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Phosphane- and Phosphite-Substituted Diiron Diselenolato Complexes as Models for [FeFe]-Hydrogenases

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Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 65th birthday

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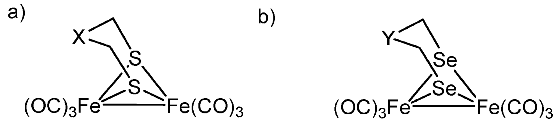
The displacement of terminal CO ligands in Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_6$ (**1**) by triphenylphosphane, trimethyl phosphite, and bis(diphenylphosphanyl)ethane (dppe) ligands is investigated. Treatment of **1** with 1 equiv. of triphenylphosphane afforded Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$(PPh$_3$) (**2**). The mono- and disubstituted phosphite complexes Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$P(OMe)$_3$(**3**)andFe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_4$-[P(OMe)$_3$]$_2$ (**4**) were obtained from the reaction of **1** with excess P(OMe)$_3$ at reflux in toluene. In contrast, the reaction of **1** with 1 equiv. of dppe in the presence of Me$_3$NO·2H$_2$O gave a mixture of Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_4$(κ^2-dppe) (**5**) and [Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$]$_2$(μ-dppe) (**6**). The newly synthesized complexes **2**–**6** were fully characterized by IR, ^{1}H NMR, ^{13}C NMR, ^{77}Se{^{1}H} NMR, and ^{31}P{^{1}H} NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray diffraction analysis. Complex **2** has proved to be a catalyst for the electrochemical reduction of the weak acid, acetic acid, to give molecular hydrogen.

Introduction

The search for alternative energy sources is a challenge for mankind. Hydrogen is one of these energy sources.[1–4] Hydrogenases are enzymes that produce dihydrogen from water. An important representative example of these enzymes was isolated from *Desulfovibrio desulfuricans*.[5,6] This enzyme can produce 9000 molecules of hydrogen per second at 30 °C (hypothetically 1 mol of this enzyme could fill an airship of 13000 m^3 in about 10 min).[6] Therefore several diiron dithiolato model compounds as biomimics for the active site of this enzyme have been described (Scheme 1a).[7–24] The catalytic properties for hydrogen generation by models of [FeFe]-hydrogenases can be modified by substitution of the CO ligands. The replacement of one or two carbonyl ligands from [FeFe]-hydrogenase model complexes by CN$^–$, phosphanes, phosphite, carbene, and isocyanide ligands have been reported in the literature.[9–11,23–30] These complexes also serve as models of the active site of [FeFe]-hydrogenases. The substitution reactions of [FeFe]-hydrogenases with bidentate ligands such as bis(phosphanes) [Ph$_2$P(CH$_2$)$_n$PPh$_2$] and diamines were also investigated.[31–36] Recently, the preparation and characterization of diiron models containing diselenolato ligands have been reported (Scheme 1b).[37–40] The ability of these complexes to act as models for the [FeFe]-hydrogenases has also been investigated. In this paper, the substitution reactions of one or two carbonyl groups of Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)-(CO)$_6$ (**1**) by PPh$_3$ or P(OMe)$_3$ are studied in order to increase the electron density at the iron atoms and to enhance its basicity. The replacement of carbonyl ligands of **1** by bis(diphenylphosphanyl)ethane (dppe) in order to obtain dissymmetrically disubstituted diiron systems is also described. In addition, the electrochemistry of the monophosphane complex **2** was investigated by cyclic voltammetry, in order to compare its electrochemistry with **1** as well as with its sulfur analogues.



Scheme 1. (a) Models of [FeFe]-hydrogenases containing dithiolato ligands (X = CH$_2$, NH, O, S). (b) Models of [FeFe]-hydrogenases containing diselenolato ligands (Y = CH$_2$, Se, NPh).

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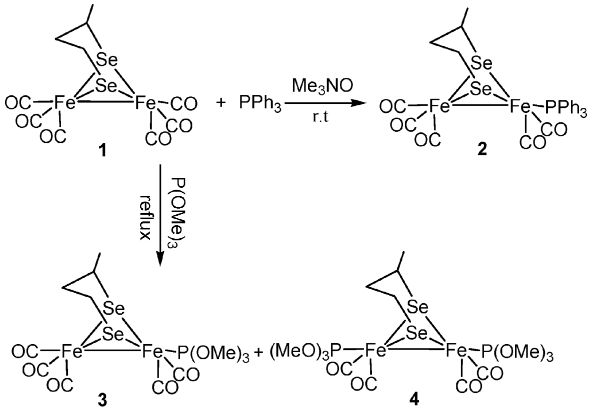
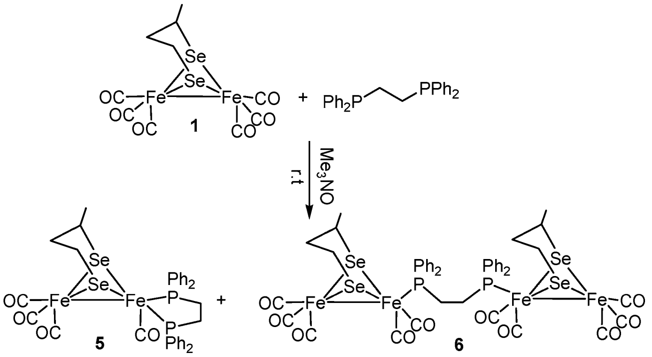
Results and Discussion

Stirring of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_6$ (**1**) at room temperature with 1 equiv. of triphenylphosphane in the presence of trimethylamine *N*-oxide dihydrate ($Me_3NO{\cdot}2H_2O$) gives the complex $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5(PPh_3)$ (**2**) (Scheme 2). The $CH_2CH_2CH(CH_3)$ moiety bridging the selenium atoms desymmetrizes the iron atoms,[41] and the PPh_3 ligand may be *cis* or *trans* to the CH_3 group in the bridge. However, only one diastereomer has been found. In contrast, heating of **1** at reflux with an excess amount of $P(OMe)_3$ in toluene for 3 h gives two complexes, namely $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$ (**3**) and $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4[P(OMe)_3]_2$ (**4**) (Scheme 2), in which one (**3**) or two (**4**) carbonyl ligands are substituted by $P(OMe)_3$.



