# Rip It off: Nitro to Nitroso Reduction by Iron Half-Sandwich Complexes

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activation of the dppe ligand to give  $[Fe^{III}(\kappa^3 O, P, P'-P(2-O-C_6H_4)(Ph)-C_2H_4 PPh_2)Cp$ <sup>+</sup>. Complexes [3]<sup>+</sup> are stable under ambient conditions, are readily purified by column chromatography and can be isolated in up to 50% yield, considering that 0.5 equiv of 1 is required as the oxygen acceptor.

## ■ INTRODUCTION

The activation of small molecules through controlled modification of common functional groups is a key aspect of modern chemical synthetic strategies by providing access to unusual or unstable moieties. With a view to increasing the sustainability of chemical processes, a fast-growing area of research seeks to undertake these activation steps with earthabundant elements of low inherent toxicity.<sup>1</sup> For example, while nitroso compounds (RNO) are known as versatile synthetic reagents<sup>2</sup> and as noninnocent, redox-active ligands<sup>3,4</sup> in various transition-metal complexes,<sup>5</sup> studies of substituted nitroso compounds are complicated by the few methods known for their synthesis<sup>6</sup> and the commercially available examples. Nevertheless, the coordination chemistry of nitroso compounds is of special interest and can be used to mimic molecular oxygen in e.g. Cu<sup>7</sup> and Fe<sup>8</sup> complexes. However, the remarkable stability of nitroso ligands also causes deactivation of iron-based enzymes, including hemoglobin, for which they are considered as the end products of nitroarene poisoning in the human body.9,11

Although nitroso ligands in iron porphyrin-based compounds and iron complexes of other macrocyclic ligand systems have been intensely studied in this context,<sup>3,10</sup> the range of complexes featuring nitroso ligands remains limited as noted above. For transition metals other than iron, such as Co,<sup>11</sup> Ni,<sup>12</sup> and Ru,<sup>13,14</sup> reduction of nitro- to nitrosoarenes is known for a broader range of complex types, whereby phosphines or carbonyl ligands commonly act as reducing agents and oxygen acceptors, forming  $O=PPh_3$  and  $CO_2$ , respectively. In some Ru-based examples, the complex itself was also able to act as the oxygen acceptor, with the extruded oxygen atom incorporated within the ancillary ligand scaffold as new *o*-formyl<sup>14</sup> and hydroxyl<sup>13</sup> functional groups. The most important features and developments of the chemistry of Ru nitroso complexes have recently been reviewed, highlighting the importance of this ligand entity.<sup>15</sup>

- <sup>57</sup>Fe Mössbauer

Despite the prevalence of nitro-substituted aryl halides as coupling partners in late-metal-catalyzed cross-coupling reactions, examples of such substrates with iron and other first-row metal catalysts are conspicuously absent. This hints at difficulties in achieving transformations of these nitrosubstituted substrates with these elements, giving merit to further investigation of the interactions of nitroarenes with iron complexes.<sup>16</sup>

The iron half-sandwich fragment is known for its stability and strong metal to ligand back-bonding properties,<sup>17</sup> making it an ideal platform upon which to further explore nitroso

Received: January 7, 2021 Published: March 12, 2021



Article

X-ray diffraction



ligand chemistry. However, few nitroso complexes of the FeCp moiety are known, and generalized synthetic procedures have proven elusive. The first such complexes were prepared from the reaction of  $[FeI(CO)_2Cp]$  with AgPF<sub>6</sub> and PhNO.<sup>18</sup> The second example known to date has been identified from the  $[Fe(NCMe){PPh_2(2-S-C_6H_4)}Cp^*]$  precursor, which upon dissociation of the labile NCMe ligand can reversibly bind nitrosoarenes formed *in situ* by reduction from their parent nitroarenes with  $(EtO)_3SiH$  as a part of an iron-based catalytic cycle (Scheme 1).<sup>19</sup> In the absence of the reducing agent the

Scheme 1. Coordination of a Nitrosoarene Prepared from in Situ Reduction of a Nitroarene Substrate  $(Top)^{19}$  and the Deoxygenation of Nitroarenes Leading to the Synthesis of Iron Nitroso Complexes Described in the Present Work (Bottom)

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iron complex directly reduced the nitro precursor, with the extruded oxygen atom being captured by the phosphine ligand. However, a convenient and general method for the preparation of iron half-sandwich nitroso complexes is still pending.

Here we present a straightforward approach to the preparation of nitroso compounds by the deoxygenation of common nitroarenes within the coordination sphere of the simple half-sandwich complex  $[Fe(dppe)Cp][BAr_4^X]$  (X = F,  $[B(3,5-(CF_3)_2-C_6H_3)_4]$ ; X = Cl,  $[B(3,5-Cl_2-C_6H_3)_4]$ ) via a bimetallic intermediate. While one metal fragment captures the nitroso moiety to give stable nitroso complexes, the other acts as an oxygen acceptor.

#### RESULTS AND DISCUSSION

The nitroso compounds  $[3a-v]^+$  were obtained from the reaction of  $[FeCl(dppe)Cp](1)^{20}$  with an excess of any one of the various nitroarenes 2 and the sodium salts of the weakly coordinating borate anions  $[BAr^{F_4}]^-$  (i.e.,  $[B(3,5-(CF_3)_2-C_6H_3)_4]^-)$  and  $[BAr^{Cl_4}]^-$  (i.e.,  $[B(3,5-Cl_2-C_6H_3)_4]^-)$  in toluene (18 h, 70 °C) (Scheme 2).

