# **ORGANOMETALLICS**

# Reaction of Aryl Diazonium Salts and Diiron(I) Dithiolato Carbonyls: Evidence for Radical Intermediates

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**Supporting Information** 

**ABSTRACT:** Treatment of  $Fe_2(pdt)(CO)_4(dppv)$  (1) with aryldiazonium salts affords the 34 e<sup>-</sup> adducts  $[Fe_2(pdt)(\mu N_2Ar)(CO)_4(dppv)]^+$  (pdt<sup>2-</sup> = 1,3-propanedithiolate, dppv = *cis*-C<sub>2</sub>H<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub>). Under some conditions, the same reaction gave substantial amounts of [1]<sup>+</sup>, the product of electron transfer. Consistent with the influence of electron transfer in



the reactions of some electrophiles with Fe(I)Fe(I) dithiolates, the reaction of  $[Me_3S_2]^+$  and  $Fe_2(pdt)(CO)_4(dppbz)$  was found to give  $[Fe_2(pdt)(CO)_4(dppbz)]^+$  as well as  $Me_2S$  and  $Me_2S_2$  (dppbz = 1,2-bis(diphenylphosphino)benzene).

# INTRODUCTION

The reactivity of diiron dithiolato carbonyls has come under intense scrutiny with the discovery that these diiron compounds are structurally related to the active site of the [FeFe]-hydrogenases.<sup>1</sup> Many efforts are underway to prepare low molecular weight analogues of these biocatalysts.<sup>2</sup> Since the diiron dithiolato center in the [FeFe]-hydrogenases features strong donor ligands in addition to CO, biomimetic modeling generally focuses on the substituted derivatives of the diiron dithiolates, especially diphosphine complexes such as Fe<sub>2</sub>(pdt)-(CO)<sub>4</sub>(dppv) (1) and Fe<sub>2</sub>(pdt)(CO)<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub> (2).<sup>2</sup>

Electrophiles (E<sup>+</sup>) attack substituted diiron(I) dithiolato complexes in one of three ways. Most commonly, electrophiles give adducts of the type  $[Fe_2(\mu-E)(SR)_2L_6]^{+,3}$  Many examples exist; cases include  $E^+ = Cl^{+,4} SMe^{+,5-7}$  and  $H^{+,8}$  The addition of NO<sup>+</sup> to diiron(I) dithiolates results in substitution, although 36 e<sup>-</sup> adducts are implicated as intermediates.<sup>9</sup> Protonation of diiron dithiolates containing chelating diphosphine ligands generally gives terminal hydride complexes, which subsequently isomerize by migration of the hydride to a bridging position.<sup>10</sup> Intermediate terminal hydrides are not observed, however, for the protonation of the symmetrical complex 2.<sup>11</sup> It is therefore unclear if terminal hydrides form upon protonation of 2 and isomerize very readily or if the protonation occurs at the Fe-Fe bond. Some electrophiles (O-atom transfer agents,<sup>12</sup> alkylating agents<sup>13</sup>) attack not at the metal but rather at sulfur (Scheme 1).

A new perspective on the stereochemistry of electrophilic attack at diiron(I) dithiolates came from our recent study of the reaction of **2** with  $[S_2Me_3]^+$ , a source of the electrophile SMe<sup>+</sup>.<sup>7</sup> The initially observed product,  $[Fe_2(pdt)(SMe)-(CO)_4(PMe_3)_2]^+$ , features a terminal MeS ligand. This complex isomerizes by a first-order pathway to the corresponding  $\mu$ -thiolato isomer (eq 1).

This result suggests that protonation of 2 may occur also at a single Fe center followed by rapid rearrangement to the observed  $\mu$ -hydride complex. To address this question and to

Scheme 1. Three Pathways Established for Addition of Electrophiles  $(E^{\scriptscriptstyle +})$  to Diiron(I) Dithiolates



more generally probe the reactivity of the diiron complexes, we extended the range of electrophiles to include diazonium cations. Some diazonium salts are highly soluble in cold organic solvents, which makes them amenable to in situ NMR analysis. The results serve as a reminder that some electrophiles function as electron-transfer agents, and the stereochemistry of the adduct reflects the stereochemistry of the open-shell diiron intermediate.