Scheme 2. Models of substituted [FeFe]-hydrogenase complexes $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5(PPh_3)$ (**2**), $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$ (**3**), and $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4[P(OMe)_3]_2$ (**4**) prepared in our laboratory.

The reaction of compound **1** with 1 equiv. of dppe in the presence of $Me_3NO{\cdot}2H_2O$ gives a mixture of the chelated diiron complex $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa^2\text{-dppe})$ (**5**) and the bridged tetrairon complex $[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (**6**), which can be separated by column chromatography (Scheme 3). Compounds **2**–**6** have been characterized by IR and multinuclear NMR spectroscopy, mass spectrometry, elemental analysis, as well as by X-ray crystallography. These complexes are air-stable in the solid state and are stable for several hours in solution. The ^1H NMR spectra for **2**–**6** exhibit a doublet at δ = 1.09, 1.28, 1.24, 1.52, and 1.03 ppm, respectively, for the methyl group of the diselenolato ligand. $^1H,^1H$ COSY, $^1H,^{13}C$ HSQC, and $^1H,^{13}C$ HMBC NMR spectroscopic experiments allowed the assignment of the other five chemically nonequivalent protons of the diselenolato ligand. These resonances are comparable to those of the unsubstituted complex **1**.[38] The $^{13}C\{^1H\}$ NMR spectra for **2**–**6** exhibit four resonances for the bridging unit. These resonances are in the same range as those observed for **1**.[38] In addition, the expected resonance for the carbonyl groups and the phosphane ligands were observed. Two signals are obtained in the $^{77}Se\{^1H\}$ NMR spectra for complexes **2**–**6** because of the presence of two different Se atoms. The $^1H\text{-}^{77}Se$ HMBC spectrum allows the assignment of the two different Se atoms. The $^{31}P\{^1H\}$ NMR spectra of **2** and **3** show one signal at δ = 72.1 and 193.1 ppm, respectively, whereas for **4** two resonances are observed at δ = 186.5 and 189.2 ppm from the nonequivalent iron atoms.



Scheme 3. Models of [FeFe]-hydrogenases containing a chelated dppe ligand (**5**) and bridged dppe ligand (**6**) prepared in our laboratory.

The $^{31}P\{^1H\}$ NMR spectrum of **5** displays signals at δ = 98.7 and 96.3 ppm ($^2J_{PP}$ = 20.3 Hz) representing an AB spin system, which indicates the presence of two nonequivalent phosphorus atoms. These resonances can be assigned to the basal-apical isomer of a diiron complex with a chelating dppe ligand.[32–34] Only one diastereoisomer has been observed. The mass spectra of **2**–**5** show the molecular ion peaks followed by the fragmentation of five CO groups in **2** and **3**, and four in **4** and **5**. Compound **6** exhibits two singlets in the $^{31}P\{^1H\}$ NMR spectrum at δ = 66.1 and 66.2 ppm. These resonances are shifted to higher fields compared to those reported for sulfur analogues.[31–34] The two signals (ratio 1:1) in the $^{31}P\{^1H\}$ NMR spectrum of **6** could be explained by the presence of two diastereoisomers in solution resulting from the flap pointing toward or away from the phosphane ligand. A temperature-dependent $^{31}P\{^1H\}$ NMR study (T = 273–333 K) shows that these two species are not in equilibrium. MS analysis shows the fragmentation of 10 CO groups and the molecular peak at m/z = 1330, which suggests the presence of a tetranuclear complex in which two diiron moieties are linked by a dppe ligand.

The IR spectra of **2**–**6** show three absorption bands in the regions of 1916–1955, 1972–1996, and 2033–2040 cm^{-1}. These data are within the same ranges observed for the unsubstituted[38] complex and for the sulfur analogues.[26,31–33]

The molecular structures of **2**–**6** were determined and are shown in Figures 1, 2, 3, 4, and 5, respectively. The coordination geometry around the iron cores in all complexes are similar to those in its sulfur analogues.[26,31–34] The central 2Fe2Se structures of all of the complexes are in the butterfly conformation, as was observed for the sulfur analogues.[26,31–34] The displacement of one or two carbonyl groups by phosphanes or phosphite has only a small effect on the Fe–Fe distances as compared to that of **1** [2.5471(15) Å].[38] The Fe–Fe bonds in **2**–**6** are longer than those in the sulfur derivatives {**2**: 2.5573(16) Å [sulfur derivative: 2.5247(6) Å[26]], **3**: 2.5881(12) Å [sulfur derivative: 2.5142(9) Å[26]], **4**: 2.5506(6) Å, **5**: 2.6180(7) Å [sulfur derivative: 2.547(7) Å[32]], **6**: 2.5506(13) Å [sulfur derivative: 2.5108(14) Å[31]]} because of the larger size of the selenium atoms.[26,31–34] The Fe–Se bonds in **2**–**6** are slightly longer (ca. 0.017 Å) than that in the unsubstituted compound **1** due to the stronger σ-donor properties of phosphanes or phosphite ligands compared to carbonyl groups.[38] The Fe–P bond lengths [**2**: 2.246(2) Å, **3**: 2.1596(17) Å, **4**: 2.1651(8) Å and 2.1601(9) Å, **5**: 2.2323(11) Å and 2.1913(9) Å, **6**: 2.2236(18) Å] are comparable to those observed for sulfur and selenium analogues.[26,31–34,40] In compounds **2**–**4** and **6** the P atoms are coordinated to Fe in an apical position, which has been proved by $^{31}P\{^{1}H\}$ NMR spectroscopy and X-ray crystallography (Figures 1, 2, 3, and 5), whereas the apical-basal isomer is observed in **5** (Figure 4). In principle, for the monosubstituted complexes **2** and **3** the phosphane ligand may occupy an apical or basal position. The X-ray crystal structure of **2** shows that the phosphane ligand occupies an apical position. In addition, the stereochemistry of **2** is complicated by the possibility of forming diastereomers. That is, one with the CH_3 group of the bridge and P moiety on the same side (*cis*) or the other with the CH_3 group of the bridge and P moiety on opposite sides (*trans*). Furthermore, each diastereomer may adopt either of two conformations obtained by inverting the flap of the $CH_2CH_2CH(CH_3)$ moiety resulting in an equatorial or axial CH_3 group and the flap pointing toward or away from the phosphane ligand. It can be seen from the X-ray structure of **2** that the CH_3 group is equatorial and *trans* to the phosphane ligand and the flap points away from the phosphane ligand. As pointed out above, the ^{31}P NMR spectrum of **2** shows only one resonance signal suggesting that only one diastereomer is present. In **3** the P ligand is basal. There are two different basal positions owing to the dissymmetry induced by the $CH_2CH_2CH(CH_3)$ bridge. In **3** the phosphite ligand occupies the basal position *syn* to the equatorial CH_3 group, and the flap points toward the phosphane ligand. In **4** the phosphane ligands are on different Fe atoms, and both occupy apical positions with the equatorial CH_3 group. Owing to the dissymmetry of the $CH_2CH_2CH(CH_3)$ moiety the two phosphane ligands are nonequivalent as already noted above in the ^{31}P NMR spectroscopic analysis. For **5**, both P atoms of the dppe are on one Fe atom with one P atom apical and the other basal. Surprisingly, the CH_3 group is *cis* and the flap points toward the apical P atom, and the CH_3 group is *syn* to the basal P atom of the dppe ligand. In **6** both P atoms of the bridging dppe ligand occupy apical positions. The CH_3 group occupies an equatorial position and is *cis* to the phosphane ligand, and the flap points toward the phosphane ligand. The stereochemistry for the two 2Fe2Se centers is the same.

