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Ferrocene-bis(phosphinimine) Nickel(II) and Palladium(II) Alkyl Complexes: Influence of the Fe-M (M = Ni, Pd) Interaction on Redox Activity and Olefin Coordination

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Supporting Information Placeholder

ABSTRACT: The synthesis of several novel nickel(II) and palladium(II) ferrocene-bis(phosphinimine) alkyl complexes containing iron-nickel and iron-palladium interactions is reported. The redox behavior of all complexes was evaluated electrochemically and chemically; in addition, reactions with weak nucleophiles, such as acetonitrile and olefins, were also investigated. DFT calculations were performed to understand the electronic structure of the alkyl metal complexes.

INTRODUCTION

Catalytic processes that can be switched by an external stimulus can offer an additional, ‘bio-like’ control of chemical transformations. Early examples showed that switchable catalysts could be used to speed up or slow down the rate of a reaction according to the presence of a specific trigger, which could be either a physical or a chemical stimulus, or to change the stereoelectronic outcome of a reaction (on/off switches). In recent years, however, more advanced tasks have been accomplished, such as turning ‘on’ and ‘off’ different forms of the same pre-catalyst in order to promote complementary reactions that take place from a mixture of different building blocks. Redox switchable catalysis uses redox reagents (chemical triggers) to turn on and off reactions. The earlier works of Wrighton et al., Long et al., and Plenio et al. illustrated the influence of the redox states of ferrocenyl units, in supporting ligands, on catalysis. Our initial work focused extensively on utilizing ferrocene-based ligands for the redox control of ring-opening polymerizations (ROP) of cyclic esters. Starting with indium, yttrium, and cerium phosphen (phosphen = 1,1’-di(2-tert-butyl-6-diphenylphosphiniminophenoxy)ferrocene) complexes, an on/off activity for the polymerization of L-lactide was observed based on the oxidation state of the iron center. These early efforts culminated in the discovery of a system that displayed redox-controlled polymerization of several cyclic monomers: first in the case of L-lactide/c-caprolactone with a titanium thiolfan complex, (thiolfan*)Ti(OiPr)2 (thiolfan* = 1,1’-di(2,4-di-tert-butyl-6-thiophenoxy)ferrocene), and then for L-lactide/cyclohexene oxide utilizing a zirconium salfan complex, (salfan)Zr(OBu)2 (salfan = 1,1’-di(2-tert-butyl-6-N-methylmethylenephenoxy)ferrocene). Recently, there have been efforts by our group and others to expand the application of redox-controlled systems beyond ROP. Such examples include ferrocene-based ligands capable of modulating monomer selectivity in palladium systems for olefin polymerization and Buchwald-Hartwig cross-coupling reactions, utilization of cobalt complexes for olefin hydrolalkoxylation, and of gold mesoionic carbenes for heterocycles synthesis. However, in all cases of redox-controlled catalysis, the ferrocene unit is distant from the primary metal center and no direct interaction exists between iron in ferrocene and the metal involved in a substrate transformation.

Various bidentate ferrocene derived ligands reported in the literature containing phosphorus, sulfur, and nitrogen-based substituents are known to promote direct iron-metal interactions. However, the use of these complexes in redox-switchable catalysis has not been investigated. For example, ferrocene-bis(phosphinimines) have been used as supporting ligands, but not in catalytic examples. Based on our interest in redox-switchable catalysis utilizing ferrocene derivatives, we decided to prepare ferrocene-bis(phosphinimine) nickel and palladium alkyl complexes containing iron-nickel and iron-palladium interactions and investigate their efficacy for redox-switchable olefin polymerization.

RESULTS AND DISCUSSION

Preparation and characterization of the ferrocene-bis(phosphinimine) metal complexes. Initial attempts to carry out a direct ligand substitution using fc(NPPh3)2 to prepare the halide-alkyl complexes of nickel and palladium were unsuccessful. However, the addition of NaBPh4 to (PPh3)2NiCl(Ph) or (COD)PdCl(Me) (COD = 1,5-cyclooctadiene) in the presence of fc(NPPh3)2 resulted in the isolation of fc(NPPh3)2NiPh[BPh4] and fc(NPPh3)2PdMe[BPh4] as red crystals in an 82.4% yield and 67.0% yield, respectively.
Scheme 1. The preparation of nickel and palladium ferrocene-bis(triphenylphosphinimine) complexes.

