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

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Abstract

Treatment of $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppv})$ (**1**) with aryl diazonium salts affords the $34e^-$ adducts $[\text{Fe}_2(\text{pdt})(\mu\text{-N}_2\text{Ar})(\text{CO})_4(\text{dppv})]^+$ ($\text{pdt}^{2-} = 1,3\text{-propanedithiolate}$, $\text{dppv} = \text{cis-C}_2\text{H}_2(\text{PPh}_2)_2$). Under some conditions, the same reaction gave substantial amounts of $[\textbf{1}]^+$, 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 $[\text{Me}_3\text{S}_2]^+$ and $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppbz})$ was found to give $[\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppbz})]^+$ as well as Me_2S and Me_2S_2 ($\text{dppbz} = 1,2\text{-bis(diphenylphosphino)benzene}$).

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 $[\text{FeFe}]$ -hydrogenases.¹ Many efforts are underway to prepare low molecular weight analogues of these biocatalysts.² Since the diiron dithiolato center in the $[\text{FeFe}]$ -hydrogenases features strong donor ligands in addition to CO, biomimetic modelling generally focuses on the substituted derivatives of the diiron dithiolates, especially diphosphine complexes $\text{Fe}_2(\text{SR})_2(\text{CO})_4(\text{PR}_3)_2$ such as $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppv})$ (**1**) and $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{PMe}_3)_2$ (**2**).²

Electrophiles (E^+) attack substituted diiron(I) dithiolato complexes in one of three ways. Most commonly, electrophiles give adducts of the type $[\text{Fe}_2(\mu\text{-E})(\text{SR})_2\text{L}_6]^{+3}$. Many examples exist, cases include $\text{E}^+ = \text{Cl}^+$,⁴ SMe^+ ,^{5–7} and H^+ .⁸ The addition of NO^+ to diiron(I) dithiolates results in substitution, although $36e^-$ adducts are implicated as intermediates.⁹ Protonation of diiron dithiolates containing chelating diphosphine ligands generally proceeds via initial attack at a single metal to give terminal hydride complexes, which subsequently isomerize by migration of the hydride to a bridging position.¹⁰ Intermediate terminal hydrides are not observed, however, for the protonation of the symmetrical complex **2**.¹¹ It is therefore unclear if terminal hydrides form upon protonation of **2**, but that they isomerize very readily or if the protonation occurs at the Fe-Fe bond. Some electrophiles (*O*-atom transfer agents,¹² alkylating agents¹³) 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 $[\text{S}_2\text{Me}_3]^+$, a source of the electrophile SMe^{+7} . The initially observed product, $[\text{Fe}_2(\text{pdt})(\text{SMe})(\text{CO})_4(\text{PMe}_3)_2]^+$, features a terminal MeS

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

ligand. This complex isomerizes via a first order pathway to the corresponding μ -thiolato isomer (eq 1).

(1)

This result suggests that protonation of **2** may also occur also at a single Fe center followed by rapid rearrangement to the observed μ -hydride. To address this question and to 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 is advantageous for this 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 $[\text{PhN}_2]\text{BF}_4$ at 0 °C resulted in good yields of the adduct $[\text{Fe}_2(\text{pdt})(\mu\text{-N}_2\text{Ph})(\text{CO})_4(\text{dppv})]\text{BF}_4$ ($[\mathbf{1}(\mu\text{-N}_2\text{Ph})]\text{BF}_4$). ^1H and ^{31}P NMR spectra of this salt are simple, indicating a symmetrical product. The formula was confirmed by ESI-mass spectrometry. Binding of the diazonium cation to the diiron center causes a shift in $\nu_{\text{CO}(\text{avg})}$ of $\sim 72\text{ cm}^{-1}$ to 2030 cm^{-1} . For comparison, protonation of **1** shifts $\nu_{\text{CO}(\text{avg})}$ by 60 cm^{-1} .¹⁴ The reaction of **1** and $[\text{4-ClC}_6\text{H}_4\text{N}_2]\text{PF}_6$ gave the corresponding chlorophenyldiazonium complex. The spectroscopic data on the $[\text{4-ClC}_6\text{H}_4\text{N}_2]^+$ and $[\text{PhN}_2]^+$ derivatives are similar. We found that $[\text{PhN}_2]\text{BF}_4$ also reacts rapidly with **2**, but we were unable to purify or identify products.

