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# Modelling the photosynthetic water oxidation center: Preparation and physical properties of a tetranuclear oxide bridged Mn complex corresponding to the native S<sub>2</sub> state

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erman,<sup>20a</sup> dimethyl 2-oxopentylphosphonate<sup>30</sup> (388 mg, 2 mmol) in 2 mL of THF was added to a rapidly stirred suspension of sodium hydride (45.6 mg, 1.9 mmol) in THF (5 mL) at -10 °C. The resulting suspension was stirred at -10 °C for 30 min, and then **44a** (229 mg, 1 mmol) in THF (5 mL) was added over 5 min. After stirring an additional 10 min at -10 °C, the mixture was allowed to warm to room temperature and then refluxed for 1 h. The reaction mixture was partitioned between ether (20 mL) and 1 M NaOH (10 mL), after which the aqueous layer was washed with ether (20 mL). The combined organic extracts were dried over anhydrous MgSO<sub>4</sub> and concentrated. Chromatography on silica gel (EtOAc-hexane, 1:1) gave **44b** (278 mg, 90%) as a colorless solid. Recrystallization from ether-hexane (3:7) gave colorless needles: mp 74-75 °C; IR (KBr) 2.94, 5.86, 6.05, 6.66  $\mu\text{m}$ ; <sup>1</sup>H NMR  $\delta$  0.81 (d, 3 H,  $J$  = 6.4 Hz), 0.90 (t, 3 H,  $J$  = 7.3 Hz), 0.98-1.84 (m, 9 H, 1.43, overlapping singlet, 9 H), 2.02 (br t, 1 H), 2.53 (t, 2 H,  $J$  = 7 Hz), 3.94 (br m, 1 H), 4.74 (br d, 1 H), 6.08 (d, 1 H,  $J$  = 16 Hz), 6.68 (dd, 1 H,  $J$  = 16, 9 Hz);  $[\alpha]^{24}_{\text{D}} + 53.2^\circ$  (c 0.43, CHCl<sub>3</sub>); chemical ionization mass spectrum,  $m/z$  (rel intensity)  $M + 1$  (22), 209 (100), 265 (26). Anal. Calcd for C<sub>18</sub>H<sub>30</sub>NO<sub>3</sub>: C, 70.10; H, 9.80. Found: C, 69.93; H, 9.65.

(+)-Pumiliotoxin C (**45**). A solution of **44b** (145 mg, 0.47 mmol) in 2 mL of ethanol was treated with hydrogen (1 atm) in the presence of 5% palladium carbon (20 mg) until the theoretical amount of hydrogen was absorbed. The catalyst was removed by filtration through Celite, and the resulting solution was concentrated. The residue was treated with 1 mL of 90% trifluoroacetic acid (TFA) at room temperature for 1 h. After removal of the excess TFA under reduced pressure, the residue was made basic with 1 N NaOH and washed with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  5 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and con-

centrated to give the  $\Delta^{1,2}$  imine, which was immediately dissolved in 5 mL of ethanol and several drops of concentrated HCl solution. Hydrogenation in the presence of 5% palladium on carbon (50 mg) for 6 h, removal of the catalyst by filtration through Celite, and concentration gave essentially pure (+)-pumiliotoxin C (109 mg, 72%) as the amine hydrochloride. Recrystallization from 2-propanol afforded the hydrochloride as colorless needles: mp 285-286 °C (sealed capillary); lit. mp 286-288 °C; <sup>1</sup>H NMR  $\delta$  (CDCl<sub>3</sub>) 0.87 (d, 3 H), 0.89 (t, 3 H), 0.90-2.54 (m, 16 H), 2.98 (br m, 1 H), 3.32 (br d, 1 H), 8.46 (br m, 1 H), 9.62 (br m, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  60.2, 58.2, 41.1, 35.0, 34.5, 29.2, 27.3, 25.3, 23.3, 20.6, 19.7, 19.2, 13.7;  $[\alpha]^{24}_{\text{D}} + 16.1^\circ$ ,  $[\alpha]^{24}_{435} + 28.8^\circ$  (c 0.50, MeOH); lit.  $[\alpha]^{20}_{\text{D}} + 16.4^\circ$ ,  $[\alpha]^{20}_{436} 28.1^\circ$  (c 1.00, MeOH); chemical ionization mass spectrum,  $m/z$  (rel intensity) 194 (100), 152 (88). The spectral data were in agreement with those reported for the natural product.<sup>28</sup>

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**Supplementary Material Available:** Tables of crystal structure data, atomic coordinates, bond lengths, bond angles, anisotropic parameters, and hydrogen atom coordinates for **5** and **18** (6 pages). Ordering information is given on any current masthead page.