Figure 1. Molecular structure drawing of [fc(NPPh3)2NiPh][BPh4] with thermal ellipsoids at 50% probability; hydrogen, solvent, and borate atoms are omitted for clarity. Selected distances (Å) and angles (°): N(1)-P(1), 1.613(2); N(2)-P(2), 1.613(2); N(1)-Ni(1), 1.898(2); N(2)-Ni(1), 1.895(2); C(11)-Ni(1), 2.051(2); Fe(1)-Ni(1), 2.8244(6); C(11)-Ni(1)-N(1), 102.4(1); C(11)-Ni(1)-N(2), 97.2(1); N(1)-Ni(1)-Fe(1), 80.94(6); N(2)-Ni(1)-Fe(1), 79.52(6).

The iron-nickel distance of 2.8244(6) Å is similar to that of a related complex [fc(S2)Ni(PMe2Ph)] (2.886(1) Å) and longer than those observed for the dicaticonic species [fc(NIm)2Ni(NCMe)][BF4]2 (2.6297(4) Å), [fc(NIm)2Ni(PPh3)][BF4]2 (2.6447(3) Å), and [fc(NPPh3)2NiCl][Cl] (2.67 Å) and [fc(NPPh3)2Ni][BPh4] (2.67 Å). The 1H NMR spectrum of [fc(NPPh3)2NiPh][BPh4] is consistent with the presence in solution of a diamagnetic species and both the nickel and palladium complexes display a wide separation between the Cp signals (0.97 ppm and 1.46 ppm, respectively), consistent with the presence of an Fe-M (M = Ni, Pd) interaction. In the 31P NMR spectra, the chemical shifts of 37.5 ppm (nickel) and 30.2 ppm (palladium) are downfield compared to that of fc(NPPh3)2 (27.2 ppm). The presence of the borate counter ion was confirmed by singlets at -5.7 ppm and -5.9 ppm for the nickel and palladium complexes, respectively, in the corresponding 11B NMR spectra.

Figure 2. Molecular structure drawing of [fc(NPPh3)2PdMe][BPh4] with thermal ellipsoids at 50% probability; hydrogen, solvent, and borate atoms are omitted for clarity. Selected distances (Å) and angles (°): N(1)-P(1), 1.613(2); N(2)-P(2), 1.613(2); N(1)-Ni(1), 1.898(2); N(2)-Ni(1), 1.895(2); C(11)-Ni(1), 1.891(3); Fe(1)-Ni(1), 2.8244(6); C(11)-Ni(1)-N(1), 102.4(1); C(11)-Ni(1)-N(2), 97.2(1); N(1)-Ni(1)-Fe(1), 80.94(6); N(2)-Ni(1)-Fe(1), 79.52(6).