The Na[BAr<sup>X</sup><sub>4</sub>] salts likely help drive the reaction through the precipitation of NaCl,<sup>21</sup> while the weakly coordinating borate anions impart solubility of the iron complex salts in toluene, making the coordinatively unsaturated Fe moiety available for the reaction with the substrates. The crude reaction mixtures can be purified by column chromatography, allowing the recovery of the excess nitroarene and isolation of the nitroso complexes  $[3a-v][BArF_4]$  together with the Fe<sup>III</sup> byproduct  $[4][BArX_4]$  (Scheme 2). In some cases the similar polarities of the salts of  $[3]^+$  and  $[4]^+$  made separation by column chromatography difficult, accounting for the variable isolated yields of the byproduct. The reaction tolerates a wide variety of substituted nitroarenes. However, reactions with nitroarenes bearing  $\pi$ -electron-donating groups such as p-F (2b), p-OMe (2h), and NR<sub>2</sub> (20,p) resulted in lower yields, independent of the borate counterion. This may be due to one or more factors, including the stronger N…O bonds in the  $\pi$ donor-substituted nitro compounds 2 or weaker Fe-N(O)bonds in the respective nitroso products (see below). Aliphatic substrates are less well behaved under these reaction conditions, with the reaction of 1 with 2-nitropropane giving several unidentified byproducts in addition to low yields of  $[3f]^+$ . The presence of acidic OH groups as in 4-nitrophenol (2g) and 4-nitrobenzoic acid (2q) resulted in the formation of the oxidized  $Fe^{III}$  phenolate [6][BAr<sup>Cl/F</sup><sub>4</sub>] and chloride [4][BAr<sup>Cl/F</sup><sub>4</sub>] complexes, respectively, rather than the nitroso compounds  $[3g]^+$  and  $[3q]^+$ . In passing we note that  $[6]^+$ appears to be the first bench-stable example of an iron halfsandwich phenolate complex to have been isolated; previous investigations were limited to reactive low-valent 14- and 16-VE complexes<sup>22</sup> and computational studies.<sup>23,24,37</sup> Reactions of 1 with  $Na[BAr^{Cl}_{4}]$  and inorganic nitro compounds, such as sodium nitrate and nitrite, failed to give nitroso complexes but rather gave [4][BAr<sup>Cl</sup><sub>4</sub>], in 11% and 29% yields, respectively. The coordinatively unsaturated species  $[Fe(dppe)Cp][BAr_4^F]$ has been shown to promote internal alkyne-vinylidene rearrangements under conditions similar to those employed here.<sup>21</sup> A competition experiment in which [FeCl(dppe)Cp] was reacted with 4 equiv of both PhC≡CPh and 2e (used for a better distinction from resonances from other aromatic entities) in the presence of  $Na[BAr_{4}^{F}]$  gave the nitroso complex  $[3e]^+$  exclusively. In the case of reactions of [FeCl(dppe)Cp], Na $[BAr^{F_4}]$ , and either of the internal alkynes **2s** and **2u**, the nitroso complexes  $[3s,u][BAr_4^F]$  were obtained in 44% and 29% yields, respectively, together with  $[4][BAr^F]_4$ in low yield (Scheme 2). It can therefore be concluded that the nitro-nitroso reduction is favored in comparison to the internal alkyne-vinylidene rearrangement under these conditions. However, in contrast to 4-nitrophenol (2g), reaction with the hydroxyl functionality in alkynol 2u was not observed, most probably due to the steric demand of the  $C(CH_3)_2OH$ fragment, and  $[3u][BAr_4^F]$  was isolated in 29% yield. Reactions with the analogous CH<sub>2</sub>OH derivative 2t, where the hydroxyl functionality is more accessible, only  $[4]^+$  and o-CH activated  $[5]^+$  (Figure 2; vide infra) were isolated as the  $[BAr_{4}^{F}]$  - salts. The ether 2v gave only trace amounts of products derived from an alkyne-vinylidene rearrangement together with  $[3v]^+$  in low yield.

In contrast to the reactions of  $[Fe(dppe)Cp]^+$  with internal alkynes, the presence of a terminal alkyne (2w) or coordinating nitrile (2x) functional group prevented the formation of the nitroso complexes  $[3w,x]^+$  and instead gave the acetylide complex [7a] (after deprotonation of the intermediate vinylidene) and the simple nitrile complex  $[7b]^+$  in over 50% yields, respectively (Scheme 3).

The latter compounds are identical with those products obtained by established procedures (Supporting Information) and were identified by e.g. NMR spectroscopy and singlecrystal X-ray diffraction (Figures S25 and S26). With the terminal alkyne and nitrile functional groups in [7a] and [7b]<sup>+</sup> effectively masked by coordination to the iron center, these complexes were subsequently reacted with an excess of 1 and Na[BAr<sup>F</sup><sub>4</sub>], resulting in bimetallic [8a]<sup>+</sup> and [8b]<sup>2+</sup>, which were isolated in low yield after purification of the reaction mixture by column chromatography. The bimetallic complexes

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Scheme 2. Synthesis and Substrate Scope of Fe Nitroso Complexes  $[3a-v][BAr_4^X]$  from [FeCl(dppe)Cp](1) and the Respective Nitroarenes  $2a-v^i$ 



<sup>*a*</sup>If the Fe<sup>III</sup> species [4]<sup>+</sup> is present, NMR-corrected yields are given. <sup>*b*</sup>PhC==CPh (1 equiv) was added during synthesis. <sup>*c*</sup>8 equiv of the nitroarene was used. <sup>*d*</sup>1 (2 equiv), Na[BArCl<sub>4</sub>] (2 equiv), and 2 (1 equiv) were used; yield based on 2. <sup>*c*</sup>Compound [6]<sup>+</sup> was formed instead. <sup>*f*</sup>A 1:Na[BArF<sub>4</sub>]:2 ratio of 5:5:1 was used; yield based on 2. <sup>*g*</sup>N,N-Dimethyl-4-nitrosoaniline instead of N,N-dimethyl-4-nitroaniline was reacted. <sup>*h*</sup>Compound [4][BArF<sub>4</sub>] was formed instead. <sup>*i*</sup>Counterions: [BArF<sub>4</sub>]<sup>-</sup> = [B(3,5-(CF<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>]<sup>-</sup>; [BArCl<sub>4</sub>]<sup>-</sup> = [B(3,5-Cl<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>]<sup>-</sup>. Note: 0.5 equiv of 1 acts as the oxygen acceptor (Scheme 3); therefore, yields higher than 50% cannot be obtained.

decompose by dissociation of the nitrile-coordinated metal fragment of  $[8b][BAr^{F}_{4}]_{2}$ , giving  $[3x][BAr^{F}_{4}]$  (Scheme 3 and Figure S19) or Fe–N(O) bond cleavage and subsequent reoxidation toward [7a]. Although attempts to similarly activate the remaining nitro functionality in  $[3m]^{+}$  to produce bimetallic  $[3y]^{2+}$  failed, the latter could instead be obtained by the reaction of 1,4-dinitrobenzene (2m) with a 5-fold excess of  $1/Na[BAr^{F}_{4}]$  (Scheme 3), also in low overall isolated yield.