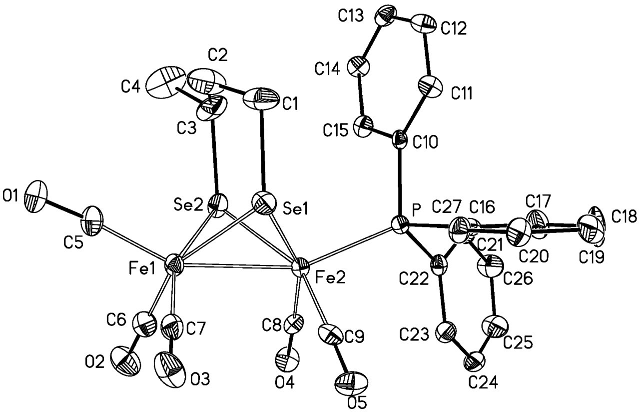


Figure 1. ORTEP drawing of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5(PPh_3)$ (**2**). Selected distances [Å] and angles [°]: Fe1–Fe2 2.5573(16), Fe1–Se1 2.3868(16), Fe1–Se2 2.3792(15), Fe2–Se1 2.3791(15), Fe2–Se2 2.3940(14); Fe1–Se1–Fe2 64.90(5), Fe1–Se2–Fe2 64.79(5).

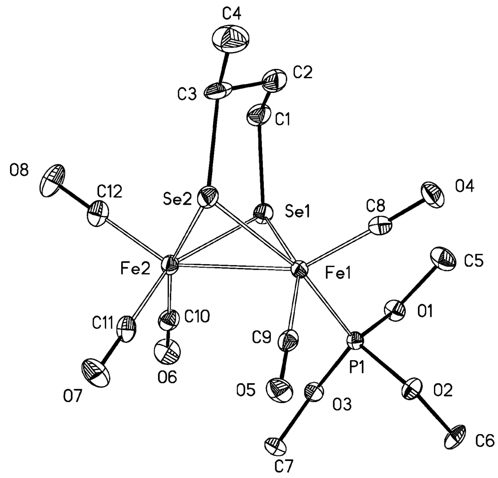


Figure 2. ORTEP drawing of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$ (**3**). Selected distances [Å] and angles [°]: Fe1–Fe2 2.5881(12), Fe1–Se1 2.3723(10), Fe1–Se2 2.3723(10), Fe2–Se1 2.3792(11), Fe2–Se2 2.3814(11); Fe1–Se1–Fe2 66.01(3), Fe1–Se2–Fe2 65.97(3).

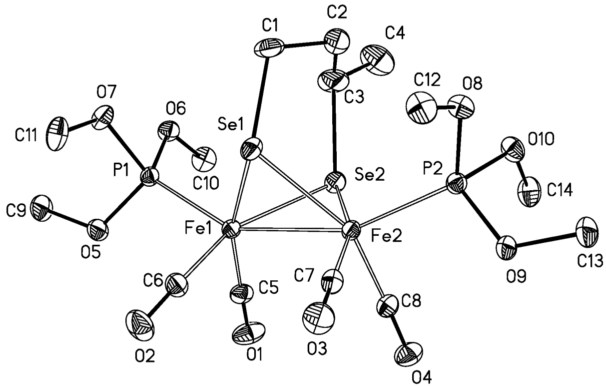


Figure 3. ORTEP drawing of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4[P(OMe)_3]_2$ (**4**). Selected distances [Å] and angles [°]: Fe1–Fe2 2.5506(6), Fe1–Se1 2.3787(5), Fe1–Se2 2.3828(5), Fe2–Se1 2.3818(5), Fe2–Se2 2.3817(5); Fe1–Se1–Fe2 64.794(16), Fe1–Se2–Fe2 64.733(16).

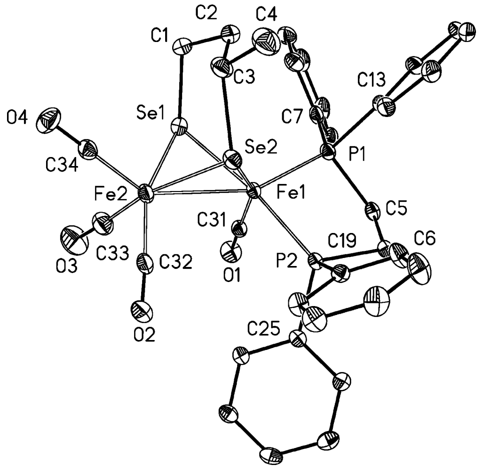


Figure 4. ORTEP drawing of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa^2\text{-dppe})$ (**5**). Selected distances [Å] and angles [°]: Fe1–Fe2 2.6180(7), Fe1–Se1 2.3685(6), Fe1–Se2 2.3738(6), Fe2–Se1 2.3839(6), Fe2–Se2 2.3924(6); Fe1–Se1–Fe2 66.853(19), Fe1–Se2–Fe2 66.636(19).

