.3 (d with <sup>183</sup>W satellites, J<sub>P-P</sub> = 6 Hz, J<sub>P-W</sub> = 245 Hz, 1P), 47.3 (d with <sup>183</sup>W satellites, J<sub>P-P</sub> = 6 Hz, J<sub>P-W</sub> = 303 Hz, 1P). Anal. Calc. for C<sub>38</sub>H<sub>36</sub>OP<sub>2</sub>SW: C, 58.03; H, 4.61. Found: C, 58.24; H, 4.71%.

### 3.4. Preparation of **7**

The reaction mixture was obtained similarly from **3** (171 mg, 0.54 mmol), S<sub>8</sub> (18 mg, 0.069 mmol), and dppe (237 mg, 0.60 mmol) under UV irradiation for 16 h, which was dried up and the residue was stirred with ether (5 mL) to give orange slurry. This mixture was filtered off and the solid was extracted with THF. Addition of ether to the concentrated extract afforded **7**·0.5Et<sub>2</sub>O as red crystals (61 mg, 16% yield). IR (KBr): 2530w ν(SH); 1821vs cm<sup>-1</sup> ν(CO). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.8–7.6 (m, 6H, Ph), 7.37 (m, 2H, Ph), 7.2–6.9 (m, 12H, Ph), 3.26 (q, 2H, OCH<sub>2</sub>CH<sub>3</sub>), 2.2 (m, 1H, PCH<sub>2</sub>), 2.0–1.8 (m, 3H, PCH<sub>2</sub>), 1.47 (s, 15H, Cp\*), 1.11 (t, 3H, OCH<sub>2</sub>CH<sub>3</sub>), –2.17 (dd, J<sub>P-H</sub> = 6.2, 1.4 Hz, 1H, SH). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 89.5, 65.8 (d, J<sub>P-P</sub> = 31 Hz, 1P each). Anal. Calc. for C<sub>39</sub>H<sub>45</sub>O<sub>1.5</sub>MoP<sub>2</sub>S: C, 64.37; H, 6.23. Found: C, 64.37; H, 6.16%.

### 3.5. Preparation of **8**

Complex **8** was prepared from **4** (819 mg, 2.03 mmol) by the same method as that for **7**, S<sub>8</sub> (65 mg, 0.25 mmol), and dppe (889 mg, 2.23 mmol), and isolated as orange crystals (376 mg, 24% yield). IR (KBr): 2512w ν(SH); 1824vs cm<sup>-1</sup> ν(CO). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.8–7.6 (m, 6H, Ph), 7.4–7.3 (m, 2H Ph), 7.2–6.9



**Fig. 3.** An ORTEP drawing for **13** (50% probability level). Hydrogen atoms are omitted for clarity.

(m, 12H, Ph), 2.2 (m, 1H, PCH<sub>2</sub>), 2.1–1.7 (m, 3H, PCH<sub>2</sub>), 1.52 (s, 15H, Cp<sup>\*</sup>), –1.62 (dd,  $J_{P-H} = 7.2, 2.0$  Hz, 1H, SH). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 58.0 (s with <sup>183</sup>W satellites,  $J_{P-W} = 257$  Hz, 1P), 43.1 (s with <sup>183</sup>W satellites,  $J_{P-W} = 288$  Hz, 1P). Anal. Calc. for C<sub>37</sub>H<sub>40</sub>OP<sub>2</sub>SW: C, 57.08; H, 5.18. Found: C, 57.14; H, 5.19%.

### 3.6. Preparation of **9**

Into a THF solution (50 mL) of [RhCl(PPh<sub>3</sub>)<sub>3</sub>] (462 mg, 0.499 mmol) cooled to –78 °C were added **5** (349 mg, 0.499 mmol) and NEt<sub>3</sub> (140 μL, 1.00 mmol) with stirring. The mixture was warmed gradually to room temperature and stirred continuously at that temperature for 2 days. The resultant solution was concentrated to ca. 10 mL and ether (50 mL) was added. After filtration, the filtrate was kept in the fridge (–20 °C) to give **9** slowly as the black crystals (370 mg, 75% yield). IR (KBr): 1971s cm<sup>–1</sup> ν(CO). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.59 (m, 2H, Ph), 7.4–7.05 (m, 28H Ph), 6.94 (m, 1H, Ph), 6.74, 6.62 (m, 2H each, Ph), 4.99 (dd,  $J_{P-H} = 1.6, 0.6$  Hz, 5H, Cp), 3.29, 3.06, 2.47, 1.86 (m, 1H each, PCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 62.6 (ddd,  $J_{P-P} = 16, 6$  Hz,  $J_{P-Rh} = 3$  Hz, 1P, Mo–dppe), 46.5 (ddd,  $J_{P-P} = 43, 16$  Hz,  $J_{P-Rh} = 177$  Hz, 1P, Rh–P), 31.9 (ddd,  $J_{P-P} = 43, 6$  Hz,  $J_{P-Rh} = 187$  Hz, 1P, Rh–P); Assignment of two latter P signals to either Rh–dppe or Rh–PPh<sub>3</sub> is uncertain. Anal. Calc. for C<sub>50</sub>H<sub>44</sub>OP<sub>3</sub>SRhMo: C, 60.99; H, 4.50. Found: C, 60.54; H, 4.76%.