The nitroso cations  $[3]^+$  are characterized by  $\nu$ (NO) bands at ~1290 and 1283 cm<sup>-1 25</sup> and by a <sup>31</sup>P{<sup>1</sup>H} NMR resonance at 97–104 ppm, the precise chemical shift being in good correlation with the electron density of the nitroso substituent (Figure S17). Electron-donating groups, such as *p*-OCH<sub>3</sub> ([**3h**]<sup>+</sup>; 103.2 ppm) and *p*-NMe<sub>2</sub> ([**3o**]<sup>+</sup>, 103.8 ppm), cause a slight low-field shift, whereas the resonance of the *p*-NO<sub>2</sub> derivative [**3m**]<sup>+</sup> is shifted to higher field and found at 101.3 ppm (Table S4). The bimetallic compounds [**8a/b**]<sup>+/2+</sup> exhibit two singlets in the <sup>31</sup>P{<sup>1</sup>H} NMR at 92.1, 102.2 and 97.0, 100.8 ppm, respectively. The symmetrical bimetallic complex [**3y**]<sup>2+</sup> revealed a low-field shift in the <sup>31</sup>P{<sup>1</sup>H} NMR (103.4 ppm) in comparison to monometallic [**3m**]<sup>+</sup> (101.3 ppm).

A correlation of the <sup>31</sup>P{<sup>1</sup>H} NMR resonances with the Hammett parameters<sup>26</sup> of the substituents attached in *meta*  $(\sigma_m)$  and *para*  $(\sigma_p)$  positions of the nitrosoarene ligand results in a linear fit (Figure S17;  $R^2 = 0.9214$ ) and allowed for the determination of parameters as yet unreported for the substituents in  $[3u]^+$  ( $\sigma_p = 0.20$ ),  $[3v]^+$  ( $\sigma_p = 0.22$ ),  $[3y]^{2+}$  ( $\sigma_p = -0.55$ ),  $[8a]^+$  ( $\sigma_p = 0.28$ ), and  $[8b]^{2+}$  ( $\sigma_p = 1.23$ ). The

<sup>13</sup>C{<sup>1</sup>H} shift of the Cp moiety also proved sensitive to the electronic nature of the nitroso ligand substituent (Figure S16). An examination of the  ${}^{13}C{}^{1}H$  NMR data reveals that the chemical shift of the Cp ligand is affected by the push-pull character between electron-donating substituents (NMe<sub>2</sub>, NPh<sub>2</sub>) and the electron-withdrawing nitroso substituent ( $\sigma_n$ = 0.91). Thus, the  $R^2$  value of the fit is enhanced from 0.8006 to 0.9495, if the push-pull-corrected  $\sigma_n^+$  parameters are considered. To the best of our knowledge  $\sigma_p^+$  is not yet available for the NPh<sub>2</sub> group ([**3p**]<sup>+</sup>) and was calculated as  $\sigma_p^+$ = -0.89 (Table S4 and Figure S16). The push-pull effect causes a bathochromic shift of the  $d \rightarrow d$  transition from red (e.g.  $[3e]^+$ , 463 nm) to blue (e.g.  $[3o]^+$ , 586 nm in benzene), giving an additional visual indication of the electronic effect. The p-NMe<sub>2</sub> substituent in  $[3o]^+$  causes a complex solvatochromic behavior (Tables S5 and S6), where polar solvents result in a hypsochromic shift from a blue to a purple solution (Figure S20).

The well-resolved <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of [3]<sup>+</sup> and conventional chemical shifts of the resonances are strongly supportive of a diamagnetic Fe<sup>II</sup> oxidation state and a neutral nitroso ligand. In contrast, the paramagnetic Fe<sup>III</sup> species [4–6]<sup>+</sup> exhibit broadened <sup>1</sup>H NMR resonances, and the <sup>31</sup>P{<sup>1</sup>H} NMR resonances are essentially indistinguishable from the background noise level (Supporting Information).<sup>27</sup>

However, despite the paramagnetic broadening, the Cp resonance of  $[4]^+$  was sufficiently well resolved to allow detection in samples of  $[3]^+$ . Consequently, in cases where full

Scheme 3. Reaction of 1 with Nitroarenes Bearing Terminal Alkynyl (2w) and Nitrile (2x) Functionalities (Top) and Synthesis of Bimetallic  $[3y]^+$  from 1,4-Dinitrobenzene (Bottom)<sup>*a*</sup>



"Ratio 1:Na[BAr<sup>F</sup><sub>4</sub>]:**2m** = 5:5:1; [3m][BAr<sup>F</sup><sub>4</sub>] (36%) was also formed. \*KO<sup>f</sup>Bu was added prior to the workup to deprotonate the vinylidene forms.

separation of  $[3]^+$  from  $[4]^+$  could not be achieved, an estimate of the yield of the nitroso complex was based on the ratio of the C<sub>5</sub>H<sub>5</sub> moieties of  $[3]^+$  (~4.7 ppm) and  $[4]^+$  (4.47 ppm). The blue, paramagnetic Fe<sup>III</sup> phenolate  $[6]^+$  was characterized by <sup>1</sup>H NMR (4.99 ppm, broad, C<sub>5</sub>H<sub>5</sub>) and UV–vis ( $\lambda_{max} = 549$ nm, blue) spectroscopy and single-crystal X-ray diffraction (Figure 2). IR bands at 1578 and 1330 cm<sup>-1</sup> clearly show the presence of a NO<sub>2</sub> functionality in  $[6]^+$ , together with an ether  $\nu_{C-O}$  band at 1261 cm<sup>-1</sup> (Table S1). The unsymmetrical dppe backbone in  $[5]^+$  resulted in two absorption maxima at 519 and 625 nm. The latter is caused by the oxygen donor, giving a blue solution similar to that of phenolate  $[6]^+$ . The cationic fragments of  $[3-6]^+$  were also identified by high-resolution mass spectrometry.