The solid state structure of $[\text{Fe}_2(\text{pdt})(\mu\text{-N}_2\text{C}_6\text{H}_4\text{-4-Cl})(\text{CO})_4(\text{dppv})]\text{PF}_6$ was confirmed crystallographically (Figure 1). The complex has idealized C_s symmetry and the diazonium ligand is bridging. Clusters with $\mu\text{-}\eta^1, \eta^1\text{-RN}_2$ ligands are preceded.¹⁵ The diazonium ligand is strongly bent ($\text{N1-N1-C38} = 120.4^\circ$) with the ClC_6H_4 group oriented away from the bulky $\text{Fe}(\text{dppv})(\text{CO})$ center. The dppv ligand is bound at the two basal sites on one Fe center. The Fe-Fe distance of $2.9653(6)\text{ \AA}$ is assigned as nonbonding. Similar Fe---Fe distances have been observed for other 36 e^- diiron dithiolate complexes with bridging alkylidene ligands.¹⁶

The reaction of **1** and $[\text{PhN}_2]^+$ 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 $[\text{PhN}_2]\text{BAr}^{\text{F}}_4$ ($\text{Ar}^{\text{F}} = \text{C}_6\text{H}_3\text{-3,5-(CF}_3)_2$). The off-white solid $[\text{PhN}_2]\text{BAr}^{\text{F}}_4$ is highly soluble in CH_2Cl_2 at low temperatures. The reaction of $[\text{PhN}_2]\text{BAr}^{\text{F}}_4$ and **1** at $-90\text{ }^\circ\text{C}$ was monitored by ^{31}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 dissolved. Upon warming the sample, signals for this intermediate disappear and only smaller broad signals are observed. Above $-30\text{ }^\circ\text{C}$, signals for $[\mathbf{1}(\mu\text{-N}_2\text{Ph})]^+$ appear, and at room temperature $[\mathbf{1}(\mu\text{-N}_2\text{Ph})]^+$ is the exclusive product. The observations suggest that (i) an unsymmetrical diamagnetic adduct forms at low temperature that is not $[\mathbf{1}(\mu\text{-N}_2\text{Ph})]^+$, and (ii) upon warming, this intermediate rearranges concomitant with the

formation of additional species that convert to $[\mathbf{1}(\mu\text{-N}_2\text{Ph})]^+$. We propose the sequence shown in eq 2.

(2)

Significantly, when the reaction of **1** and $[\text{PhN}_2]\text{BAr}^{\text{F}}_4$ was monitored by IR spectroscopy *at room temperature*, we observed ~1:1 of $[\mathbf{1}(\mu\text{-N}_2\text{Ph})]^+$ and the previously characterized¹⁷ $S = 1/2$ species $[\mathbf{1}]^+$. It therefore is likely that the broadened NMR spectra arise from presence of $[\mathbf{1}]^+$. Such mixed valence cations are known to adopt the structures that feature a vacant apical site on one Fe center:^{17,18}

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.^{6,7,19} IR analysis of its reaction with **1** at low temperatures revealed the clean formation of $[\mathbf{1}]^+$. A similar result was obtained for the reaction of $[\text{Me}_3\text{S}_2]\text{BF}_4$ and $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppbz})$ (**3**), except that $[\mathbf{3}]^+$ is particularly stable (eq 3).

Using ^1H NMR spectroscopy, we also confirmed that $[\text{Me}_3\text{S}_2]\text{BF}_4$ reacts with ferrocene to give ferrocenone and a 2:1 mixture of Me_2S and Me_2S_2 . Treating **3** with $[\text{PhN}_2]\text{BF}_4$ also afforded $[\mathbf{3}]^+$.