(30) Prepared from methyl butyrate by the procedure described in Corey, E. J.; Kwiatkowski, G. T. *J. Am. Chem. Soc.* **1966**, *88*, 5653.

## Communications to the Editor

### Modelling the Photosynthetic Water Oxidation Center: Preparation and Physical Properties of a Tetranuclear Oxide Bridged Mn Complex Corresponding to the Native S<sub>2</sub> State

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Elucidating the precise structure and mode of action of the Mn aggregate responsible for photosynthetic water oxidation/oxygen evolution represents an area of intense research at the present time. It is generally believed that four Mn atoms per photosystem II (PS II) reaction center are essential for activity.<sup>2</sup> The Mn aggregate is capable of cycling between five oxidation levels (S<sub>0</sub>-S<sub>4</sub>) during the catalytic cycle<sup>3</sup> but can also adopt an additional "super-reduced" oxidation level, labeled S<sub>-1</sub>, under certain conditions.<sup>4</sup> We have been seeking inorganic model complexes of

this biological unit to assist in elucidation of the precise structural changes and concomitant substrate transformations during turnover. We recently reported the synthesis of complexes containing the [Mn<sub>4</sub>O<sub>2</sub>] core with structural features similar to the enzyme and isolable in three oxidation levels corresponding to the native S<sub>-1</sub>, S<sub>0</sub>, and S<sub>1</sub> levels.<sup>5</sup> Since the EPR active S<sub>2</sub> level has allowed the most detailed study of the biological unit to date, we have turned our attention to the synthesis of an Mn<sub>4</sub> complex in this important oxidation level (3 Mn<sup>III</sup>, Mn<sup>IV</sup>) and herein report the successful attainment of this objective.

A stirred slurry of brown "manganic acetate" (0.54 g)<sup>6</sup> in degassed MeCN (25 mL) was treated dropwise with Me<sub>3</sub>SiCl (0.66 mL). To the resulting solution was added imidazole (HIm, 0.25 g) in MeCN (15 mL), followed by NaClO<sub>4</sub> (0.29 g) in MeCN (10 mL). The final red-brown solution was stirred for a further 10 min, filtered, and left undisturbed for 2 days at ambient temperature. The resulting dark brown crystals were collected by filtration, washed with MeCN, and dried; yield ~ 20%. The product was identified by analysis<sup>7</sup> and crystallographic

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(6) Prepared by a slight modification to the standard reaction of Mn(OAc)<sub>2</sub> with KMnO<sub>4</sub> in hot glacial acetic acid, as described by Lis, T. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2042. Full details, together with a more detailed discussion of the preparation of **1**, will be provided in the full report of this work.