By way of example, the electrochemical properties of  $[3k]^+$ ,  $[3m]^+$ , and  $[3p]^+$  were studied by cyclic voltammetry in dichloromethane solutions containing 0.05 M [NBu<sub>4</sub>][BAr<sup>Cl</sup><sub>4</sub>] supporting electrolyte. The *p*-CH<sub>3</sub> and *p*-NPh<sub>2</sub> derivatives  $[3k,p]^+$  showed one reversible one-electron redox process at -470 and -480 mV (vs FcH/FcH<sup>+</sup>), respectively. These values are similar to those of 1 (-420 mV) and strongly support assignment of the redox wave to an Fe<sup>II/III</sup> oxidation process.<sup>28</sup> In addition, compound  $[3p]^+$  exhibits an irreversible oxidation process with an anodic peak potential of 0.52 mV, ascribed to the triaryl amine moiety. The *p*-NO<sub>2</sub> derivative  $[3m]^+$  showed an irreversible reduction process at -0.96 mV. To further establish the iron oxidation state in complexes  $[3]^+$ , <sup>57</sup>Fe Mössbauer parameters were obtained from  $[3m,o]^+$  by way of example and compared with those of neutral (1) and

cationic (Fe(NCPh)(dppe)Cp][BAr<sup>Cl</sup><sub>4</sub>]) Fe<sup>II</sup> and Cl ([4]<sup>+</sup>) and O-functionalized ([6]<sup>+</sup>) Fe<sup>III</sup> half-sandwich complexes (Table 1 and Figure 1). Data were collected at 80 K and fitted

Table 1. <sup>57</sup>Fe Mössbauer Data for 1,  $[3m]^+$ ,  $[4]^+$ ,  $[6]^+$  and a Fe<sup>II</sup> Benzonitrile Complex in Comparison with Literature Data

compound	IS (mm/s)	QS (mm/s)	$\Gamma (mm/s)$
1	0.430(3)	1.903(5)	0.128(4)
1 <sup>28</sup>	0.44	1.92	0.13
$[3m]^+$	0.228(9)	0.845(16)	0.174(12)
[ <b>3</b> 0] <sup>+</sup>	0.257(5)	1.113(10)	0.155(7)
<b>[4]</b> <sup>+</sup>	0.419(17)	0.76(3)	0.27(3)
$[4(F)]^{+a}$	0.426	0.92	nr
<b>[6</b> ] <sup>+</sup>	0.47(5)	0.82(8)	0.44(8)
[Fe(NCPh)(dppe)Cp] <sup>+</sup>	0.356(3)	1.932(7)	0.120(6)
[Fe(NCCH <sub>3</sub> )(dppe)Cp] <sup>+ 28</sup>	0.39	2.01	0.14

<sup>*a*</sup>Value of the fluoride derivative of  $[4]^+$  taken from ref 30. nr = not reported.



Figure 1. <sup>57</sup>Fe Mössbauer spectra of 1, [3m]<sup>+</sup>, [3o]<sup>+</sup>, and [6]<sup>+</sup>.

with Lorentzian line shapes by least-squares methods (Figures S2 and S15). The isomer shift (IS) and quadruple splitting (QS) values of 1 and the benzonitrile complex [Fe(NCPh)-(dppe)Cp][BAr<sup>Cl</sup><sub>4</sub>] are consistent with previous measurements, confirming the Fe<sup>II</sup> oxidation state.<sup>28</sup> The IS parameter in [FeX(dppe)Cp]<sup>n+</sup> complexes is predominantly affected by the nature of the ligand X and decreases in the order O (0.47) > Cl (0.42) > NC (0.36) > N(O) (0.23/0.26), while the selectron character at the metal ion increases.<sup>29</sup>

In the case of the nitroso complexes  $[3m,o]^+$  the substantial metal to ligand d,p back-bonding increases the amount of *s*-electron density at the metal indirectly, resulting in IS values similar to those recently reported for the Fe<sup>II</sup> hydride complex [FeH(dppe)Cp\*]<sup>27,31</sup> and significantly lower than those of the Fe<sup>III</sup> compounds [4]<sup>+</sup> and [6]<sup>+</sup>. Indeed, a comparison of Fe<sup>II</sup> and Fe<sup>III</sup> chlorides 1 and [4]<sup>+</sup> also reveals that the IS values in these half-sandwich complexes are rather insensitive to the iron oxidation state. This can be explained by the equilibrating donating/back-bonding effects of the Fe<sup>--</sup>Cp interaction and the not insignificant ligand character involved in the oxidation

of 1.<sup>29</sup> The QS parameter decreases from 1 to  $[4]^+$ , revealing a more symmetrical charge distribution in the oxidized complex  $[4]^+$ . Similarly low values are found for Fe<sup>III</sup> phenolate  $[6]^+$ . The QS value is also affected by the electronic properties of the *para* substituent in nitroso complexes  $[3]^+$ . Exchange of a *p*-NO<sub>2</sub> group in  $[3m]^+$  by *p*-NMe<sub>2</sub> in  $[3o]^+$  increases the QS value from 0.845(16) to 1.113(10), caused by the reduced  $\pi$  acidity of the ligand in  $[3o]^+$ , resulting in a more asymmetrical charge distribution around the metal.

Although both values are similar to those of Fe<sup>III</sup> complexes  $[4]^+$  and  $[6]^+$ , the sharp signals in NMR experiments reveal a diamagnetic Fe<sup>II</sup> configuration for the nitroso complexes. Clearly the QS values are sensitive to both the nature of the ligand environment and the oxidation state of the metal ion. The half-height width (line broadening,  $\Gamma$ ) increases in the order Fe<sup>II</sup> (0.13) <  $[3o]^+$  (0.16)  $\approx [3m]^+$  (0.17) < Fe<sup>III</sup>-Cl (0.27) < Fe<sup>III</sup>-O (0.44). Thus, although a comparison of complexes with ligands of different nature can be misleading,<sup>31</sup>  $\Gamma$  reveals that nitroso complexes  $[3m,o]^+$  exhibit properties similar to those of other Fe<sup>II</sup> compounds, evidencing a Fe<sup>II</sup>/N(O)R<sup>0</sup> metal/ligand couple.

Compounds  $[3d,m,o,s]^+$ ,  $[4]^+$ ,  $[5]^+$ ,  $[6]^+$ , and  $[9]^{2+}$  ( $[9]^{2+} = [{Fe(dppe)Cp}_2(\mu-dppe)]^{2+}$ ; Figure 2 and Figures S1–S5)



**Figure 2.** ORTEP drawings of the molecular structures of  $[3m]^+$  (top left; probability level 30%),  $[6]^+$  (top right; probability level 50%),  $[3s]^+$  (bottom left; probability level 50%), and  $[5]^+$  (bottom right; probability level 30%) showing their atom-numbering scheme. H atoms, the  $[Bar^{F}_{4}]^-$  (**3m**,**s**, **5**) or  $[BAr^{Cl}_{4}]^-$  (**3s**) counterion, disordered parts (see ESI) and the phenyl rings of the dppe fragments have been atoms are omitted for clarity. Selected bond properties are summarized in Table 2. Selected bond properties (Å):  $[5]^+$ , Fe-P 2.154(9)-2.2757(7), Fe-O 1.863(2), Fe-Ct<sub>Cp</sub> 1.7355(4);  $[6]^+$ , Fe1-P1 2.2460(8), Fe1-P2 2.2589(8), Fe-O 1.8828(18), C-N 1.457(3), N-O 1.228(3) and 1.233(3), Fe-Ct<sub>Cp</sub> 1.7495(4). For a comparison of bond parameters of nitroso complexes  $[3]^+$ , see Table 2.

could be further characterized by single-crystal X-ray diffraction. The Fe–P distances (Table 2) in  $[3d,m,o,s]^+$  are comparable to those of other Fe nitroso complexes<sup>19</sup> and cationic, N-ligated complexes, such as  $[Fe(NCMe)(dppe)Cp]^+$  (Figure S8), which further supports the description of compounds  $[3]^+$  in terms of an Fe<sup>II</sup> metal atom and a neutral nitroso ligand.