# RESULTS AND DISCUSSION

Treatment of **1** with [PhN<sub>2</sub>]BF<sub>4</sub> at 0 °C resulted in good yields of the adduct [Fe<sub>2</sub>(pdt)( $\mu$ -N<sub>2</sub>Ph)(CO)<sub>4</sub>(dppv)]BF<sub>4</sub> ([1( $\mu$ -N<sub>2</sub>Ph)]BF<sub>4</sub>). <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of this salt are simple, indicating a symmetrical product. The formula of the cation was confirmed by ESI-mass spectrometry. Binding of the

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diazonium cation to the diiron center causes a shift in  $\nu_{CO(av)}$  of ~72 cm<sup>-1</sup> to 2030 cm<sup>-1</sup>. For comparison, protonation of 1 shifts  $\nu_{CO(av)}$  by 60 cm<sup>-1.14</sup> The reaction of 1 and [4-ClC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>]PF<sub>6</sub> gave the corresponding chlorophenyldiazonium complex. The spectroscopic data on the 4-ClC<sub>6</sub>H<sub>4</sub>N<sub>2</sub><sup>+</sup> and PhN<sub>2</sub><sup>+</sup> derivatives are similar. We found that [PhN<sub>2</sub>]BF<sub>4</sub> also reacts rapidly with **2**, but we were unable to purify or identify products.

The solid-state structure of  $[Fe_2(pdt)(\mu-N_2C_6H_4-4-Cl)-(CO)_4(dppv)]PF_6$  was confirmed crystallographically (Figure 1). The complex has idealized  $C_c$  symmetry, and the diazonium



Figure 1. Structure of the cation in  $[1(\mu-N_2C_6H_4Cl)]PF_6$  with thermal ellipsoids set at 35%. Hydrogen atoms, phenyl carbon thermal ellipsoids, and the counteranion were omitted for clarity. Selected bond distances (Å): Fe1–Fe2, 2.9653(6); Fe1–N1, 1.941(2); Fe2–N1, 1.973(3); Fe1–P1, 2.2256(9); Fe1–P2, 2.2271(9); Fe1–C39, 1.789(3); Fe1–S1, 2.3280(8); Fe1–S2, 2.3244(9); Fe2–S2, 2.3321(8); Fe2–S1, 2.3176(9); Fe2–C1, 1.827(4); Fe2–C3, 1.824(3); Fe2–C2, 1.823(4); N1–N2, 1.235(3); C35–Cl42, 1.744(3).

ligand is bridging. Clusters with  $\mu$ - $\eta^1$ , $\eta^1$ -RN<sub>2</sub> ligands are precedented.<sup>15</sup> The diazonium ligand is strongly bent (N1–N2–C38 = 120.4°) with the ClC<sub>6</sub>H<sub>4</sub> group oriented away from the bulky Fe(dppv)(CO) center. The dppv ligand is bound at the two basal sites on one Fe center. The Fe---Fe distance of 2.9653(6) Å is assigned as nonbonding. Similar Fe---Fe distances have been observed for other 36 e<sup>-</sup> diiron dithiolate complexes with bridging alkylidene ligands.<sup>16</sup>

The reaction of 1 and  $[PhN_2]^+$  was examined in situ to gain insights into the reaction pathway, i.e., the possible formation of intermediates. Such experiments were hindered by the poor

solubility of the typical diazonium salts (and, to a lesser extent, the low solubility of 1) in cold dichloromethane. This problem was addressed by the use of the organoborate salt  $[PhN_2]BAr_4^F$  $(Ar^{F} = C_{6}H_{3}-3,5-(CF_{3})_{2})$ . The off-white solid  $[PhN_{2}]BAr^{F_{4}}$  is highly soluble in CH<sub>2</sub>Cl<sub>2</sub> at low temperatures. The reaction of  $[PhN_2]BAr_4^F$  and 1 at -90 °C was monitoried by <sup>31</sup>P NMR spectroscopy. The initial spectrum reveals the immediate formation of a single new, unsymmetrical intermediate. Under our reaction conditions, ca. 50% of 1 remains undissolved. Upon warming the sample, signals for this intermediate disappear and only weak broad signals are observed. Above -30 °C, signals for  $[1(\mu-N_2Ph)]^+$  appear, and at room temperature  $[1(\mu-N_2Ph)]^+$  is the exclusive product. The observations suggest that (i) an unsymmetrical diamagnetic adduct forms at low temperature that is not  $[1(\mu N_2Ph$ )<sup>+</sup>, and (ii) upon warming, this intermediate rearranges concomitant with the formation of additional species that convert to  $[1(\mu-N_2Ph)]^+$ . We propose the sequence shown in eq 2.