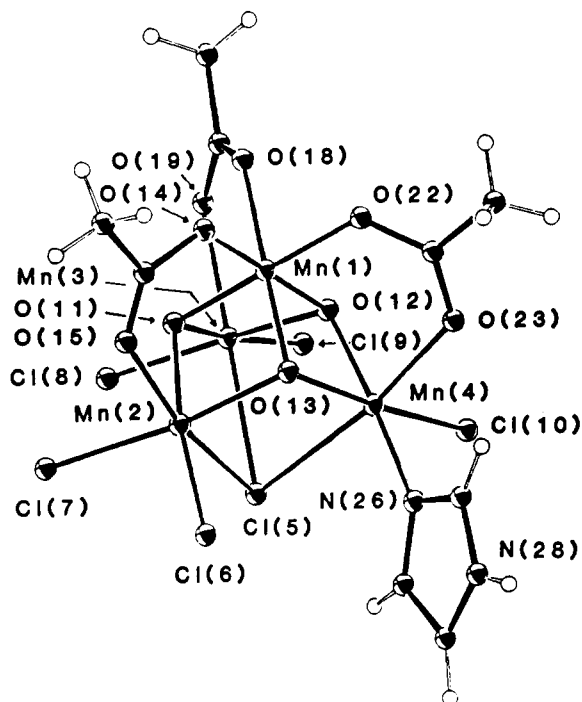
(7) Anal. Calcd for C<sub>18</sub>H<sub>27.5</sub>N<sub>7.5</sub>O<sub>9</sub>Cl<sub>6</sub>Mn<sub>4</sub>: C, 23.36; H, 3.00; N, 11.35; Cl, 22.98; Mn, 23.75. Found: C, 22.96; H, 3.06; N, 11.48; Cl, 22.98; Mn, 23.17.

<sup>†</sup> Alfred P. Sloan Research Fellow, 1987-89.

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**Figure 1.** The structure of the anion of **1** showing the labeling scheme. Selected bond distances (Å) are as follows: Mn(1)···Mn(2), 2.818 (4); Mn(1)···Mn(3), 2.818 (5); Mn(1)···Mn(4), 2.806 (5); Mn(2)···Mn(3), 3.323 (5); Mn(2)···Mn(4), 3.285 (5); Mn(3)···Mn(4), 3.246 (5); Mn(1)–O(11), 1.844 (13); Mn(1)–O(12), 1.858 (14); Mn(1)–O(13), 1.797 (13); Mn(2)–O(11), 1.962 (13); Mn(2)–O(13), 1.955 (12); Mn(3)–O(11), 1.999 (14); Mn(3)–O(12), 2.002 (14); Mn(4)–O(12), 1.885 (13); Mn(4)–O(13), 1.977 (13); Cl(5)–Mn(2,3,4), 2.630 (7), 2.633 (6), 2.608 (7); Mn(1)–O(14,18,22), 1.950 (14), 1.958 (13), 1.958 (15); Mn(2)–O(15), 2.212 (14); Mn(3)–O(19), 2.198 (15); Mn(4)–O(23), 2.144 (14); Mn(2)–Cl(6,7), 2.251 (6), 2.263 (6); Mn(3)–Cl(8,9), 2.264 (7), 2.270 (7); Mn(4)–Cl(10), 2.280 (7); Mn(4)–N(26), 1.978 (16).

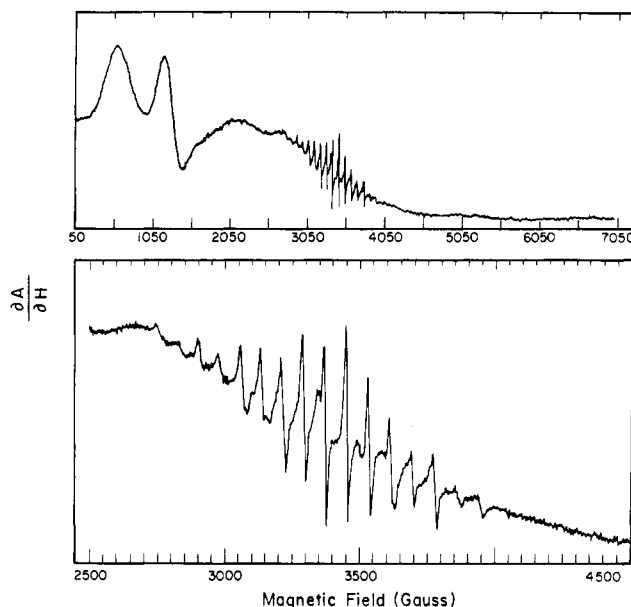
means<sup>8</sup> to be  $(\text{H}_2\text{Im})_2[\text{Mn}_4\text{O}_3\text{Cl}_6(\text{HIm})(\text{OAc})_3] \cdot 1.5\text{MeCN}$  (**1**;  $\text{H}_2\text{Im}^+ = \text{imidazolium cation}$ ). The structure of the anion of **1** is shown in Figure 1. The central  $[\text{Mn}_4(\mu_3\text{-O})_3(\mu_3\text{-Cl})]^{6+}$  core is best considered as a  $\text{Mn}_4$  pyramid with Mn(1) at the apex,  $\mu_3\text{-Cl}$  atom Cl(5) bridging the basal plane, and a  $\mu_3\text{-O}$  bridging each of the remaining three faces; alternatively, the core can be described as a severely distorted  $\text{Mn}_4\text{O}_3\text{Cl}$  cubane. A bridging  $\text{AcO}^-$  across each Mn(1)–Mn(2,3,4) edge, five terminal Cl atoms, and a terminal HIm group complete distorted octahedral Mn coordination. The unique HIm ligand destroys idealized  $C_{3v}$  symmetry. Mn···Mn separations fall into two types; Mn(1)···Mn(2,3,4) (av. 2.814 Å) are distinctly shorter than those between basal Mn atoms (av. 3.285 Å), consistent with the differing bridging modes. Charge considerations necessitate a mixed-valence  $\text{Mn}_3^{\text{III}}\text{Mn}^{\text{IV}}$  description,<sup>9</sup> and, based on metal–ligand bond distances, Mn(1) is assigned as the  $\text{Mn}^{\text{IV}}$  center.