The Fe–N and N–O bond lengths are in good agreement with those of Fe porphyrin nitroso complexes featuring a lowspin Fe<sup>II</sup> center.<sup>10</sup> The N–O distances of  $[3d,m,o,s]^+$  (1.251(3)–1.272(12) Å), featuring more electron donating dppe ancillary ligands, are slightly elongated relative to the carbonyl complex  $[Fe{N(O)-Ph}(CO)_2Cp]^+$  (1.226(3) Å),<sup>18</sup> indicating greater Fe–N(O) back-bonding. The Fe–O==NR binding mode was not observed in any of the compounds studied here.<sup>8</sup> The donor–acceptor electronic effects observed in the NMR and optical properties are also reflected in the C– N bond lengths toward the *para* substituents, which decrease from 1.465(3) (*p*-NO<sub>2</sub>,  $[3m]^+$ ) to 1.363(4) Å (*p*-NMe<sub>2</sub>,  $[3o]^+$ ).

The strength of the Fe-N interaction in the nitroso complexes was investigated by displacement reactions with acetonitrile. Complexes  $[3m][BAr_4^F]$  (p-NO<sub>2</sub>) and [3o]- $[BAr_{4}^{F}]$  (p-NMe<sub>2</sub>), representing both extremes of the electronic scale, were chosen by way of example. Electronpoor  $[3m]^+$  displayed a high barrier toward displacement of the nitroso ligand and converted only slowly to the acetonitrile complex  $[Fe(NCMe)(dppe)Cp]^+$  in refluxing NCMe, with 10% conversion after 4 h and 90% of [3m]<sup>+</sup> being recovered. A 12 h reaction gave  $\sim 63\%$  conversion (Figure S19), demonstrating the high stability of  $[3m]^+$ . In addition, it should be noted that 1,4-dinitrobenzene was also formed in this reaction, by reoxidation of the released p-nitroso nitrobenzene ligand. In contrast, the blue color of electronrich  $[3o]^+$  vanishes completely within 10-20 min in acetonitrile at ambient temperature. These results also help explain the lower yields of the electron-rich nitroso complexes  $[3h,o,p]^+$  (Scheme 2), which are more prone toward a release of the nitroso ligand during the workup and purification processes.

The electronic differences of the nitroso ligand substituents are also reflected in the Fe–N distances and degree of  $\eta^1/\eta^2$ disorder in the solid-state structures. The more labile p-NMe<sub>2</sub> derivative, [30]<sup>+</sup>, offers a relatively long Fe-N distance (1.841(3) Å) and absence of the  $\eta^2$  coordination mode of the N(O)R moiety in the structural model, consistent with limited Fe-N back-bonding. The derivatives bearing more electron withdrawing p-NO<sub>2</sub> ([3m]<sup>+</sup>) and p-C $\equiv$ CPh ([3s]<sup>+</sup>) moieties offer shorter Fe- $\eta^1$ -N(O) distances (1.820(2) and 1.707(9) Å, respectively) and feature more significant contributions from the disordered  $\eta^2$ -N(O) component in the structural models ( $[3m]^+$ , 10%;  $[3s]^+$ , 52%). The C<sub>6</sub>-N= O torsion angle of the  $\eta^1$ -bonded nitroso functionality toward the phenyl plane follows the trend of a decrease of electron density in the order  $[3o]^+ > [3s]^+ > [3m]^+$  via  $47.9(2)^\circ <$  $61.0(7)^{\circ} < 66.58(14)^{\circ}$ . The  $\eta^2$ -coordination mode induces a rather coplanar orientation of the NO and phenyl fragments (Table 2). The Fe–O distances decrease in the order  $\sim$ 2.7 Å  $(\eta^1 \text{ entities}) \gtrsim 2.1 \text{ Å} (\eta^2 \text{ entities}) \gtrsim 1.87 \text{ Å for phenolate}$ complexes  $[5]^+$  and  $[6]^+$ .

Recent investigations by Ishii and co-workers highlighted the use of Na[BAr<sup>F</sup><sub>4</sub>] for the activation of 1 by halide abstraction in nonpolar/noncoordinating solvents. The electronically and coordinatively unsaturated [Fe(dppe)Cp]<sup>+</sup> complex is able to activate internal alkynes via an alkyne–vinylidene rearrangement.<sup>21</sup> Other halide abstracting agents such as AgPF<sub>6</sub> and NaBPh<sub>4</sub> resulted in a complex mixture of products. However, the use of [BAr<sup>F</sup><sub>4</sub>]<sup>-</sup> is not without difficulty, due to its rather elaborate purification and high propensity for disorder of the CF<sub>3</sub> groups in the solid state,<sup>32</sup> which can complicate crystallization processes.

To address some of these potential concerns, the non-fluorinated, but still weakly coordinating,  $[B(3,5-Cl_2-C_6H_3)_4]^-$  anion was explored in these studies.<sup>32</sup> A comparison between reactions promoted by the more soluble Na[BAr<sup>F</sup><sub>4</sub>] salt and