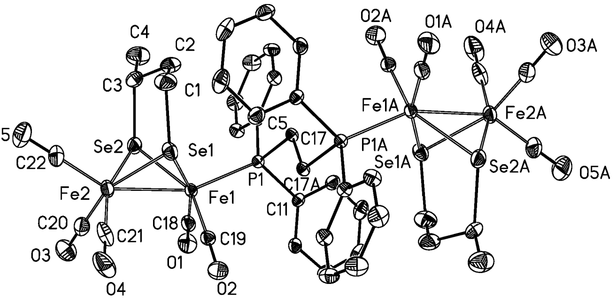


Figure 5. ORTEP drawing of $[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (**6**). Selected distances [Å] and angles [°]: Fe1–Fe2 2.5506(13), Fe1–Se1 2.3871(12), Fe1–Se2 2.3743(12), Fe2–Se1 2.3904(13), Fe2–Se2 2.3774(13); Fe1–Se1–Fe2 64.54(4), Fe1–Se2–Fe2 64.93(4).

Electrochemical Investigations

Cyclic voltammograms of **2** were recorded in order to identify the electrochemical oxidation and reduction processes and to test the ability of these complexes to catalyze the reduction of weak acids to form dihydrogen. Complex **2** was studied in dichloromethane. As expected for the replacement of CO by a phosphane ligand, the phosphane complex **2** is more easily oxidized than the unsubstituted complex **1** with an anodic peak potential of +0.35 V vs. ferrocene compared to +0.76 V for **1**.[38] There is a reasonable degree of reversibility to the oxidation process. The reduction peak for **2**, whose height is also close to that expected for a one-electron process, appears at –2.00 V and is irreversible (Figure 6). As expected, the potential is more negative than that observed for **1** (–1.83 V).[38] As noted elsewhere,[42] replacement of CO by a phosphane ligand causes a shift of both the anodic and cathodic peaks in the negative direction. The shifts seen for **2**, 0.41 and 0.17 V, respectively, may be compared with shifts of 0.62 and 0.18 V seen upon replacing CO by PPh_3 in a sulfur analogue similar to **2**, $Fe_2[\mu\text{-}S(CH_2)_3S](CO)_6$.[26]

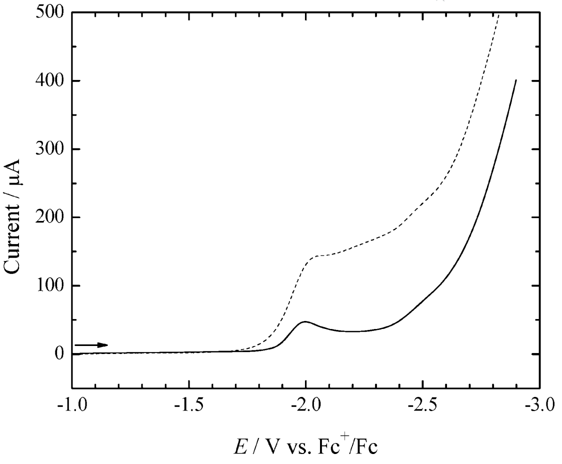


Figure 6. Cyclic voltammograms of 1.0 mM **2** in CH_2Cl_2 with 0.10 M Bu_4NPF_6 and a scan rate of 0.10 V s^{-1}. Solid: **2** alone. Dashed: **2** + 10.5 mM CH_3COOH. Return sweeps omitted for clarity.

Addition of acetic acid results in catalytic reduction at the main peak rather than a separate, more negative peak as seen with **1**[38] (dashed curve, Figure 6). Thus, **2** is capable of catalyzing the production of dihydrogen by the reduction of weak acids.

Conclusions

The present study showed that the desymmetrized $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_6$ (**1**) reacts with PPh_3 and $P(OMe)_3$ producing the mono- and disubstituted complexes **2**–**4**; only one diastereoisomer has been observed in complexes **2**–**4**. By using the bidentate ligand dppe, a mixture of the chelated diiron (**5**) and the bridged tetrairon (**6**) complexes were obtained as observed for the sulfur-PDT derivatives. For $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa^2\text{-dppe})$ (**5**) we have also obtained only one diastereoisomer with an apical-basal position of the dppe ligand, whereas two diastereoisomers have been detected for $[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (**6**) as indicated by the ^{31}P NMR spectra. The results of the X-ray diffraction analysis show that the Fe–Fe distances in **2**–**6** are significantly longer than those in their sulfur analogues due to the larger size of the selenium atom. The stereochemistry is complicated by the fact that the phosphane ligand may occupy an apical or basal position (and there are two basal P diastereomers: one with the P and CH_3 group *syn* and the other *anti*), and for each of these (apical and two basal) there are two diastereomers (*cis* and *trans*), each of which can exist as two conformers with an axial or equatorial CH_3 group owing to the "flap" of the bridge, which can point toward or away from the P ligand. The electrochemical investigations of **2** showed oxidation and reduction behavior that is consistent with substitution of a CO group, as in **1** with a phosphane ligand. Catalytic reduction of acetic acid was seen at the first reduction peak of **2**.