### 3.7. Preparation of **10**

This complex was prepared similarly from [RhCl(PPh<sub>3</sub>)<sub>3</sub>] (185 mg, 0.200 mmol) and **6** (157 mg, 0.200 mmol) by using KOBu<sup>t</sup> (34 mg, 0.30 mmol) in place of NEt<sub>3</sub>. The yield of **10** as black crystals was 147 mg (69%). IR (KBr): 1970s cm<sup>–1</sup> ν(CO). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.73 (m, 2H, Ph), 7.5–7.2 (m, 28H Ph), 6.90 (m, 1H, Ph), 6.66, 6.58 (m, 2H each, Ph), 5.08 (dd,  $J_{P-H} = 1.6, 0.4$  Hz, 5H, Cp), 3.48, 3.14, 2.66, 1.93 (m, 1H each, PCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 50.4 (ddd,  $J_{P-P} = 42, 5$  Hz,  $J_{P-Rh} = 193$  Hz, 1P, Rh–P), 33.7 (ddd,  $J_{P-P} = 42, 15$  Hz,  $J_{P-Rh} = 172$  Hz, 1P, Rh–P), 33.3 (ddd with <sup>183</sup>W satellites,  $J_{P-P} = 15, 5$  Hz,  $J_{P-Rh} = 2$  Hz,  $J_{P-W} = 376$  Hz, 1P, W–dppe). Assignment of two former P signals to either Rh–dppe or Rh–PPh<sub>3</sub> is uncertain. Anal. Calc. for C<sub>50</sub>H<sub>44</sub>OP<sub>3</sub>SRhMo: C, 55.99; H, 4.14. Found: C, 55.85; H, 4.41%.

### 3.8. Preparation of **11**

Into a THF solution (40 mL) of [IrCl(coe)<sub>2</sub>]<sub>2</sub> (90 mg, 0.10 mmol) was added PPh<sub>3</sub> (53 mg, 0.20 mmol). The mixture was stirred at room temperature for 30 min and then cooled to –78 °C. After addition of **5** (140 mg, 0.201 mmol) and KOBu<sup>t</sup> (34 mg, 0.30 mmol), the mixture was warmed gradually to room temperature with stirring. The resultant solution was concentrated to ca. 2 mL and ether (20 mL) was added with stirring. After filtration, the filtrate was kept at –78 °C to give **11** as black crystals (17 mg). IR (KBr): 1959s cm<sup>–1</sup> ν(CO). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.7–7.0 (m, 30H, Ph), 6.99 (m, 1H, Ph), 6.73, 6.63 (m, 2H each, Ph), 5.01 (dd,  $J_{P-H} = 1.6, 0.4$  Hz, 5H, Cp), 3.30, 3.16, 2.37, 1.70 (m, 1H each, PCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 70.1 (dd,  $J_{P-P} = 17, 3$  Hz, 1P, Mo–dppe), 33.4 (dd,  $J_{P-P} = 21, 17$  Hz, 1P, Ir–P), 12.7 (dd,  $J_{P-P} = 21, 3$  Hz, 1P, Ir–P). Analytically pure **11** was not available, since it gradually decomposed when redissolved in solvents for recrystallization.

### 3.9. Preparation of **12**

This complex was obtained from **6** (79 mg, 0.10 mmol), [IrCl(coe)<sub>2</sub>]<sub>2</sub> (45 mg, 0.050 mmol), PPh<sub>3</sub> (27 mg, 0.10 mmol), and KOBu<sup>t</sup> (18 mg, 0.16 mmol) as black crystals (22 mg) by the same procedure as described above. IR (KBr): 1959s cm<sup>–1</sup> ν(CO). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.7–7.0 (m, 30H, Ph), 6.89 (m, 1H, Ph), 6.64, 6.58 (m,

2H each, Ph), 5.09 (dd,  $J_{P-H} = 2.2, 0.6$  Hz, 5H, Cp), 3.45, 3.19, 2.54, 1.77 (m, 1H each, PCH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 37.6 (dd with <sup>183</sup>W satellites,  $J_{P-P} = 15, 4$ ,  $J_{P-W} = 380$  Hz, 1P, W–dppe), 34.4 (dd,  $J_{P-P} = 21, 15$  Hz, 1P, Ir–P), 13.7 (dd,  $J_{P-P} = 21, 4$  Hz, 1P, Ir–P). Purification of **12** was also unsuccessful due to its instability in solutions.