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Table 2. Selected	Bond Pr	operties (.	Å/deg)	) of Nitroso	Complexes	$[3d,m,o,s]^+$
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[3d] <sup>+ a</sup>	[ <b>3m</b> ] <sup>+</sup>	[ <b>3</b> 0] <sup>+</sup>	[ <b>3s</b> ] <sup>+</sup>
<i>p</i> -Br	<i>p</i> -NO <sub>2</sub>	<i>p</i> -NMe <sub>2</sub>	p-C≡CPh
100/0	90.5/9.5	100/0	47.8/52.2
1.7517(3)-1.7578(3)	1.7493(4)	1.7498(4)	1.7351(5)
2.2186(7)-2.2453(6)	2.2279(8)	2.2309(9)	2.2345(12)
	2.2234(8)	2.2361(9)	2.2538(10)
1.835(2)	1.820(2)	1.841(3)	$1.707(9) (\eta^1)$
1.827(2)			$2.132(7) (\eta^2)$
2.7289(17)	2.740(2)	2.712(2)	$2.632(2) (\eta^1)$
2.7424(17)	2.114(19)		2.108(5) $(\eta^2)$
1.267(3)	1.255(3)	1.251(3)	$1.272(12) (\eta^{1})$
1.252(3)			$1.323(10) (\eta^2$
1.452(3)	1.459(3)	1.457(4)	1.452(5)
1.471(3)			
111.16(19)	110.51(19)	112.4(2)	$109.7(8) (\eta^1)$
111.55(19)			111.9(6) $(\eta^2)$
122.12(16)	125.02(17)	123.0(2)	123.5(6) $(\eta^1)$
124.89(17)			70.8(4) $(\eta^2)$
49.00(14)	66.58(14) $(\eta^1)$	47.9(2)	$61.0(7) (\eta^1)$
54.29(14)	$7(2) (\eta^2)$		15.7(9) $(\eta^2)$
	1.216(3)		
	1.225(3)		
	$1465(3)^d$	$1.363(4)^{e}$	
	$[3d]^{+ \alpha}$ p-Br 100/0 1.7517(3)-1.7578(3) 2.2186(7)-2.2453(6) 1.835(2) 1.827(2) 2.7289(17) 2.7424(17) 1.267(3) 1.252(3) 1.452(3) 1.452(3) 1.471(3) 111.16(19) 111.55(19) 122.12(16) 124.89(17) 49.00(14) 54.29(14)	$\begin{array}{ c c c c c } & [3d]^{+a} & [3m]^{+} \\ p \cdot Br & p \cdot NO_2 \\ 100/0 & 90.5/9.5 \\ \hline 1.7517(3) - 1.7578(3) & 1.7493(4) \\ 2.2186(7) - 2.2453(6) & 2.2279(8) \\ & 2.2234(8) \\ \hline 1.835(2) & 1.820(2) \\ \hline 1.827(2) & & & \\ 2.7289(17) & 2.740(2) \\ 2.7424(17) & 2.114(19) \\ 1.267(3) & 1.255(3) \\ \hline 1.252(3) & & \\ 1.452(3) & 1.459(3) \\ \hline 1.452(3) & 1.459(3) \\ \hline 1.471(3) & & \\ 111.16(19) & 110.51(19) \\ \hline 111.55(19) & & \\ 122.12(16) & 125.02(17) \\ \hline 124.89(17) & & \\ 49.00(14) & 66.58(14)(\eta^{1}) \\ 54.29(14) & 7(2)(\eta^{2}) \\ \hline \end{array}$	$\begin{bmatrix} [3d]^{+ a} & [3m]^{+} & [3o]^{+} \\ [00/0 & 90.5/9.5 & 100/0 \\ 1.7517(3)-1.7578(3) & 1.7493(4) & 1.7498(4) \\ 2.2186(7)-2.2453(6) & 2.2279(8) & 2.2309(9) \\ 2.2234(8) & 2.2309(9) \\ 2.2234(8) & 2.2361(9) \\ 1.835(2) & 1.820(2) & 1.841(3) \\ 1.827(2) & & & & \\ 2.7289(17) & 2.740(2) & 2.712(2) \\ 2.7424(17) & 2.114(19) & & \\ 1.267(3) & 1.255(3) & 1.251(3) \\ 1.252(3) & & & & \\ 1.452(3) & 1.459(3) & 1.457(4) \\ 1.471(3) & & & & \\ 111.16(19) & 110.51(19) & 112.4(2) \\ 111.55(19) & & & & \\ 122.12(16) & 125.02(17) & 123.0(2) \\ 124.89(17) & & & & \\ 49.00(14) & 66.58(14) (\eta^1) & 47.9(2) \\ 54.29(14) & 7(2) (\eta^2) & & \\ 1.216(3) \\ 1.225(3) & & & & \\ 1.225(3) & & & & \\ 1.225(3) & & & & \\ 1.216(3) \\ 1.225(3) & & & & \\ 1.225(3) & & & & \\ 1.225(3) & & & & \\ 1.225(3) & & & & \\ 1.225(3) & & & & \\ 1.216(3) \\ 1.225(3) & & & & \\ 1.225(3) & & & & \\ 1.216(3) \\ 1.225(3) & & & \\ 1.225(3) & & & & \\ 1.216(3) \\ 1.225(3) & & & \\ 1.225(3) & & & \\ 1.216(3) \\ 1.225(3) & & & \\ 1.225(3) & & & \\ 1.255(3) & & & \\ 1.255(3) & & & \\ 1.255(3) & & & \\ 1.255(3) & & & \\ 1.225(3) & & & \\ 1.25$

9.5% of  $\eta^2$  coordination in  $[3m]^+$  are not discussed, due to the lower precision of the data, except noted.

Na[BAr<sup>Cl</sup><sub>4</sub>]<sup>-</sup> gave similar product distributions, but often with higher yields of the key compounds [3]<sup>+</sup> from the fluorinated salt. For example, in the case of [3b,m]<sup>+</sup> the [BAr<sup>F</sup><sub>4</sub>]<sup>-</sup> counterion significantly enhanced the yield of the products [3b,m][BAr<sup>F</sup><sub>4</sub>] vs [3b,m][BAr<sup>Cl</sup><sub>4</sub>] (Scheme 2), which might be due to either a better solubility of fluorinated counterions in general or the lower amount of water in the respective sodium salt (see the Supporting Information). Nevertheless, many of the resulting products are difficult to crystallize or precipitate using [BAr<sup>F</sup><sub>4</sub>]<sup>-</sup>, whereas the chlorinated version readily gave many of the products as solid materials.<sup>32</sup>

The formation of the Fe<sup>III</sup> byproduct  $[4]^+$  is unlikely to be due to the oxidation of 1 by the nitroarenes, given the increased yields of complexes  $[3]^+$  in excess nitroarene. Furthermore, the reaction of 1 with the nitroso derivative of **20**, which is an even stronger electron acceptor ( $\sigma_p(NO) =$ 0.91;  $\sigma_p(NO_2) = 0.78)^{26}$  and would consequently facilitate an electron transfer, did not result in  $[4]^+$  but rather gave  $[30][BArF_4]$  in 89% yield (Scheme 2). The formation of  $[4]^+$ can be attributed to the reaction of {Fe(dppe)Cp}<sup>+</sup> with dichloromethane.<sup>31</sup> The further byproduct  $[5]^+$  (Scheme 2 and Figure 2) was obtained as a blue solid in various quantities (usually <10%). Compound  $[5]^+$  most probably originates by abstraction of an oxygen atom from the nitro substrate and subsequent internal rearrangement (see Scheme 4).