Experimental Section

General Comments: All reactions were performed by using standard Schlenk and vacuum-line techniques under an inert gas. The ^1H, $^{13}C\{^1H\}$, $^{77}Se\{^1H\}$ $^{31}P\{^1H\}$, and 2D NMR ($^1H,^1H$ COSY, $^1H,^{13}C$ HSQC, $^1H,^{13}C$ HMBC, $^1H,^{77}Se$ HMBC) spectra were recorded with either a Bruker Avance 200 or 400 MHz spectrometer by using the solvent residual peak or a concentrated solution of SeO_2 in D_2O as the reference. The ^{77}Se chemical shifts are reported relative to neat Me_2Se [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$ ppm].[43] External standard 85% H_3PO_4 was used as a reference for $^{31}P\{^1H\}$ spectral measurements. The mass spectra were recorded with a Finnigan MAT SSQ 710 instrument. The IR spectra were measured with a Perkin–Elmer System 2000 FT-IR spectrometer. Elemental analyses were performed with a Leco CHNS-932 apparatus. Silica gel 60 (0.015–0.040 mm) was used for column chromatography, and TLC was performed by using Merck TLC aluminum sheets (Silica gel 60 F_{254}). $Fe_3(CO)_{12}$ was purchased from Aldrich, solvents from Fisher Scientific, and other chemicals from Acros, and were used without further purification. All of the solvents used were dried and distilled prior to use according to standard methods. $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_6$ (**1**) was prepared according to a literature procedure.[38]

Preparation of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5PPh_3$ (2): A solution of **1** (60 mg, 0.12 mmol) and $Me_3NO\cdot 2H_2O$ (24 mg, 0.22 mmol) in MeCN was stirred at room temperature for 10 min. Then, triphenylphosphane (32 mg, 0.12 mmol) was added and the mixture stirred for 2 h. The resulting dark red mixture was concentrated to dryness under vacuum. The obtained solid was redissolved in a minimum amount of CH_2Cl_2 and the solution column-chromatographed (SiO_2/hexane). From the major red fraction, which was eluted with hexane/diethyl ether (2:1), **2** was obtained as a red solid, and was recrystallized from pentane at –25 °C. Yield 67 mg (77%). M.p. 193–194 °C. $C_{27}H_{23}Fe_2O_5PSe_2$ (728.05): calcd. C 44.54, H 3.18; found C 44.49, H 3.35. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.58 (m, 1 H, $SeCH_2CH_AH_B$), 1.09 (d, ^3J = 6.8 Hz, 3 H, CH_3), 1.27 (m, 1 H, $SeCH_2CH_AH_B$), 1.71 (m, 1 H, $SeCH_CH_D$), 2.00 (m, 1 H, SeCH), 2.03 (m, 1 H, $SeCH_CH_D$), 7.24–7.67 (m, 15 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 17.4 ($SeCH_2$), 25.7 (CH_3), 27.9 (SeCH), 38.5 ($SeCH_2CH_2$), 128.3, 130.1, 133.6, 136.0, 136.8 (PPh_3), 206.9, 210.3, 214.1, 214.3 (CO) ppm. $^{77}Se\{^1H\}$ NMR (76 MHz, $CDCl_3$): δ = 135 ($SeCH_2$), 467 (SeCH) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ = 72.1 (PPh_3) ppm. FTIR (KBr): $\tilde{\nu}$ = 2037 (vs), 1978 (vs), 1926 (w) cm^{-1}. MS (DEI = 70 eV): m/z (%) = 728 (1) [M^+], 672 (3) [M^+ – 56; 2 CO], 644 (3) [M^+ – 84; 3 CO], 588 (10) [M^+ – 140; 5 CO].

Preparation of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$ (3) and $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4[P(OMe)_3]_2$ (4): A solution of trimethyl phosphite [$P(OMe)_3$; 67 mg, 0.54 mmol] and **1** (90 mg, 0.18 mmol) in toluene (25 mL) was heated under reflux for 3 h. The resulting dark red mixture was concentrated to dryness under vacuum. The obtained solid was redissolved in a minimum amount of CH_2Cl_2 and the solution column-chromatographed (SiO_2/hexane). Products **3** and **4** were obtained from the first and the second fraction, respectively, by using hexane/CH_2Cl_2 (2:1) and then pure CH_2Cl_2 as eluents. Complex **3** was recrystallized from hexane at –25 °C and **4** from ethyl ether at 0 °C.

$Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$ (3): Yield 38 mg (36%). M.p. 74–75 °C. $C_{12}H_{17}Fe_2O_8PSe_2$ (589.84): calcd. for $6C_{12}H_{17}Fe_2O_8PSe_2\cdot 1$hexane C 25.84, H 3.24; found C 25.67, H 3.14. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.06 (m, 1 H, $SeCH_2CH_AH_B$), 1.28 (d, ^3J = 8.4 Hz, 3 H, CH_3), 1.68 (m, 1 H, $SeCH_2CH_AH_B$), 2.06 (m, 1 H, $SeCH_CH_D$), 2.47 (m, 1 H, SeCH), 2.57 (m, 1 H, $SeCH_CH_D$), 3.72 [s, 9 H, $P(OMe)_3$] ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 29.4 ($SeCH_2$), 32.8 (CH_3), 37.1 (SeCH), 38.6 ($SeCH_2CH_2$), 52.0, 52.4 $P(OMe)_3$, 210.4, 210.9 (CO) ppm. $^{77}Se\{^1H\}$ (76 MHz, $CDCl_3$): δ = 396 ($SeCH_2$), 403 (SeCH) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ = 193.9 $P(OMe)_3$ ppm. FTIR (KBr): $\tilde{\nu}$ = 2040 (s), 1985 (vs, sh), 1931 (w) cm^{-1}. MS (DEI = 70 eV): m/z (%) = 590 (60) [M^+], 562 (9) [M^+ – 28; CO], 534 (12) [M^+ – 56; 2 CO], 506 (7) [M^+ – 84; 3 CO], 450 (23) [M^+ – 140; 5 CO].

$Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4[P(OMe)_3]_2$ (4): Yield 57 mg (46%). M.p. 155–156 °C. $C_{14}H_{26}Fe_2O_{10}P_2Se_2$ (685.91): calcd. C 24.51, H 3.82; found C 24.69, H 3.86. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.11 (m, 1 H, $SeCH_2CH_AH_B$), 1.24 (d, ^3J = 6.6 Hz, 3 H, CH_3), 1.53 (m, 1 H, $SeCH_2CH_AH_B$), 1.74 (m, 1 H, $SeCH_CH_D$), 1.89 (m, 1 H, SeCH), 2.39 (m, 1 H, $SeCH_CH_D$), 3.71, 3.77 [s, 18 H, 2 $P(OMe)_3$] ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 16.1 ($SeCH_2$), 25.2 (CH_3), 26.1 (SeCH), 38.6 ($SeCH_2CH_2$), 51.4, 51.5, 51.8, 51.9 $P(OMe)_3$, 213.1, 213.4, 214.4, 214.7 (CO) ppm. $^{77}Se\{^1H\}$ NMR (76 MHz, $CDCl_3$): δ = 252 ($SeCH_2$), 402 (SeCH) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ = 186.5, 189.2 [$P(OMe)_3$] ppm. FTIR (KBr): $\tilde{\nu}$ = 2040 (m), 1996 (vs), 1955 (vs, sh) cm^{-1}. MS (DEI = 70 eV): m/z (%) = 686 (12) [M^+], 630 (9) [M^+ – 56; 2 CO], 602 (2) [M^+ – 84; 3 CO], 574 (16) [M^+ – 112; 4 CO].

Synthesis of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa^2\text{-dppe})$ (5) and $[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (6): A solution of **1** (98 mg, 0.20 mmol) and $Me_3NO\cdot 2H_2O$ (45 mg, 0.40 mmol) dissolved in MeCN was stirred at room temperature for 10 min. A solution of dppe (80 mg, 0.20 mmol) dissolved in CH_2Cl_2 (2 mL) was added and the combined solutions were stirred for 1 h. Then the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel using hexane/CH_2Cl_2 (1:2) as the eluent. Complex **5** was obtained from the first red fraction and recrystallized from hexane/CH_2Cl_2 at –25 °C. A second red brownish band provided complex **6**, which was also recrystallized from hexane/CH_2Cl_2 at –25 °C.

$Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa^2\text{-dppe})$ (5): Yield 33 mg (20%). M.p. 208–209 °C. $C_{34}H_{32}Fe_2O_4P_2Se_2$ (836.17): calcd. C 48.84, H 3.86; found C 48.45, H 3.88. ^1H NMR: δ = 0.91 (m, 1 H, SeCH), 1.24 (m, 1 H, $SeCH_2CH_AH_B$), 1.52 (d, ^3J = 6.2 Hz, 3 H, CH_3), 1.69 (m, 1 H, $SeCH_CH_D$), 1.90 (m, 1 H, $SeCH_2CH_AH_B$), 2.15 (m, 1 H, $SeCH_CH_D$), 2.52, 2.93 (m, 4 H, PCH_2CH_2P), 7.24–7.46 (m, 20 H, 2 PPh_2) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 21.2 (SeCH), 27.5 ($SeCH_2$), 29.2 (CH_3), 29.7 ($SeCH_2CH_2$), 45.8, 47.8 (PCH_2CH_2P) 128.6, 130.3, 132.4 (2 PPh_2), 210.2 (CO) ppm. $^{77}Se\{^1H\}$NMR (76 MHz, $CDCl_3$): δ = 234 ($SeCH_2$), 402 (SeCH) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 96.3 (d, $^2J_{PP}$ = 20.3 Hz), 98.7 (d, $^2J_{PP}$ = 20.3 Hz) ppm. FTIR (KBr): $\tilde{\nu}$ = 2037 (s), 1975 (vs), 1919 (w) cm^{-1}. MS (DEI = 70 eV): m/z (%) = 836 (8) [M^+], 808 (2) [M^+ – 28; CO], 752 (9) [M^+ – 84; 3 CO], 724 (38) [M^+ – 112; 4 CO].

$[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (6): Yield 101 mg (76%). M.p. 193–194 °C. $C_{44}H_{40}Fe_4O_{10}P_2Se_4$ (1329.95): calcd. for $3C_{44}H_{40}Fe_4O_{10}P_2Se_4\cdot 2$hexane C 41.22, H 3.58; found C 41.61, H 3.58. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.69 (m, 2 H, 2 SeCH), 0.85 (m, 2 H, 2 $SeCH_2CH_AH_B$), 1.03 (d, ^3J = 6.4 Hz, 6 H, 2 CH_3), 1.35 (m, 2 H, 2 $SeCH_CH_D$), 1.56 (m, 2 H, 2 $SeCH_2CH_AH_B$), 1.87 (m, 2 H, 2 $SeCH_CH_D$), 2.65, 2.81 (m, 4 H, PCH_2CH_2P), 7.03–7.51 (m, 20 H, 2 PPh_2) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ = 17.9 ($SeCH_2$), 25.5 (SeCH), 27.7 ($SeCH_2CH_2$), 30.3, 32.4 (PCH_2CH_2P), 39.1 (CH_3), 125.1, 127.9, 128.8, 137.4 (2 PPh_2), 210.8 (CO) ppm. $^{77}Se\{^1H\}$ NMR (76 MHz, $CDCl_3$): δ = 313 ($SeCH_2$), 409 (SeCH) ppm. $^{31}P\{^1H\}$ NMR

Table 1. Crystal data and refinement details for the X-ray structure determinations.