Conclusions

This work describes the first diazonium derivative of a diiron dithiolate. The adducts show no tendency to decarbonylate to the $34 e^-$ derivatives, in contrast to the lability of isoelectronic $[\text{Fe}_2(\text{pdt})(\text{NO})(\text{CO})_4(\text{dppv})]^+.$ ⁹ The new reagent $[\text{PhN}_2]\text{BAr}^{\text{F}}_4$ 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** affording 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 $\text{NO}^+.$ ²⁰ It is well known that diazonium salts are good oxidants (e.g., for $[\text{Fc}_6\text{H}_4\text{N}_2]^{+/0}$ $E = -0.07 \text{ V}$ for $\text{Fc}^{+/0}$).²⁰

The detection of odd-electron intermediates expands the range of reactions of diiron dithiolates. It is well known that $1e^-$ oxidation of $\text{Fe}_2(\text{pdt})(\text{CO})_6\text{-xL}_x$ gives products wherein one Fe center adopts a “rotated structure.”^{17,18} 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 vs symmetrical diphosphine complexes, such as **1** vs **2**. Although exhibiting similar cyclic voltammograms,^{17,22} $[1]^+$ and $[2]^+$ differ in terms of their stability, with $[2]^+$ being highly unstable and the dppv (and dppbz) cation being readily detectable.

Experimental Section

Methods have been recently reported.²³ The diazonium salts $[N_2Ph]BF_4$ $[4-ClC_6H_4N_2]PF_6$ were prepared according to literature procedures.²⁴

$[N_2Ph]BAr^F_4$

A mixture of 0.380 g (2.5 mmol) of $[N_2Ph]BF_4$ and 1.799 g (2.5 mmol) of $KBAr^F_4$ was pre-cooled to $-30\text{ }^\circ\text{C}$ and then treated with 20 mL of CH_2Cl_2 . This mixture was allowed to warm to $0\text{ }^\circ\text{C}$ and then vigorously stirred for 60 min. The resulting cloudy yellow mixture was filtered to remove KBF_4 , and the supernatant was concentrated to $\sim 5\text{ mL}$. An off-white precipitate formed upon addition of 30 mL of hexane and was collected by filtration. Yield: 1.94 g (80% based on $KBAr^F_4$). 1H NMR (CD_2Cl_2): δ 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, $BAr^F_4^-$), 7.57 (bs, 4H, $BAr^F_4^-$). Anal. Calcd for $C_{38}H_{17}BF_{24}N_2$ (found): C, 47.13 (47.69); H, 1.77 (1.75); N, 2.89 (2.83). IR (CH_2Cl_2): $\nu_{NN} = 1567\text{ cm}^{-1}$.

$[Fe_2(pdt)(\mu-N_2Ph)(CO)_4(dppv)]BF_4$

A mixture of 0.509 g (0.70 mmol) of **1**²⁵ and 0.150 g (0.78 mmol) of $[N_2Ph]BF_4$ was cooled to $0\text{ }^\circ\text{C}$ and dissolved in 10 mL of CH_2Cl_2 . 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_2Cl_2 was filtered through Celite and diluted with hexane to give the product. Yield: 0.59 g (86%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 81.4 (s). 1H NMR (CD_2Cl_2): δ 7.3 – 6.9 (m, Ph), 4.56 (s, C_2H_2), 3.28 (m, SCH_2), 2.90 (m, SCH_2), 2.86 (m, $CH_2CH_2CH_2$), 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).

[Fe₂(pdt)(μ-N₂C₆H₄Cl)(CO)₄(dppv)]PF₆

As in the preceding procedure, a CH₂Cl₂ solution of 0.397 g (0.55 mmol) of **1** was treated with 0.156 g (0.55 mmol) of [N₂C₆H₄-4-Cl]PF₆. Standard workup afforded the product. Yield: 0.437 g (92.5%). ³¹P{¹H} NMR (CD₂Cl₂): δ –145.2 (sept, *J*_{P-F} = 733), 81.9 (s). ¹H NMR (CD₂Cl₂): δ 8.5 – 6.9 (m, Ph), 4.47 (bs, C₂H₂), 3.26 (m, *J*_{H-H} = 9, SCH₂), 2.93 (m, *J*_{H-H} = 9, SCH₂), 2.85 (m, CH₂CH₂CH₂), 2.69 (m, CH₂CH₂CH₂). IR (CH₂Cl₂, cm^{–1}): 2090, 2040, 1975. Anal. Calcd (Found) for C₃₉H₃₂ClF₆Fe₂N₂O₄P₃S₂: C, 46.34 (45.84); H, 3.19 (3.82); N, 2.77 (2.16).