### 3.10. Preparation of **13**

Upon standing a CH<sub>2</sub>Cl<sub>2</sub> solution (3 mL) of **9** (32 mg, 0.032 mmol) at room temperature, purple crystals of **13**·2CH<sub>2</sub>Cl<sub>2</sub> precipitated, the yield of which was 10 mg (39%) after a week. IR (KBr): 1676s cm<sup>–1</sup> ν(CO). Anal. Calc. for C<sub>66</sub>H<sub>62</sub>O<sub>2</sub>P<sub>4</sub>S<sub>2</sub>Cl<sub>4</sub>Mo<sub>2</sub>Rh<sub>2</sub>: C, 49.01; H, 3.87. Found: C, 48.58; H, 3.71%. Due to the quite poor solubility to the common solvents, NMR spectra could not be recorded.

### 3.11. Preparation of **14**

Similar procedure using **10** (33 mg, 0.031 mmol) gave **14**·2CH<sub>2</sub>Cl<sub>2</sub> as purple crystals (4.1 mg, 16% yield). IR (KBr): 1656s cm<sup>–1</sup> ν(CO). The IR spectrum is totally in good agreement with that of **13** except for the shift of the ν(CO) band by 20 cm<sup>–1</sup>. Anal. Calc. for C<sub>66</sub>H<sub>62</sub>O<sub>2</sub>P<sub>4</sub>S<sub>2</sub>Cl<sub>4</sub>W<sub>2</sub>Rh<sub>2</sub>: C, 44.27; H, 3.49. Found: C, 43.91; H, 3.71%. Due to the quite poor solubility to the common solvents, NMR spectra could not be recorded.

### 3.12. X-ray crystallography

Single crystals of **7**·0.5Et<sub>2</sub>O, **8**, **9**·THF·0.5Et<sub>2</sub>O, and **10**·THF·0.5Et<sub>2</sub>O were sealed in glass capillaries under argon, while that of **13**·2CH<sub>2</sub>Cl<sub>2</sub> was mounted on a cryoloop with paratone oil. Diffraction studies were done by a Rigaku Mercury CCD diffractometer equipped with a graphite monochromatized Mo K $\alpha$  source at 20 °C for **7**, **8**, **9**, and **10** and at –160 °C for **13**. Details are summarized in Table 4. Data collections were performed by using the CRYSTALCLEAR program package [23]. All data were corrected for Lorentz and polarization effects as well as absorption.

Structure solution and refinements were conducted by using the CRYSTALSTRUCTURE program package [24]. The positions of non-hydrogen atoms were determined by Patterson methods (PATTY [25]) and subsequent Fourier synthesis (DIRDIF99 [26]), which were refined anisotropically by full-matrix least-squares techniques. Hydrogen atoms except for those attached to the disordered atoms were placed at the calculated positions and included at the final stages of the refinements with fixed parameters. For **7** and **8**, the SH hydrogens were unable to be located and not included in the refinements of their structures. For **13**, due to the unsatisfactory quality of the data, all C atoms were refined isotropically.

Preliminary X-ray data for **10**·THF·0.5Et<sub>2</sub>O: formula, C<sub>56</sub>H<sub>54.50</sub>O<sub>2.50</sub>P<sub>3</sub>SRhW;  $F_w = 1179.28$ ; space group,  $P2_1/a$  (no. 14);  $a = 11.395(5)$  Å,  $b = 34.50(1)$  Å,  $c = 13.779(6)$  Å,  $\beta = 111.962(2)^\circ$ ,  $V = 5023(4)$  Å<sup>3</sup>;  $Z = 4$ ;  $\rho_{\text{calc}} = 1.559$  g cm<sup>–3</sup>; crystal size,  $0.10 \times 0.10 \times 0.10$  mm<sup>3</sup>; no. of unique reflections, 11 358; no. of variables, 603;  $R_1$  value with  $I > 2\sigma(I)$  and  $wR_2$  value with all data, 0.0386 and 0.187; GOF, 1.066.