A further feature of the reaction is the rapid color change from dark to intense blue upon the addition of the borate salts Na[BAr<sup>X</sup><sub>4</sub>] to the mixtures of **1** and **2**. Reactions of **1** and Na[BAr<sup>X</sup><sub>4</sub>] in the absence of nitro compounds, e.g. upon addition of toluene, diphenylacetylene, or *N*,*N*-dimethylaniline instead, did not show such behavior, nor has such a distinctive color change been reported for similar halide abstraction reactions of [FeX(dppe)Cp'] complexes carried out in Scheme 4. Proposed Mechanism for the Synthesis of *o*-Fluoro-Substituted Complex  $[3r]^+$  via Intermediates  $[A-C]^{+/2+a}$ 



<sup>*a*</sup>Yield based on 1, considering 2 equiv of 1 for the formation of  $[3r][BAr^{F}_{4}]$ , according to the proposed mechanism.

different solvents or mediated by other reagents.<sup>33,34</sup> Several attempts, e.g. within the formation of [**3b,d,s**]<sup>+</sup>, were carried out to isolate or crystallize this first-formed, highly air sensitive blue species, which appears to be stable for only a few hours in solution, judging by the discharge of the characteristic color. To date, the blue species formed en route to e.g. [**3b,d,s**]<sup>+</sup> have resulted in oily precipitates, containing small quantities of orange crystals, identified via single-crystal X-ray diffraction as

the bimetallic complex  $[9][BAr^{Cl}_4]_2$  (Figure S5). The additional bridging dppe ligand within  $[9]^{2+}$  evinces decomposition of the precursor complex. In addition to  $[9]^{2+}$ , varying amounts of the Fe<sup>III</sup> species  $[4]^+$  were also obtained from the attempts to isolate the key blue intermediates in these reactions.

The sole nitroarene that resulted in a stable blue solution at ambient temperature on reaction with 1 and  $Na[BAr_{4}^{F}]$  was 1fluoro-2-nitrobenzene 2r (Scheme 4). This blue compound was identified as  $[C]^{2+}$  by NMR, IR, and UV-vis spectroscopy (Table S3 and Figures S13, S14, and S8, respectively). The intense blue color of  $[\mathbf{C}]^{2+}$  ( $\lambda_{max} = 695 \text{ nm}$ ) is consistent with the presence of an Fe-O bond (Tables S2 and S3), also observed for phenolates  $[5]^+$  and  $[6]^+$ , and is shifted >100 nm to lower energy in comparison to the primary absorption band in 1 (588 nm). The  $\eta^6/\pi$ -coordinated complex [Fe( $\eta^6$ - $C_6H_5Me$ )(dppe)Cp]<sup>+</sup> is not responsible for this color.<sup>35</sup> The bimetallic nature of  $[C]^{2+}$  was confirmed by complete conversion of 1 to  $[C]^{2+}$  following a reaction with 0.5 equiv of 2r over 30 min at 60 °C (Figure S13). Allowing the reaction to proceed for 18 h at 70 °C gave [3r][BAr<sup>F</sup><sub>4</sub>] in 50% yield; if two molecules of 1 are considered to produce  $[3r]^+$ , then the yield is quantitative (Schemes 2 and  $\overline{4}$ ). The suggestion of a bimetallic structure for  $[C]^{2+}$  is further supported by the IR spectrum of this complex, with both asymmetric and symmetric  $\nu(NO_2)$  stretching vibrations shifted toward lower energy by 7 and 12 cm<sup>-1</sup> in comparison with the free nitroarene 2r (Table S1 and Figure S13), indicating that the nitro functionality acts as a donor ligand and the overall symmetry of the NO<sub>2</sub> group is retained, excluding the presence of monometallic  $[B]^+$ .

The  ${}^{31}P{}^{1}H$  NMR of  $[C]^{2+}$  showed one singlet at 98.5 ppm and a small signal at 97.3 ppm (<10%), which can be ascribed to traces of the product  $[3r]^+$  (97.3 ppm) (Table S3). A further indicative parameter for a complete conversion of 1 into  $[\mathbf{C}]^{2+}$  is the <sup>13</sup>C{<sup>1</sup>H} NMR resonance of the Cp moiety, which progressively moves to lower field in the order 76.9 < 84.1 < 90.3 ppm during conversion of 1 to  $[\mathbf{C}]^{2+}$  and  $[\mathbf{3r}]^+$ . The <sup>13</sup>C{<sup>1</sup>H} NMR signals of the 1-fluoro-2-nitrobenzene entity in  $[\mathbf{C}]^{2+}$  are also easily distinguished from those of  $2\mathbf{r}$ and  $[3r]^+$ . The C–NO<sub>2</sub> carbon resonance shifts to significantly lower field during the reaction from 137.62 ppm (2r) to 137.94 pmm ( $[C]^{2+}$ ), supporting the presumption that both NO<sub>2</sub> oxygen atoms act as donor atoms and therefore reduce the electron density at the bonded C atom (Figure S12). However, the C-F probe does not undergo significant changes, either in the <sup>19</sup>F NMR, where 2r and  $[C]^{2+}$  both show a signal at -118.0 ppm, or within the  ${}^{13}C{}^{1}H{}$  NMR (C-F: 2r, 155.6 ppm;  $[C]^{2+}$ , 155.5 ppm), and there are small changes in the  ${}^{1}J_{C,F}$  coupling constants of 263.9 Hz (2r) and 265.6 Hz ( $[C]^{2+}$ ). The conversion from the putative  $\mu_2$ -NO<sub>2</sub> mode in  $[C]^{2+}$  to the NO ligand in  $[3r]^+$  gives rise to diagnostic changes in the NMR resonances, which shift from -118.0 to -123.4 ppm (<sup>19</sup>F NMR), 137.94 to 159.2 ppm  $({}^{13}C{}^{1}H{} NMR, C-NO, {}^{2}J_{C,F} = 12.2 Hz)$ , and 155.5 to 149.9 ppm (C-F,  ${}^{1}J_{C,F}$  = 252.2 Hz, Table S3) on completion of the reaction. The  $d \to d$  transition shifts from 695 nm  $[\mathbf{C}]^+$  to a value found for other examples of the orange-red nitroso complexes  $[3]^+$  ( $\lambda_{d \to d}$  < 470 nm) as well as  $[Fe(dppe)Cp^*]^{+31}$ and  $[Fe(CO)_2(O_2NPh)Cp]^+$  ( $\lambda \approx 430 \text{ nm}$ ).<sup>28,34</sup> With these various pieces of evidence in hand, a mechanism for the formation of  $[3]^+$  and  $[5]^+$  may be proposed (Scheme 4). Precursor 1 is activated by chloride abstraction with the

formation of low-valent  $[A]^+$ , which is readily coordinated by an oxygen atom of the nitroarene substrate.