The solid-state magnetochemistry of **1** is intriguing. The effective magnetic moment ( $\mu_{\text{eff}}$ ) per molecule increases gradually with decreasing temperature from 8.82  $\mu_B$  at 300.0 K to a maximum of 9.54  $\mu_B$  at 60 K, below which  $\mu_{\text{eff}}$  decreases to 7.16  $\mu_B$  at 5.0 K. These data are qualitatively in agreement at this stage with the model proposed by de Paula et al.<sup>10</sup> for the native  $S_2$  state.

(8) Crystallographic data at  $-158^\circ\text{C}$ : orthorhombic, space group  $Pbca$ ;  $a = 14.307$  (14) Å,  $b = 14.668$  (14) Å,  $c = 31.319$  (36) Å,  $Z = 4$ ;  $R = 0.0810$ ,  $R_w = 0.0870$ ; using 2513 unique intensities with  $I > 2.33\sigma(I)$ . All non-hydrogen atoms were refined anisotropically except the disordered MeCN molecules. Only hydrogen atoms of the anion, included as fixed atom contributors, were used in the final refinement cycles.

(9) The average metal oxidation state of +3.25 was confirmed by a standard iodimetric redox titration which gave a value of  $+3.23 \pm 0.03$ .

(10) The complex is  $\text{Mn}_4\text{O}_3\text{Cl}_4(\text{OAc})_3(\text{py})_3$ ; its EPR spectrum in a  $\text{CH}_2\text{Cl}_2/\text{toluene}$  glass also displays the two low-field fine structure features and a hyperfine-structured feature at  $g \sim 2$ : Vincent, J. B.; Christou, G.; Chang, H.-R.; Li, O.; Hendrickson, D. N., work in progress. Complex **1** is insoluble in  $\text{CH}_2\text{Cl}_2$ .



**Figure 2.** X-band EPR spectrum of complex **1** in a DMF/toluene glass at 60 K and an expansion of the  $g = 2$  region.

In this model, the  $S_2$  state consists of an aggregate comprising two inequivalent pairs of Mn ions. The  $\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}$  pair is strongly antiferromagnetically coupled to give an  $S = 1/2$  state which is ferromagnetically coupled to the  $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$  pair, the latter being itself weakly antiferromagnetically coupled. The observed increase in  $\mu_{\text{eff}}$ /molecule as the temperature is decreased from 300 to 60 K might reflect the ferromagnetic interaction between the two Mn ion pairs. Exact values of the magnetic exchange parameters for **1**, however, are the objectives of detailed analysis of the susceptibility and EPR data currently in progress.