## 4. Supplementary material

CCDC 739958, 739959, 739960, and 739961 contain the supplementary crystallographic data for **7**, **8**, **9**, and **13**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table 4**Crystal data for **7**-0.5Et<sub>2</sub>O, **8**, **9**-THF-0.5Et<sub>2</sub>O, and **13**-2CH<sub>2</sub>Cl<sub>2</sub>.

|   | <b>7</b> -0.5Et <sub>2</sub> O                                       | <b>8</b>   | <b>9</b> -THF-0.5Et <sub>2</sub> O                                     | <b>13</b> -2CH <sub>2</sub> Cl <sub>2</sub>  |
|---|--|--|--|--|
| Formula                                 | C <sub>39</sub> H <sub>45</sub> O <sub>1.50</sub> P <sub>2</sub> SMo | C <sub>37</sub> H <sub>40</sub> OP <sub>2</sub> SW     | C <sub>56</sub> H <sub>57</sub> O <sub>2.50</sub> P <sub>3</sub> SMoRh | C <sub>66</sub> H <sub>62</sub> O <sub>2</sub> P <sub>4</sub> S <sub>2</sub> Cl <sub>4</sub> Mo <sub>2</sub> Rh <sub>2</sub> |
| <i>F</i> <sub>w</sub>                   | 727.73   | 778.58   | 1093.89  | 1614.73  |
| Crystal system                          | Monoclinic   | Monoclinic   | Monoclinic   | Tetragonal   |
| Space group                             | <i>P</i> <sub>2</sub> <sub>1</sub> / <i>a</i> (no. 14)               | <i>P</i> <sub>2</sub> <sub>1</sub> / <i>a</i> (no. 14) | <i>P</i> <sub>2</sub> <sub>1</sub> / <i>a</i> (no. 14)                 | <i>I</i> <sub>4</sub> <sub>1</sub> / <i>a</i> (no. 88)   |
| <i>a</i> (Å)                            | 17.415(1)  | 17.156(4)  | 11.414(2)  | 31.517(4)  |
| <i>b</i> (Å)                            | 11.2257(5)   | 11.002(3)  | 34.586(6)  | –  |
| <i>c</i> (Å)                            | 18.484(1)  | 18.956(5)  | 13.793(3)  | 12.609(2)  |
| β (°)                                   | 90.547(1)  | 109.9291(9)  | 111.9698(5)  | 90   |
| <i>V</i> (Å <sup>3</sup> )              | 3613.3(3)  | 3364(2)  | 5050(2)  | 12 525(3)  |
| <i>Z</i>                                | 4  | 4  | 4  | 8  |
| ρ <sub>calc</sub> (g cm <sup>-3</sup> ) | 1.338  | 1.537  | 1.439  | 1.713  |
| Crystal size (mm <sup>3</sup> )         | 0.50 × 0.50 × 0.50   | 0.50 × 0.20 × 0.10                                     | 0.20 × 0.10 × 0.10   | 0.10 × 0.05 × 0.05   |
| μ (cm <sup>-1</sup> )                   | 5.39   | 36.23  | 7.523  | 12.92  |
| 2θ minimum, maximum (°)                 | 6, 55  | 6, 55  | 6, 55  | 6, 44  |
| Unique reflections                      | 8169 ( <i>R</i> <sub>int</sub> = 0.023)                              | 7537 ( <i>R</i> <sub>int</sub> = 0.047)                | 11 540 ( <i>R</i> <sub>int</sub> = 0.054)                              | 3818 ( <i>R</i> <sub>int</sub> = 0.248)  |
| Data of <i>I</i> > 2σ( <i>I</i> )       | 6559   | 5536   | 4880   | 1271   |
| Variables                               | 470  | 418  | 624  | 236  |
| Transmission factor                     | 0.555–0.764  | 0.308–0.696  | 0.699–0.928  | 0.728–0.937  |
| <i>R</i> <sub>1</sub> <sup>a</sup>      | 0.033  | 0.0374   | 0.0388   | 0.0564   |
| <i>wR</i> <sub>2</sub> <sup>b</sup>     | 0.103  | 0.122  | 0.1475   | 0.1977   |
| Goodness-of-fit (GOF) <sup>c</sup>      | 1.036  | 1.041  | 1.027  | 1.024  |

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  (*I* > 2σ(*I*)).<sup>b</sup>  $wR_2 = [\sum (w(F_o^2 - F_c^2))^2] / \sum w(F_o^2)^2$  (all data).<sup>c</sup>  $GOF = [\sum w(|F_o| - |F_c|)^2] / \{(\text{no. observed}) - (\text{no. variables})\}^{1/2}$ .

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