Significantly, when the reaction of 1 and  $[PhN_2]BAr_4^F$  was monitored by IR spectroscopy *at room temperature*, we observed a ~1:1 ratio of  $[1(\mu-N_2Ph)]^+$  and the previously characterized<sup>17</sup> S = 1/2 species  $[1]^+$ . It therefore is likely that the broadened NMR spectra arise from the presence of  $[1]^+$ . Such mixed-valence cations are known to adopt the structures that feature a vacant apical site on one Fe center.<sup>17,18</sup>

We sought evidence for electron transfer in other reactions of diiron(I) dithiolates. As the electrophile, we selected  $Me_3S_2^+$ , which has been used by us and others.<sup>6,7,19</sup> IR analysis of its reaction with 1 at low temperatures revealed the clean formation of  $[1]^+$ . A similar result was obtained for the reaction of  $[Me_3S_2]BF_4$  and  $Fe_2(pdt)(CO)_4(dppbz)$  (3), except that  $[3]^+$  is particularly stable (eq 3).

$$Fe_{2}(pdt)(CO)_{4}(dppbz) + [Me_{3}S_{2}]^{T}$$

$$\rightarrow [Fe_{2}(pdt)(CO)_{4}(dppbz)]^{+} + Me_{2}S + 0.5Me_{2}S_{2}$$

$$[3]^{+}$$
(3)

Using <sup>1</sup>H NMR spectroscopy, we also confirmed that  $[Me_3S_2]BF_4$  reacts with ferrocene to give ferrocenium and a 2:1 mixture of  $Me_2S$  and  $Me_2S_2$ . Treating 3 with  $[PhN_2]BF_4$  also afforded  $[3]^+$ .

### CONCLUSIONS

This work describes the first diazonium derivative of a diiron dithiolate. The adducts show no tendency to decarbonylate to the 34 e<sup>-</sup> derivatives, in contrast to the lability of isoelectronic  $[Fe_2(pdt)(NO)(CO)_4(dppv)]^{+,9}$  The new reagent  $[PhN_2]$ -BAr<sup>F</sup><sub>4</sub> represents a useful derivative of the time-honored diazonium salts. According to our spectroscopic measurements, the properties of the  $PhN_2^+$  component of the salt are unaffected by the change in counterion.

The reaction of diazonium salts with 1 afforded apparent adducts, including one proposed to feature a terminal diazonium ligand. Also observed are products resulting from electron-transfer reactions. Connelly and Geiger have previously indicated that single electron transfer is associated with the use of diazonium salts, not unlike related reactions involving NO<sup>+</sup>.<sup>20</sup> It is well known that diazonium salts are good oxidants (e.g., for  $[FC_6H_4N_2]^{+/0} E = -0.07$  V for  $Fc^{+/0}$ ).<sup>20</sup>

The detection of odd-electron intermediates expands the range of reactions of diiron dithiolates. It is well known that 1 e<sup>-</sup> oxidation of  $Fe_2(pdt)(CO)_{6-x}L_x$  gives products wherein one Fe center adopts a "rotated structure".<sup>17,18</sup> The rotated structure is geometrically predisposed to bind both Lewis bases such as  $CO^{21}$  as well as the radicals:



We propose that such S = 1/2 species are intermediates in other reactions of diiron(I) dithiolates.

One surprising and puzzling observation in these studies is the differing behavior of the unsymmetrical versus symmetrical diphosphine complexes, such as 1 versus 2. Although exhibiting similar cyclic voltammograms, <sup>17,22</sup> [1]<sup>+</sup> and [2]<sup>+</sup> differ in terms of their stability, with [2]<sup>+</sup> being highly unstable and the dppv (and dppbz) cation being readily detectable.

#### EXPERIMENTAL SECTION

Methods have been recently reported.<sup>23</sup> The diazonium salts  $[N_2Ph]BF_4$  and  $[4\text{-}ClC_6H_4N_2]PF_6$  were prepared according to literature procedures.<sup>24</sup>