	2	**3**	**4**	**5**	**6**
Empirical formula	$C_{27}H_{23}Fe_2O_5PSe_2$	$C_{12}H_{17}Fe_2O_8PSe_2$	$C_{14}H_{26}Fe_2O_{10}P_2Se_2$	$C_{34}H_{32}Fe_2O_4P_2Se_2$	$C_{44}H_{40}Fe_4O_{10}P_2Se_4 \cdot 2CH_2Cl_2$
M_r [g mol^{-1}]	728.04	589.85	685.91	836.16	1499.79
T [°C]	–90(2)	–90(2)	–90(2)	–90(2)	–90(2)
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$Pbca$	$P2_1/n$	$P2_1/n$
a [Å]	11.5652(5)	8.4457(2)	16.3859(5)	19.2256(5)	12.5031(7)
b [Å]	15.2712(8)	23.3951(9)	16.6265(4)	9.6723(3)	16.3825(9)
c [Å]	16.5167(8)	10.0243(4)	17.8597(4)	19.5069(6)	13.5152(6)
α [°]	90	90	90	90	90
β [°]	108.486(3)	103.832(2)	90	115.157(2)	98.663(3)
γ [°]	90	90	90	90	90
V [Å^3]	2766.6(2)	1923.24(12)	4865.7(2)	3283.35(17)	2736.8(2)
Z	4	4	8	4	2
ρ [g cm^{-3}]	1.748	2.037	1.873	1.692	1.820
μ [cm^{-1}]	37.73	54.11	43.61	32.36	40.06
Measured data	18398	12801	32744	22695	18250
Data with $I > 2\sigma(I)$	3882	3307	4571	5446	3907
Unique data/R_{int}	6277/0.0819	4351/0.0701	5567/0.0585	7499/0.0638	6250/0.0755
wR_2 (all data, on F^2)[a]	0.1856	0.1259	0.0776	0.0889	0.1638
R_1 [$I > 2\sigma(I)$][a]	0.0762	0.0544	0.0335	0.0422	0.0674
s[b]	1.094	1.092	1.023	1.026	1.019
Residual density [e Å^{-3}]	2.300/–1.889	2.370/–1.633	0.684/–0.786	0.911/–0.467	2.259/–1.956
Absorption method	none	none	none	none	none
CCDC no.	705054	705055	705056	705057	705058

[a] Definition of the R indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

(200 MHz, $CDCl_3$): δ = 66.1, 66.2 (2 PPh_2) ppm. FTIR (KBr): $\tilde{\nu}$ = 2033 (vs), 1972 (vs), 1916 (w) cm^{-1}. MS (DEI = 70 eV): m/z (%) = 1330 (2) [M$^+$], 1176 (7) [M$^+$ – 154; 2 Ph], 1120 (5) [M$^+$ – 210; 2 Ph + 2 CO], 1064 (10) [M$^+$ – 266; 2 Ph + 4 CO], 1036 (16) [M$^+$ – 294; 2 Ph + 5 CO], 931 (88) [M$^+$ – 399; 3 Ph + 6 CO], 903 (45) [M$^+$ – 427; 3 Ph + 7 CO].

Crystal Structure Determination: The intensity data for the compounds were collected with a Nonius KappaCCD diffractometer by using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[44,45] The structures were solved by direct methods (SHELXS)[46] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[47] All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. All non-disordered non-hydrogen atoms were refined anisotropically.[47] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations (Table 1). CCDC-705054 (for **2**), -705055 (for **3**), -705056 (for **4**), -705057 (for **5**), and -705058 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical Measurements: The electrochemical procedures, apparatus, and sources and treatment of solvent and electrolyte have been described.[38,48] Solutions were purged with argon, the glassy carbon disk working electrode (0.0707 cm^2) was from Bioanalytical Systems, the instrument was a Princeton Applied Research Model 2273 Parstat, and the experiments were conducted at room temperature. The laboratory reference electrode was a silver wire in contact with 0.010 M $AgNO_3$ in acetonitrile with 0.10 M tetrabutylammonium hexafluorophosphate. The potential of the ferrocenium ion/ferrocene couple was frequently measured with respect to this reference, and all potentials have been reported vs. ferrocene.

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[1] S. Shima, O. Pilak, S. Vogt, M. Schick, M. S. Stagni, W. M. Klaucke, E. Warkentin, R. K. Thauer, U. Ermler, *Science* **2008**, *321*, 572–575.
[2] R. Cammack, M. Frey, R. Robson, *Hydrogen as a Fuel: Learning from Nature*, Taylor & Francis, London, **2001**.
[3] R. H. B. Coontz, *Science* **2004**, *305*, 957–975.
[4] A. Melis, L. Zhang, M. Forestier, M. L. Ghirardi, M. Seibert, *Plant Physiol.* **2000**, *122*, 127–136.
[5] B. R. Glick, W. G. Martin, S. M. Martin, *Can. J. Microbiol.* **1980**, *26*, 1214–1223.
[6] E. C. Hatchikian, N. Forget, V. M. Fernandez, R. Williams, R. Cammack, *Eur. J. Biochem.* **1992**, *209*, 357–365.
[7] X. Zhao, I. P. Georgakaki, M. L. Miller, J. C. Yarbrough, M. Y. Darensbourg, *J. Am. Chem. Soc.* **2001**, *123*, 9710–9711.
[8] X. Zhao, C. Y. Chiang, M. L. Miller, M. V. Rampersad, M. Y. Darensbourg, *J. Am. Chem. Soc.* **2003**, *125*, 518–524.
[9] F. Gloaguen, J. D. Lawrence, M. Schmidt, S. R. Wilson, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2001**, *123*, 12518–12527.
[10] E. J. Lyon, I. P. Georgakaki, J. H. Reibenspies, M. Y. Darensbourg, *J. Am. Chem. Soc.* **2001**, *123*, 3268–3278.
[11] J. D. Lawrence, H. Li, T. B. Rauchfuss, M. Benard, M. M. Rohmer, *Angew. Chem. Int. Ed.* **2001**, *40*, 1768–1771.
[12] M. Razavet, S. C. Davies, D. L. Hughes, J. E. Barclay, D. J. Evans, S. A. Fairhurst, X. Liu, C. J. Pickett, *Dalton Trans.* **2003**, 586–595.
[13] R. C. Linck, T. B. Rauchfuss, *Bioorganometallics* **2006**, 403–435.
[14] H. Li, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2002**, *124*, 726–727.

[15] S. Ott, M. Kritikos, B. Åkermark, L. Sun, *Angew. Chem. Int. Ed.* **2003**, *42*, 3285–3288.

[16] C. Tard, X. Liu, S. K. Ibrahim, M. Bruschi, L. De Gioia, S. C. Davies, X. Yang, L.-S. Wang, G. Sawers, C. J. Pickett, *Nature* **2005**, *433*, 610–613.

[17] L.-C. Song, Z.-Y. Yang, H.-Z. Bian, Q.-M. Hu, *Organometallics* **2004**, *23*, 3082–3084.

[18] D. Seyferth, R. S. Henderson, L.-C. Song, *Organometallics* **1982**, *1*, 125–133.