X-band EPR spectra (3.8–90 K) were run for microcrystalline **1** and for a DMF/toluene glass of **1**. The powder spectra are relatively uninformative (broad  $g \approx 2$  and  $g \approx 4$  signals), presumably due to spin–spin relaxation. As can be seen in Figure 2, however, the glass EPR spectrum exhibits considerable fine and manganese hyperfine structure. This 60 K spectrum displays two low-field transitions at  $\sim 500$  and  $\sim 1250$  G as well as a hyperfine-structured signal centered at  $\sim 3300$  G. Experiments at frequencies other than X-band are underway to understand this fine structure. It is interesting that the intensity and resolution of the hyperfine-structured signal at  $g \approx 2$  are maximized at  $\sim 60$  K, the temperature at which  $\mu_{\text{eff}}$ /molecule undergoes a maximum. Some support for the fact that the spectrum shown in Figure 2 is that for the tetranuclear complex **1** can be drawn from the similarity of this spectrum to the 7.5 K spectrum obtained from an analogous, structurally characterized, uncharged  $\text{Mn}^{\text{IV}}\text{Mn}_3^{\text{III}}$  complex<sup>10</sup> in noncoordinating  $\text{CH}_2\text{Cl}_2/\text{toluene}$  glass; experiments are underway to further eliminate the possibility that **1** breaks into two binuclear complexes in DMF/toluene and that one or both give rise to the EPR signal shown in Figure 2. The Mn hyperfine structured  $g \sim 2$  signal seen in the spectrum of **1** is due to molecules in an  $S = 1/2$  state. Some 16 Mn hyperfine lines can be seen on this  $g \sim 2$  signal, whereas 17–19 Mn hyperfine lines have been reported<sup>11,12</sup> for the  $g = 2$  signal of the  $S_2$  state of PSII. The intensity pattern of the 16-line signal of **1** (Figure 2) is in keeping with appreciable hyperfine coupling to only two Mn ions, each with a different hyperfine-coupling constant. A more detailed EPR and ENDOR examination of this molecule is in progress.

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In summary, a potential model of the important  $S_2$  state of the oxygen evolution enzyme has been obtained, based on the following similarities with the latter: (i) a metal nuclearity of four and the presence of oxide bridges; (ii) an average metal oxidation state of +3.25; (iii) two types of inequivalent Mn atoms; (iv) both "short" (av 2.814 Å) and "long" (av 3.285 Å) Mn...Mn separations (EXAFS data on  $S_1$  indicate corresponding values of 2.69 (3) and ~3.3 Å<sup>3b,13</sup>); (v) observed spin states and hyperfine EPR features consistent with those of the native site.

Finally, terminal Mn-Cl linkages (av 2.266 Å) are not to be found in the native unit based on available data, and attempts to remove them from **1** are in progress, but whether a  $\mu_3$ -Cl as found in **1** might be present is uncertain, especially given the long bond lengths (av 2.624 Å) which might make its spectroscopic identification more difficult. It is thus tempting to speculate whether such a  $\mu_3$ -bridging requirement in some  $S_n$  states of the native system might be the origin of the recognized "Cl-dependence" of oxygen evolution.<sup>14</sup> Further studies are in progress, and additional  $Mn_4$  species at this oxidation level are under characterization.<sup>10,15</sup>

**Acknowledgment.** This work was supported by NSF Grant CHE-8507748 (to G.C.) and NIH Grant HL-13652 (to D.N.H.). We thank the Bloomington Academic Computing Service for a gift of computer time.