**[N<sub>2</sub>Ph]BAr<sup>F</sup>**<sub>4</sub>. A mixture of 0.380 g (2.5 mmol) of  $[N_2Ph]BF_4$  and 1.799 g (2.5 mmol) of KBAr<sup>F</sup><sub>4</sub> was precooled to -30 °C and then treated with 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. This mixture was allowed to warm to 0 °C and then vigorously stirred for 60 min. The resulting cloudy yellow mixture was filtered to remove KBF<sub>4</sub>, and the supernatant was concentrated to ~5 mL. An off-white precipitate formed upon addition of 30 mL of hexane and was collected by filtration. Yield: 1.94 g (80% based on KBAr<sup>F</sup><sub>4</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  8.31 (t,  $J_{H-H} = 8$ , 1H, *p*-H from  $[N_2C_6H_5]^+$ ), 8.35 (d,  $J_{H-H} = 8$ , 2H, *o*-H from  $[N_2C_6H_5]^+$ ), 8.02 (dd,  $J_{H-H} = 8$ , 2H, *m*-H from  $[N_2Ph]^+$ ), 7.72 (m, 8H, BAr<sup>F</sup><sub>4</sub>), 7.57 (bs, 4H, BAr<sup>F</sup><sub>4</sub>). Anal. Calcd for C<sub>38</sub>H<sub>17</sub>BF<sub>24</sub>N<sub>2</sub> (Found): C, 47.13 (47.69); H, 1.77 (1.75); N, 2.89 (2.83). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{NN} = 1567$  cm<sup>-1</sup>.

[Fe<sub>2</sub>(pdt)(μ-N<sub>2</sub>Ph)(CO)<sub>4</sub>(dppv)]BF<sub>4</sub>. A mixture of 0.509 g (0.70 mmol) of 1<sup>25</sup> and 0.150 g (0.78 mmol) of [N<sub>2</sub>Ph]BF<sub>4</sub> was cooled to 0 °C and dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. The resulting dark red reaction mixture was stirred until the IR spectrum indicated the complete consumption of starting materials (~45 min). The product precipitated as a deep red powder upon addition of 30 mL of hexane. An extract of the crude product in CH<sub>2</sub>Cl<sub>2</sub> was filtered through Celite and diluted with hexane to give the product. Yield: 0.59 g (86%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 81.4 (s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.3–6.9 (m, Ph), 4.56 (s, C<sub>2</sub>H<sub>2</sub>), 3.28 (m, SCH<sub>2</sub>), 2.90 (m, SCH<sub>2</sub>), 2.86 (m,

 $\begin{array}{l} CH_2CH_2CH_2),\ 2.69\ (m,\ CH_2CH_2CH_2).\ IR\ (CH_2Cl_2,\ cm^{-1}):\ 2088,\ 2039,\ 1972.\ ESI-MS\ (m/z):\ 613.2\ ([Fe_2(pdt)(CO)_2(dppv)(N_2Ph)]^+),\ 803.2\ ([Fe_2(pdt)(CO)_3(dppv)(N_2Ph)]^+),\ 831.21\ ([Fe_2(pdt)-(CO)_4(dppv)(N_2Ph)]^+).\ Anal.\ Calcd\ (Found)\ for\ C_{39}H_{33}BF_4Fe_2N_2O_4P_2S_2:\ C,\ 51.01\ (50.12);\ H,\ 3.62\ (3.86);\ N,\ 3.05\ (2.92). \end{array}$ 

[Fe<sub>2</sub>(pdt)(μ-N<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl)(CO)<sub>4</sub>(dppv)]PF<sub>6</sub>. As in the preceding procedure, a CH<sub>2</sub>Cl<sub>2</sub> solution of 0.397 g (0.55 mmol) of 1 was treated with 0.156 g (0.55 mmol) of [N<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-4-Cl]PF<sub>6</sub>. Standard workup afforded the product. Yield: 0.437 g (92.5%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ –145.2 (sept,  $J_{P-F} = 733$ ), 81.9 (s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.5 – 6.9 (m, Ph), 4.47 (bs, C<sub>2</sub>H<sub>2</sub>), 3.26 (m,  $J_{H-H} = 9$ , SCH<sub>2</sub>), 2.93 (m,  $J_{H-H} = 9$ , SCH<sub>2</sub>), 2.85 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.69 (m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2090, 2040, 1975. Anal. Calcd (Found) for C<sub>39</sub>H<sub>32</sub>ClF<sub>6</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>4</sub>P<sub>3</sub>S<sub>2</sub>: C, 46.34 (45.84); H, 3.19 (3.82); N, 2.77 (2.16).