Although an excess of 2 helps to capture  $[\mathbf{A}]^+$  and shift the equilibrium toward monometallic  $[\mathbf{B}]^+$ , bimetallic  $[\mathbf{C}]^{2+}$  is considered as the key species, due to the maintained symmetry of the  $\nu(NO_2)$  stretching vibrations in the IR spectrum (Figure S14). Bimetallic  $[\mathbf{C}]^{2+}$  undergoes a homolytic N...O bond cleavage and dissociates into nitroso complex  $[3\mathbf{r}]^+$ , with formal  $N^{III} \rightarrow N^I$  reduction and formation of the oxoiron species  $[\mathbf{D}]^+$ , containing a {Fe<sup>IV</sup>=O} entity commonly found in oxoiron<sup>IV</sup> heme complexes.<sup>36,36</sup> This mechanism is supported by recent computational studies, suggesting that oxygen can be removed from the N<sup>+</sup>-O<sup>-</sup> entity in pyridine *N*-oxides by iron half-sandwich complexes [Fe<sup>II</sup>(O  $\leftarrow$ NC<sub>5</sub>H<sub>5</sub>)Ph-(L)Cp<sup>\*</sup>] (L = CO, Cl, NMe<sub>2</sub>, etc.).<sup>37</sup>

The computational model indicates that the N-O bond is cleaved, forming a  $Fe^{IV}=O$  or  $Fe^{III}-\dot{O}^-$  intermediate with concomitant release of pyridine. The abstracted oxygen is subsequently inserted into the Fe-Ph bond, forming the phenolate ligand. In the case of the reactions described here, a similar process would allow the N-O cleavage product derived from  $[C]^{2+}$  to be captured as the nitroso complex  $[3]^+$ , together with the formation of the  $Fe^{IV} = O$  species  $[D]^+$ . An internal C,H activation process of  $[D]^+$  gives  $[5]^+$ , whereby one of the adjacent phenyl groups of the dppe ligand is oxidized at its ortho position. This process requires a reaction temperature of 60 °C and does not occur under ambient conditions. It also competes with a decomposition process of [D]<sup>+</sup>, resulting in small amounts of [FcH]<sup>+</sup> (Supporting Information) and insoluble material remaining on the top of a column. The hydrogen radical formed during this internal oxidation process is most probably consumed by one of the formed byproducts.

## CONCLUSION

Activation of the iron half-sandwich complex [FeCl(dppe)Cp] (1) by chloride abstraction with Na[BAr<sup> $X_4$ </sup>] in toluene permits reactions with a range of common nitro aromatics to give the cationic iron nitroso complexes  $[Fe{N(O)-C_6H_4R}(dppe)-$ Cp]<sup>+</sup> ([3]<sup>+</sup>). Complexes [3]<sup>+</sup> are obtained in up to quantitative yields, feature a wide range of substituents, are stable under ambient conditions, and can be purified using column chromatography. Structural characterization via X-ray diffraction for R = p-Br, p-NO<sub>2</sub>, p-NMe<sub>2</sub>, p-(C $\equiv$ CPh) proved their constitution. The Fe-nitroso interaction involves a high degree of  $Fe \rightarrow N(O)$  back-bonding, evinced by a range of spectroscopic and structural data. Terminal alkynyl and cyano functionalities are superior binding entities in comparison to the  $NO_2 \rightarrow NO$  reduction process. The reaction is most probably initiated by coordination of two {Fe(dppe)Cp}<sup>+</sup> fragments toward the nitro functionality, resulting in the formation of the blue, bimetallic [{Fe(dppe)Cp}<sub>2</sub>{ $\mu,\kappa^2O,O'$ - $O_2NAr$ ]<sup>2+</sup> species in solution. This air- and moisture-sensitive compound could be spectroscopically identified in the case of reactions of 1 and  $Na[BAr_{4}^{F}]$  with 2-fluoronitrobenzene. The bimetallic species undergoes a N-O bond cleavage, resulting in nitroso complexes  $[3]^+$  and a Fe<sup>IV</sup>=O/Fe<sup>III</sup>-O<sup>-</sup> species. This process is similar to heme-based degradations of RNO<sub>2</sub> poisonings, where the respective nitroso complexes terminate the process, due to their superior stability. The reaction reported herein mimics this process using the iron source as both the nitrosoaryl and oxygen scavenger. The Fe<sup>IV</sup>=O species undergoes an internal rearrangement via C<sub>1</sub>H activation

of a dppe-related phenyl group, resulting in  $[Fe^{III}(\kappa^3 O, P, P' - P(2 - O - C_6H_4)(Ph) - C_2H_4 - PPh_2)Cp]^+$ , proven by single-crystal X-ray diffraction. The results could explain difficulties in the conversion of nitroarenes in iron catalysis.

## ASSOCIATED CONTENT

### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00042.

Experimental prodecures and spectroscopic data of the new compounds described herein (PDF)

#### Accession Codes

CCDC 2005644–2005654 and 2014131–2014133 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data\_request/cif, or by emailing data\_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

M.K. gratefully acknowledges support from the Forrest Research Foundation for a Forrest Research Fellowship. This work was further supported in part by the University of Western Australia Research Priorities Fund. The authors gratefully acknowledge the facilities and the scientific and technical assistance of Microscopy Australian at the Centre for Microscopy, Characterisation & Analysis (CMCA) and The University of Western Australia, a facility funded by the University, State and Commonwealth Governments. S.A.M. gratefully acknowledges the Australian Research Council (ARC) for a Future Fellowship (FT200100243). We gratefully acknowledge helpful discussions with Professor A. S. Weller and advice concerning the synthesis of  $Na[BAr^{Cl}_{4}]$ .

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