**Supplementary Material Available:** Fractional coordinates and isotropic and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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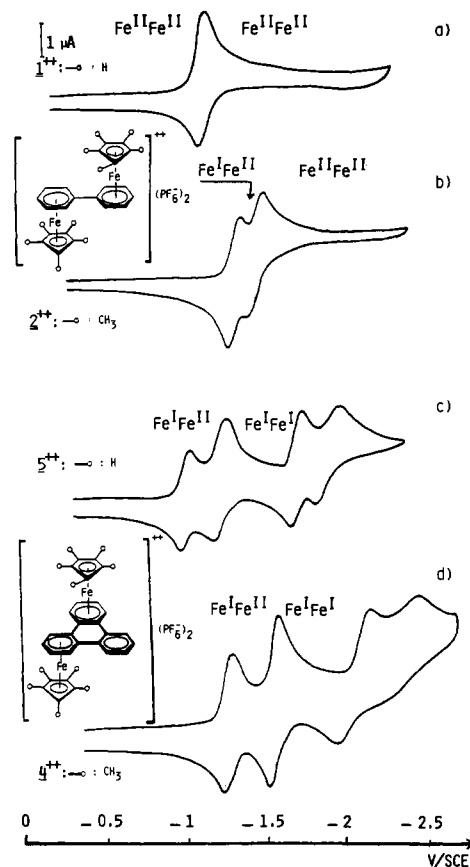
### Organodiiron "Electron Reservoir" Complexes Containing a Polyaromatic Ligand: Syntheses, Stabilization, Delocalized Mixed Valences, and Intramolecular Coupling

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Transition-metal complexes with stable redox series have attracted attention recently because of their potential applications to technological devices.<sup>1</sup> Mononuclear organoiron sandwiches have already disclosed properties of electron-transfer (ET) catalysts.<sup>2</sup> We now report a novel series of diiron complexes of



**Figure 1.** CV of the dicationic diiron complexes of biphenyl [(a) Cp,  $1^{2+}$ ; (b) Cp\*,  $2^{2+}$ ] and of triphenylene [(c) Cp,  $5^{2+}$ ; (d) Cp\*,  $4^{2+}$ ] at  $-35^\circ\text{C}$  with 0.1 M  $n\text{-Bu}_4\text{N}^+\text{BF}_4^-$  on Hg cathode. Same trend on Pt. Internal standard: ferrocene. The CV's of  $3^{2+}$  resemble those of  $2^{2+}$  (b). For values of  $E_p$ ,  $\Delta E_p$ , and  $i_a/i_c$ , see text and supplementary material.  $E_p$ 's vary with scan rates only for the fourth wave of  $4^{2+}$  and  $5^{2+}$  (slow ET).

polyaromatics which can be reduced either in four single-electron steps or in a single two-electron step depending on the stereoelectronic design of the ligands. Also included are the first spectroscopic and structural characteristics of the bicyclohexadienylidene ligand.

We find that the cyclic voltammogram (CV) of the precursor  $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$  dication  $[(\text{FeCp})_2(\text{biphenyl})]^{2+}(\text{PF}_6^-)_2$ ,  $1^{2+}$ ,<sup>3</sup> shows, at  $-35^\circ\text{C}$ , only one two-electron wave (Figure 1a), i.e., the mixed valence  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$  is not observable (at  $20^\circ\text{C}$ , two waves were reported in the polarogram with  $\Delta E = 100\text{ mV}^{3a}$  which is now attributable to an EC mechanism). The reduction of  $[\text{Fe}^{\text{II}}\text{Cp}(\eta^6\text{-arene})]^+\text{PF}_6^-$  by  $\text{LiAlH}_4$  in THF  $-50^\circ\text{C}$  is known to result in  $\text{ET}^{4,5}$   $\text{Fe}^{\text{II}} \rightarrow \text{Fe}^{\text{I}}$ . Applied to  $1^{2+}$ , this reaction provides a deep blue, EPR-silent (4.2 K) solution of **1** (unstable above  $-30^\circ\text{C}$ ) which, thus, cannot contain  $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$  or  $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$  species.<sup>6</sup> The working hypothesis is that a reversible structural and electronic rearrangement intervenes, concomitant to the second ET, and that the resulting energy gain lowers the potential of this second ET. Such a process is well documented in the  $2e^-$  reduction of  $\eta^6\text{-arene-Ru}^{\text{II}}$ ,  $-\text{Rh}^{\text{II}}$ ,  $-\text{Ir}^{\text{II}}$ ,<sup>8</sup> and  $-\text{Cr}^{\text{II}}$  complexes to  $\eta^4\text{-arene}$  analogues,

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<sup>‡</sup> Université du Maine (Mössbauer study).

<sup>§</sup> Université de Rennes I (X-ray crystal structure).

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