Electrochemical studies performed on [fc(NPPh3)2NiPh][BPh4] displayed a complicated and uninformative redox behavior (Figure S40). Attempts to perform a chemical oxidation using acetyl ferrocenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ([AcFc][BArF], Scheme 2 and Figure S26) or AgBF4 (Figure S27) and a reduction using cobaltocene (Figure S24) on an NMR reaction scale did not result in the formation of any new species. Utilizing KC8 as a reducing agent resulted only in the formation of nickel black and liberation of fc(NPPh3)2 (Scheme 2, Figure S25). On the other hand, electrochemical studies performed on [fc(NPPh3)2PdMe][BPh4] (Figure S41) displayed several quasi-reversible redox processes in the range of 0 – 1.25 V (vs. Fc/Fc+) suggesting that a more potent oxidant than a ferrocenium salt may be used. Similarly to the nickel case, utilizing [16Fe][BAR5] as an oxidant led to the formation of a new species.
formation of several minor species, with the starting material remaining the predominant species (Scheme 2, Figure S28). However, in the presence of excess AgBF₄, the formation of a single species was observed in the ³¹P NMR spectrum (Figure S37). A closer look at the in situ generated complex via ¹H, ¹¹B, and ¹⁹F NMR spectroscopies (Figures S36 and S38-39) revealed the loss of the methyl group and the presence of tetrafluoroborate as the predominant counter ion in solution. The existence of palladium-fluorine interactions in the newly formed palladium complex, in the absence of a coordinating solvent, can be postulated based on the broad signals observed in the ¹⁹F NMR spectrum. Scaling up the reaction and the addition of THF resulted in the isolation of [fc(NPPh₃)₂Pd(THF)][BF₄]₂ (Scheme 2) as dark golden plates in a 73.2% yield. The results of an X-ray diffraction study are displayed in Figure 3 along with selected distances and angles. The coordination environment around the palladium center is a distorted square planar geometry (τ = 0.14). The palladium-iron distance of 2.6493(8) Å is significantly shorter than in [fc(NPPh₃)₂PdMe][BPh₄] and is now comparable with those observed for [fc(Nlm)₃Pd(NCMe)][BF₄]₂ (2.6297(4) Å), [fc(Nlm)₃Pd[PPPh₃]][BF₄]₂ (2.6447(3) Å),⁴⁴ and [fc(NPPh₃)₂Pd(Cl)][Cl] (2.67 Å).⁴³ In the ¹H NMR spectrum, the separation between the Cp signals (1.76 ppm) is slightly larger (1.46 ppm) than for the parent complex, [fc(NPPh₃)₂PdMe][BPh₄]. In the ³¹P NMR spectrum, the chemical shift of 37.4 ppm is downfield from that of [fc(NPPh₃)₂PdMe][BPh₄] (30.2 ppm). The presence of the BF₄ ions was confirmed by ¹¹B NMR spectroscopy showing a singlet at -0.4 ppm and ¹⁹F NMR spectroscopy showing two singlets at -152.0 and -152.1 ppm. The presence of two signals in the ¹⁹F NMR spectrum is due to two naturally occurring boron isotopes, ¹¹B and ¹⁰B, both of which are NMR active.

Figure 3. Molecular structure drawing of [fc(NPPh₃)₂Pd(THF)][BF₄]₂ with thermal ellipsoids at 50% probability; hydrogen, solvent, and borate atoms are omitted for clarity. Selected distances (Å) and angles (°): N(1)-P(1), 1.618(4); N(2)-P(2), 1.613(4); N(1)-Pd(1), 2.040(4); N(2)-Pd(1), 2.042(4); O(1)-Pd(1), 2.142(3); Fe(1)-Pd(1), 2.6493(8); O(1)-Pd(1)-N(1), 99.9(1); O(1)-Pd(1)-N(2), 97.7(1); N(1)-Pd(1)-Fe(1), 80.9(1); N(2)-Pd(1)-Fe(1), 81.5(1).

Next, we looked at the strength of the Fe-M (M = Ni, Pd) interaction. Previous reports by Cabrera et al.⁴¹ and Jess et al.⁴⁴ showed that the Fe-M interactions in similar complexes are weak enough that a small molecule, such as acetonitrile, can disrupt them. The resulting acetonitrile adducts, in the case of palladium complexes, are non-symmetrical species that can be readily detected by heteronuclear NMR spectroscopy. Consequently, solutions of [fc(NPPh₃)₂NiPh][BPh₄] and [fc(NPPh₃)₂PdMe][BPh₄] in a mixture of acetonitrile and methylene chloride (1:1 vol %) both display singlets with no apparent shift, suggesting that the acetonitrile-palladium and acetonitrile-nickel interactions are not sufficient enough to overcome the metal-metal interactions in these complexes.