Fe<sub>2</sub>(pdt)(CO)<sub>4</sub>(dppbz) (3). This complex was prepared analogously to 1. A solution of 0.432 g (1.12 mmol) of  $Fe_2(pdt)(CO)_6$  in 50 mL of toluene was treated with a solution of 0.084 g (1.12 mmol) of Me<sub>3</sub>NO in 15 mL of MeCN. After stirring for 10 min, the reaction mixture was treated with a solution of 0.50 g (1.12 mmol) of dppbz in 50 mL of toluene. The solution was strirred at 70 °C for 5 h. The solvent was removed under vacuum. The residue, a green-brown solid, was extracted into 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, and the product precipitated as a light-green-brown powder upon the addition of 100 mL of hexanes. The product was rinsed with 60 mL of hexanes. Yield: 0.69 g (80%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  89.1 (s) (apical-basal 94.5%),  $\delta$ 81.1 (s) (basal-basal 5.5%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.7-7.1 (m, C<sub>6</sub>H<sub>r</sub> 24H), 1.99 (m, SCH<sub>2</sub> 2H), 1.67 (m, SCH<sub>2</sub> 2H), 0.48 (bs, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub> 2H). IR  $(CH_2CI_2)$ :  $\nu_{CO}$  2020 (m), 1950 (m), 1905 (s) cm<sup>-1</sup>. Anal. Calcd (Found) for  $C_{37}H_{30}Fe_2O_4P_2S_2$ : C, 57.24 (57.15); H, 3.89 (3.94).

**Selected in Situ and IR and NMR Studies.** Several experiments were conducted (solvent: dichloromethane) to probe the role of electron-transfer reactions.

- (1) A solution of 15 mg (0.019 mmol) of 3 and 18.8 mg (0.019 mmol) of  $[Me_3S_2]BAr^F_4$  was prepared at -78 °C. Upon warming to room temperature, the IR spectrum ( $\nu_{CO}$  region) confirmed clean formation of  $[3]^+$ . Very similar results were obtained using  $[PhN_2]BF_4$  in place of  $[Me_3S_2]BAr^F_4$ .
- (2) Treatment of a solution of 3 with 1 equiv of FcBF<sub>4</sub> gave an IR spectrum ( $\nu_{CO}$  region) that matched that assigned to  $[3]^+$  in experiment 1.
- (3) Addition of 4.7 mg (0.025 mmol) of ferrocene to a solution of 5.0 mg (0.025 mmol) of  $[Me_3S_2]BF_4$  in 0.8 mL of  $CD_2Cl_2$  resulted in the slow (5 min) development of a deep blue-green color. <sup>1</sup>H NMR analysis of the mixture confirmed the formation of a 2:1 mixture of Me\_2S ( $\delta$  2.00) and Me\_2S<sub>2</sub> ( $\delta$  2.46).
- (4) Treatment of a CH<sub>2</sub>Cl<sub>2</sub> solution of 13.5 mg (0.028 mmol) of 2 at -78 °C with a solution of 27.5 mg (0.028 mmol) of [PhN<sub>2</sub>]BAr<sup>F</sup><sub>4</sub> in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> resulted in a rapid color change from red to black. The mixture was allowed to warm to room temperature, and the <sup>31</sup>P NMR spectrum revealed many signals. ESI-MS analysis showed strong peak envelopes at m/z= 587 ([2N<sub>2</sub>Ph]<sup>+</sup>) and 559 ([2Ph]<sup>+</sup>).

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Selected spectroscopic details. Crystallographic analysis. This material is available free of charge via the Internet at http:// pubs.acs.org.

#### AUTHOR INFORMATION

#### Notes

The authors declare no competing financial interest.

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# REFERENCES

(1) Fontecilla-Camps, J. C.; Volbeda, A.; Cavazza, C.; Nicolet, Y. *Chem. Rev.* **2007**, *107*, 4273.

(2) Tard, C.; Pickett, C. J. Chem. Rev. 2009, 109, 2245.

(3) Arabi, M. S.; Mathieu, R.; Poilblanc, R. Inorg. Chim. Acta 1977, 23, L17.

(4) Haines, R. J.; de Beer, J. A.; Greatrex, R. J. Chem. Soc., Dalton Trans. 1976, 1749.

(5) Treichel, P. M.; Crane, R. A.; Matthews, R.; Bonnin, K. R.; Powell, D. J. Organomet. Chem. **1991**, 402, 233.

(6) Georgakaki, I. P.; Miller, M. L.; Darensbourg, M. Y. Inorg. Chem. 2003, 42, 2489.

(7) Olsen, M. T.; Gray, D. L.; Rauchfuss, T. B.; De Gioia, L.; Zampella, G. *Chem. Commun.* **2011**, 47, 6554.

(8) Tschierlei, S.; Ott, S.; Lomoth, R. Energy Environ. Sci. 2011, 4, 2340.