Fe₂(pdt)(CO)₄(dppbz) (3**)**

This complex was prepared analogously to **1**, a solution of 0.432 g (1.12 mmol) of Fe₂(pdt)(CO)₆ in 50 mL of toluene was treated with a solution of 0.084 g (1.12 mmol) of Me₃NO 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 stirred at 70 °C for 5 h. The solvent was removed in vacuum. The residue, a green-brown solid, was extracted into 10 mL of CH₂Cl₂, 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%). ³¹P{¹H} NMR (CD₂Cl₂, 25 °C): δ 89.1 (s) (apical-basal 94.5%), δ 81.1 (s) (basal-basal 5.5%). ¹H NMR (CD₂Cl₂): δ 7.7 – 7.1 (m, C₆H_x 24H), 1.99 (m, SCH₂ 2H), 1.67 (m, SCH₂ 2H), 0.48 (bs, CH₂CH₂CH₂ 2H). IR (CH₂Cl₂): ν_{CO} 2020 (m), 1950 (m), 1905 (s) cm^{–1}. Anal. Calcd (found) for C₃₇H₃₀Fe₂O₄P₂S₂: C, 57.24 (57.15); H, 3.89 (3.94).

Selected In-situ and IR and NMR Studies

Several experiments were conducted 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 [Me₃S₂]BAr^F₄ was prepared at –78 °C. Upon warming to room temperature, the IR spectrum (ν_{CO} region) confirmed clean formation of [**3**]⁺. Very similar results were obtained using [PhN₂]BF₄ in place of [Me₃S₂]BAr^F₄.
2. Treatment of a solution of **3** with one equiv of FcBF₄ gave an IR spectrum (ν_{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) [Me₃S₂]BF₄ in 0.8 mL of CD₂Cl₂ resulted in the slow (5 min.) development of a deep blue green color. ¹H NMR analysis of the mixture confirmed the formation of a 2:1 mixture of Me₂S (δ 2.00) and Me₂S₂ (δ 2.46).
4. Treatment of a CH₂Cl₂ solution of 13.5 mg (0.028 mmol) of **2** at –78 °C with a solution of 27.5 mg (0.028 mmol) of [PhN₂]BAr^F₄ in 5 mL of CH₂Cl₂ resulted in a rapid color change from red to black. The mixture was allowed to warm to room temperature, and the ³¹P NMR spectrum revealed many signals. ESI-MS analysis showed strong peak envelopes at *m/z* = 587 ([**2**N₂Ph]⁺) and 559 ([**2**Ph]⁺).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. Fontecilla-Camps JC, Volbeda A, Cavazza C, Nicolet Y. Chem Rev. 2007; 107:4273. [PubMed: 17850165]
2. Tard C, Pickett CJ. Chem Rev. 2009; 109:2245. [PubMed: 19438209]
3. Arabi MS, Mathieu R, Poilblanc R. Inorg Chim Acta. 1977; 23:L17.
4. Haines RJ, de Beer JA, Greatrex R. J Chem Soc, Dalton Trans. 1976:1749.
5. Treichel PM, Crane RA, Matthews R, Bonnin KR, Powell D. J Organomet Chem. 1991; 402:233.
6. Georgakaki IP, Miller ML, Darensbourg MY. Inorg Chem. 2003; 42:2489. [PubMed: 12691553]
7. Olsen MT, Gray DL, Rauchfuss TB, De Gioia L, Zampella G. Chem Commun. 2011; 47:6554.
8. Tschierlei S, Ott S, Lomoth R. Ener & Envir Sci. 2011; 4:2340.
9. Olsen MT, Bruschi M, De Gioia L, Rauchfuss TB, Wilson SR. J Am Chem Soc. 2008; 130:12021. [PubMed: 18700771] Olsen MT, Justice AK, Gloaguen F, Rauchfuss TB, Wilson SR. Inorg Chem. 2008; 47:11816. [PubMed: 19007207]