Due to the lack of redox activity in [fc(NPPh₃)₂NiPh][BPh₄], we did not investigate its reactivity with olefins. On the other hand, although [fc(NPPh₃)₂PdMe][BPh₄] did not show a reversible redox process, we wanted to determine whether the compound would display the same redox behavior during a polymerization process. However, we did not observe any polymerization activity at ambient temperature in the reactions with ca. 100 equiv. of norbornene, styrene, 1-hexene, or ethylene (1.0 atm) in CD₂Cl₂, suggesting that the palladium-olefin interactions are also too weak to overcome the iron-palladium interaction. Elevating the reaction temperature resulted in the rapid formation of palladium black and no additional reactivity.
The lack of activity of [fc(NPPh3)2PdMe][BPh4] toward olefin polymerization prompted an investigation into alternative phosphinimine ligands. It is possible that a more electron rich derivative, such as the analogous tricyclohexylphosphinimine, would yield a palladium complex with a weaker Fe-Pd interaction.\textsuperscript{41} However, we could not prepare [fc(NPCy3)2PdMe][BPh4] (Scheme S1) although we used various methods, possibly due to the large steric bulk of the supporting ligand disfavoring the formation of a square planar fc(NPCy3)2PdCl(Me) intermediate. Alternatively, we prepared a new ferrocene-bis(phosphinimine) derivative, fc(PEt3)2 (Scheme 3), combining a more electron rich phosphine and a reduced steric environment compared with the fc(NPPh3)2 analogue. The reduction of the steric environment manifests itself in the isolation of a stable halide-alkyl complex, fc(PEt3)2PdCl(Me) (Scheme 3) that was not achieved either with fc(NPPh3)2 or fc(NPCy3)2. The lack of symmetry in [fc(NPCy3)2PdMe][BPh4] (Scheme S1) although we used various methods, possibly due to the large steric bulk of the supporting ligand disfavoring the formation of a square planar fc(NPCy3)2PdCl(Me) intermediate. Alternatively, we prepared a new ferrocene-bis(phosphinimine) derivative, fc(PEt3)2 (Scheme 3), combining a more electron rich phosphine and a reduced steric environment compared with the fc(NPPh3)2 analogue. The reduction of the steric environment manifests itself in the isolation of a stable halide-alkyl complex, fc(PEt3)2PdCl(Me) (Scheme 3) that was not achieved either with fc(NPPh3)2 or fc(NPCy3)2. The lack of symmetry in fc(NPCy3)2PdCl(Me) is clearly observed by a multitude of signals, specifically, the presence of eight separate signals (3.70 – 4.30 ppm) in the 31P NMR spectrum. Furthermore, we could not prepare [fc(NPCy3)2PdMe][BPh4] (Scheme S1) although we used various methods, possibly due to the large steric bulk of the supporting ligand disfavoring the formation of a square planar fc(NPCy3)2PdCl(Me) intermediate. Alternatively, we prepared a new ferrocene-bis(phosphinimine) derivative, fc(PEt3)2 (Scheme 3), combining a more electron rich phosphine and a reduced steric environment compared with the fc(NPPh3)2 analogue. The reduction of the steric environment manifests itself in the isolation of a stable halide-alkyl complex, fc(PEt3)2PdCl(Me) (Scheme 3) that was not achieved either with fc(NPPh3)2 or fc(NPCy3)2. The lack of symmetry in fc(NPCy3)2PdCl(Me) is clearly observed by a multitude of signals, specifically, the presence of eight separate signals (3.70 – 5.56 ppm) for the Cp protons in the 1H NMR spectrum and two singlets (43.4 and 45.1 ppm) in the 31P NMR spectrum.

Chloride abstraction from fc(PET3)2PdCl(Me) was accomplished with NaBPh4 affording [fc(PET3)2PdMe][BPh4] (Scheme 3) as an orange crystalline material in a 79.3% yield. The solid-state molecular structure of [fc(PET3)2PdMe][BPh4] (Figure 4) was determined using single-crystal X-ray diffraction. The coordination environment around the palladium center is in a slightly distorted square planar geometry with a τ value of 0.20. The iron-palladium distance of 2.7806(5) Å is similar to that of [fc(NPPh3)2PdMe][BPh4] (2.7957(5) Å). The 1H NMR spectrum of [fc(PET3)2PdMe][BPh4] shows a wide separation of 1.66 ppm between the signals of the Cp protons. A downfield shift in the resonance signal of [fc(NPET3)2PdMe][BPh4] (57.3 ppm) compared to both fc(PET3)2 (28.9 ppm) and fc(PET3)2PdCl(Me) (43.4 and 45.1 ppm) was observed in the 31P NMR spectra. The BPh4 ion appears at -5.7 ppm in the 11B NMR spectrum, similar to the fc(NPPh3)2 nickel and palladium analogues.