(9) Olsen, M. T.; Bruschi, M.; De Gioia, L.; Rauchfuss, T. B.; Wilson, S. R. J. Am. Chem. Soc. **2008**, 130, 12021. Olsen, M. T.; Justice, A. K.; Gloaguen, F.; Rauchfuss, T. B.; Wilson, S. R. Inorg. Chem. **2008**, 47, 11816.

(10) Ezzaher, S.; Capon, J.-F.; Gloaguen, F.; Kervarec, N.; Pétillon, F. Y.; Pichon, R.; Schollhammer, P.; Talarmin, J. C. R. Chim. 2008, 11, 906. Ezzaher, S.; Capon, J.-F.; Gloaguen, F.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Pichon, R.; Kervarec, N. Inorg. Chem. 2007, 46, 3426. Barton, B. E.; Rauchfuss, T. B. Inorg. Chem. 2008, 47, 2261. Adam, F. I.; Hogarth, G.; Kabir, S. E.; Richards, I. C. R. Chim. 2008, 11, 890.

(11) Fauvel, K.; Mathieu, R.; Poilblanc, R. Inorg. Chem. 1976, 15, 976. Jablonskytė, A.; Wright, J. A.; Pickett, C. J. Dalton Trans. 2010, 39, 3026.

(12) Kramer, A.; Lingnau, R.; Lorenz, I. P.; Mayer, H. A. Chem. Ber.
1990, 123, 1821. Darensbourg, M. Y.; Weigand, W. Eur. J. Inorg. Chem.
2010, 994. Liu, T.; Li, B.; Singleton, M. L.; Hall, M. B.; Darensbourg, M. Y. J. Am. Chem. Soc. 2009, 131, 8296.

(13) Zhao, X.; Chiang, C.-Y.; Miller, M. L.; Rampersad, M. V.; Darensbourg, M. Y. J. Am. Chem. Soc. 2003, 125, 518.

(14) Barton, B. E.; Zampella, G.; Justice, A. K.; De Gioia, L.; Rauchfuss, T. B.; Wilson, S. R. *Dalton Trans.* **2010**, *39*, 3011.

(15) Samkoff, D. E.; Shapley, J. R.; Churchill, M. R.; Wasserman, H.
J. *Inorg. Chem.* 1984, 23, 397. Yan, X.; Batchelor, R. J.; Einstein, F. W.
B.; Sutton, D. *Inorg. Chem.* 1996, 35, 7818. Sutton, D. *Chem. Rev.* 1993, 93, 905.

(16) Bonnet, J. J.; Mathieu, R.; Poilblanc, R.; Ibers, J. A. J. Am. Chem. Soc. 1979, 101, 7487.

(17) Justice, A. K.; De Gioia, L.; Nilges, M. J.; Rauchfuss, T. B.; Wilson, S. R.; Zampella, G. *Inorg. Chem.* **2008**, *47*, 7405.

(18) Liu, T.; Darensbourg, M. Y. J. Am. Chem. Soc. 2007, 129, 7008. Justice, A. K.; Rauchfuss, T. B.; Wilson, S. R. Angew. Chem., Int. Ed. 2007, 46, 6152.

(19) Treichel, P. M.; Rublein, E. K. J. Organomet. Chem. 1996, 512, 157.

(20) Connelly, N. G.; Geiger, W. E. Chem. Rev. 1996, 96, 877.

(21) Justice, A. K.; Nilges, M.; Rauchfuss, T. B.; Wilson, S. R.; De Gioia, L.; Zampella, G. *J. Am. Chem. Soc.* **2008**, *130*, 5293. Thomas, C. M.; Liu, T.; Hall, M. B.; Darensbourg, M. Y. *Inorg. Chem.* **2008**, *47*, 7009.

(22) Singleton, M. L.; Jenkins, R. M.; Klemashevich, C. L.; Darensbourg, M. Y. C. R. Chim. 2008, 11, 861.

(23) Olsen, M. T.; Rauchfuss, T. B.; Wilson, S. R. J. Am. Chem. Soc. 2010, 132, 17733.

(24) Flood, D. T. Organic Syntheses; Wiley: New York, 1943; Collect. Vol. 2, p 295. Rutherford, K. G.; Redmond, W.; Rigamonti, J. J. Org. Chem. 1961, 26, 5149.

(25) Justice, A. K.; Zampella, G.; De Gioia, L.; Rauchfuss, T. B.; van der Vlugt, J. I.; Wilson, S. R. *Inorg. Chem.* **2007**, *46*, 1655.

Note