[19] D. Seyferth, R. S. Henderson, L.-C. Song, *J. Organomet. Chem.* **1980**, *192*, C1.

[20] U. P. Apfel, Y. Halpin, H. Görls, J. G. Vos, B. Schweizer, G. Linti, W. Weigand, *Chem. Biodivers.* **2007**, *4*, 2138–2148.

[21] J. Windhager, R. A. Seidel, U. P. Apfel, H. Görls, G. Linti, W. Weigand, *Eur. J. Inorg. Chem.* **2008**, *10*, 2023–2041.

[22] J. Windhager, M. Rudolph, S. Bräutigam, H. Görls, W. Weigand, *Eur. J. Inorg. Chem.* **2007**, *18*, 2748–2760.

[23] J. Windhager, H. Görls, H. Petzold, G. Mloston, G. Linti, W. Weigand, *Eur. J. Inorg. Chem.* **2007**, *28*, 4462–4471.

[24] L.-C. Song, Z. Y. Yang, H. Z. Bian, Y. Liu, H. T. Wang, X. F. Liu, Q. M. Hu, *Organometallics* **2005**, *24*, 6126–6135.

[25] L.-C. Song, Z. Y. Yang, Y. J. Hua, H. T. Wang, Y. Liu, Q. M. Hu, *Organometallics* **2007**, *26*, 2106–2110.

[26] P. Li, M. Wang, C. He, G. Li, X. Liu, C. Chen, B. Akermark, L. Sun, *Eur. J. Inorg. Chem.* **2005**, 2506–2513.

[27] E. J. Lyon, I. P. Georgakaki, J. H. Reibenspies, M. Y. J. Darensbourg, *J. Am. Chem. Soc.* **2001**, *123*, 3268–3278.

[28] J. F. Capon, S. E. Hassnaoui, P. Schollhammer, J. Talarmin, *Organometallics* **2005**, *24*, 2020–2022.

[29] J. W. Tye, J. Lee, H. Wang, R. Mejia-Rodriguez, J. H. Reibenspies, M. B. Hall, M. Y. J. Darensbourg, *Inorg. Chem.* **2005**, *44*, 5550–5552.

[30] L. Duan, M. Wang, P. Li, Y. Na, N. Wang, L. Sun, *Dalton Trans.* **2007**, 1277–1283.

[31] W. Gao, J. Ekström, J. Liu, C. Chen, L. Eriksson, L. Weng, B. Akermark, L. Sun, *Inorg. Chem.* **2007**, *46*, 1981–1991.

[32] S. Ezzaher, J. F. Capon, F. Gloaguen, F. Y. Pétillon, P. Schollhammer, J. Talarmin, *Inorg. Chem.* **2007**, *46*, 3426–3428.

[33] S. Ezzaher, J. F. Capon, F. Gloaguen, F. Y. Pétillon, P. Schollhammer, J. Talarmin, *Inorg. Chem.* **2007**, *46*, 9863–9872.

[34] A. K. Justice, G. Zampella, L. D. Gioia, T. B. Rauchfuss, J. I. V. D. Vlugt, S. R. Wilson, *Inorg. Chem.* **2007**, *46*, 1655–1664.

[35] S. Ezzaher, J. F. Capon, F. Gloaguen, F. Y. Petillon, P. Schollhammer, J. Talarmin, *Inorg. Chem.* **2009**, *48*, 2–4.

[36] P. Y. Orain, J. F. Capon, N. Kervarec, F. Gloaguen, F. Y. Petillon, R. Pichon, P. Schollhammer, J. Talarmin, *Dalton Trans.* **2007**, 3745–3756; J.-F. Capon, F. Gloaguen, F. Y. Pétillon, P. Schollhammer, J. Talarmin, *Eur. J. Inorg. Chem.* **2008**, 4671–4681; S. Ezzaher, J.-F. Capon, N. Dumontet, F. Gloaguen, F. Y. Pétillon, P. Schollhammer, J. Talarmin, *J. Electroanal. Chem.* **2009**, *626*, 161–170.

[37] S. Gao, J. Fan, S. Sun, X. Peng, X. Zhao, J. Hou, *Dalton Trans.* **2008**, 2128–2135.

[38] M. K. Harb, T. Niksch, J. Windhager, H. Görls, R. Holze, L. T. Lockett, N. Okumura, D. H. Evans, R. S. Glass, D. L. Lichtenberger, M. El-khateeb, W. Weigand, *Organometallics* **2009**, *28*, 1039–1048.

[39] U. P. Apfel, Y. Halpin, M. Gottschaldt, H. Görls, J. G. Vos, W. Weigand, *Eur. J. Inorg. Chem.* **2008**, 5112–5118.

[40] L.-C. Song, B. Gai, H. T. Wang, Q. M. Hu, *J. Inorg. Biochem.*, accepted; DOI: 10.1016/j.jinorgbio.2009.02.002.

[41] J. L. Stanley, Z. M. Heiden, T. B. Rauchfuss, S. R. Wilson, *Organometallics* **2008**, *27*, 119–125.

[42] G. A. N. Felton, C. A. Mebi, B. J. Petro, A. K. Vannucci, D. H. Evans, R. S. Glass, D. L. Lichtenberger, *J. Organomet. Chem.*, accepted, DOI:10.1016/j.jorganchem.2009.03.017.

[43] R. C. Burns, M. J. Collins, R. J. Gillespie, G. J. Schrobilgen, *Inorg. Chem.* **1986**, *25*, 4465–4469.

[44] B. V. Nonius, *COLLECT, Data Collection Software*, The Netherlands, **1998**.

[45] Z. Otwinowski, W. Minor, "Processing of X-ray Diffraction Data Collected in Oscillation Mode" in *Methods in Enzymology*, vol. 276 (*Macromolecular Crystallography, Part A*), Academic Press, San Diego, **1997**, pp. 307–326.

[46] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

[47] G. M. Sheldrick, *SHELXL-97 (Release 97-2)*, University of Göttingen, Germany, **1997**.

[48] N. A. Macías-Ruvalcaba, D. H. Evans, *J. Phys. Chem. B* **2005**, *109*, 14642–14647.

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