10. Ezzaher S, Capon JF, Gloaguen F, Kervarec N, Pétillon FY, Pichon R, Schollhammer P, Talarmin J. C R Chim. 2008; 11:906. Ezzaher S, Capon JF, Gloaguen F, Pétillon FY, Schollhammer P, Talarmin J, Pichon R, Kervarec N. Inorg Chem. 2007; 46:3426. [PubMed: 17397148] Barton BE, Rauchfuss TB. Inorg Chem. 2008; 47:2261. [PubMed: 18333613] Adam FI, Hogarth G, Kabir SE, Richards I. C R Chim. 2008; 11:890.
11. Fauvel K, Mathieu R, Poilblanc R. Inorg Chem. 1976; 15:976. Jablonskyt A, Wright JA, Pickett CJ. Dalton Trans. 2010; 39:3026. [PubMed: 20221536]
12. Kramer A, Lingnau R, Lorenz IP, Mayer HA. Chem Ber. 1990; 123:1821. Darensbourg MY, Weigand W. Eur J Inorg Chem. 2010:994. Liu T, Li B, Singleton ML, Hall MB, Darensbourg MY. J Am Chem Soc. 2009; 131:8296. [PubMed: 19507910]
13. Zhao X, Chiang CY, Miller ML, Rampersad MV, Darensbourg MY. J Am Chem Soc. 2003; 125:518. [PubMed: 12517165]
14. Barton BE, Zampella G, Justice AK, De Gioia L, Rauchfuss TB, Wilson SR. Dalton Trans. 2010; 39:3011. [PubMed: 20221534]
15. Samkoff DE, Shapley JR, Churchill MR, Wasserman HJ. Inorg Chem. 1984; 23:397. Yan X, Batchelor RJ, Einstein FWB, Sutton D. Inorg Chem. 1996; 35:7818. Sutton D. Chem Rev. 1993; 93:905.
16. Bonnet JJ, Mathieu R, Poilblanc R, Ibers JA. J Am Chem Soc. 1979; 101:7487.
17. Justice AK, De Gioia L, Nilges MJ, Rauchfuss TB, Wilson SR, Zampella G. Inorg Chem. 2008; 47:7405. [PubMed: 18620387]
18. Liu T, Darensbourg MY. J Am Chem Soc. 2007; 129:7008. [PubMed: 17497786] Justice AK, Rauchfuss TB, Wilson SR. Angew Chem, Int Ed. 2007; 46:6152.
19. Treichel PM, Rublein EK. J Organomet Chem. 1996; 512:157.
20. Connelly NG, Geiger WE. Chem Rev. 1996; 96:877. [PubMed: 11848774]
21. Justice AK, Nilges M, Rauchfuss TB, Wilson SR, De Gioia L, Zampella G. J Am Chem Soc. 2008; 130:5293. [PubMed: 18341276] Thomas CM, Liu T, Hall MB, Darensbourg MY. Inorg Chem. 2008; 47:7009. [PubMed: 18597449]
22. Singleton ML, Jenkins RM, Klemashevich CL, Darensbourg MY. C R Chim. 2008; 11:861.
23. Olsen MT, Rauchfuss TB, Wilson SR. J Am Chem Soc. 2010; 132:17733. [PubMed: 21114298]
24. Flood DT. Org Synth. 1943:295. Coll. Vol. 2. Rutherford KG, Redmond W, Rigamonti J. J Org Chem. 1961; 26:5149.
25. Justice AK, Zampella G, De Gioia L, Rauchfuss TB, van der Vlugt JJ, Wilson SR. Inorg Chem. 2007; 46:1655. [PubMed: 17279743]

Figure 1.

Structure of the cation in [1(μ-N₂C₆H₄Cl)]PF₆ with thermal ellipsoids set at 35%. Hydrogen atoms and the counter anion 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).

Scheme 1.

Three pathways established for addition of electrophiles (E^+) to diiron(I) dithiolates.