**Figure 4.** Molecular structure drawing of [fc(NPET3)2PdMe][BPh4] displayed irreversible redox events similar to those for [fc(NPPh3)2PdMe][BPh4] (Figure S43). Attempts to perform a chemical oxidation using excess AgBF4 only resulted in a partial counter ion exchange while a new palladium species was not observed. The addition of acetonitrile to a methylene chloride solution of [fc(NPET3)2PdMe][BPh4] yielded the same results as were observed for [fc(NPPh3)2NiPh][BPh4] and [fc(NPPh3)2PdMe][BPh4]. No change in the chemical shift or formation of a non-symmetrical species was observed in the 31P NMR spectrum. Furthermore, the species is thermally sensitive and gradually decomposes at ambient temperature to form a new major species (Figures S33-S34). A loss of the methyl group and the widening in the Cp proton separation was observed in the 1H NMR spectrum as well as a further downfield shift of the signal in the 31P NMR spectrum (Figures S34), reminiscent of the formation of [fc(NPET3)2Pd(THF)][BF4] from [fc(NPET3)2PdMe][BPh4]. Decomposition was also clearly observed in the presence of styrene while no olefin-palladium interaction was observed at ambient temperature (Figure S35). Increasing the temperature only accelerated the rate of decomposition of the palladium-methyl species.

The lack of reactivity toward nucleophiles is not surprising when comparing the structural parameters of [fc(NPPh3)2PdMe][BPh4] and [fc(PET3)2PdMe][BPh4]. Although PET3 is a more electron rich phosphine than PPh3, there are no significant observable differences in various distances or the geometries around palladium (Table 1). Therefore, in these two examples, a change in the phosphine substituent did not heavily impact the electronic properties of the resulting ferrocene-phosphinimine palladium complex. However, a decrease in the steric bulk of the phosphinimine ligand, upon a transition from a phenyl to an ethyl group, may explain the decrease in the
thermal stability of [fc(NPPh₃)₂PdMe][BPh₄] and the observed loss of the methyl ligand.

Table 1. Summary of structural parameters and NMR spectroscopic data for nickel and palladium complexes.

<table>
<thead>
<tr>
<th></th>
<th>[fc(NPPh₃)₂NiPh]⁺</th>
<th>[fc(NPPh₃)₂PdMe]⁺</th>
<th>[fc(NPPh₃)₂Pd(THF)]³⁺</th>
<th>[fc(NPEt₃)₂PdMe]⁺</th>
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<tr>
<td>Fe-M (Å)</td>
<td>2.82(4)</td>
<td>2.79(5)</td>
<td>2.65(9)</td>
<td>2.78(6)</td>
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<tr>
<td>M-C (Å)</td>
<td>1.89(1)</td>
<td>2.05(2)</td>
<td>-</td>
<td>2.06(2)</td>
</tr>
<tr>
<td>M-N (Å)</td>
<td>1.89(2), 1.98(2)</td>
<td>2.03(1), 2.07(1)</td>
<td>2.04(4), 2.04(2)</td>
<td>2.04(2), 2.05(2)</td>
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<tr>
<td>N-P (Å)</td>
<td>1.61(2), 1.61(2)</td>
<td>1.66(1), 1.62(1)</td>
<td>1.61(4), 1.61(4)</td>
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<tr>
<td>τ</td>
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<td>0.16</td>
<td>0.14</td>
<td>0.20</td>
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<td>^1H NMR Cp-H (ppm)</td>
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<td>3.63, 5.39</td>
<td>2.97, 4.63</td>
</tr>
<tr>
<td>^11B NMR (ppm)</td>
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<td>-5.9</td>
<td>-0.4</td>
<td>-5.7</td>
</tr>
<tr>
<td>^31P NMR (ppm)</td>
<td>37.5</td>
<td>30.2</td>
<td>37.4</td>
<td>57.3</td>
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DFT calculations. The extent of the Fe-M interaction can also be determined from DFT calculations. Geometry optimizations for [fc(NPPh₃)₂NiPh]⁺, [fc(NPPh₃)₂PdMe]⁺, and [fc(NPEt₃)₂PdMe]⁺ were performed for the present study employing ADF2013.01, 57-59 using the PW91 functional60 and no frozen electron cores. Although the counterion was omitted, all the atoms of the cations were included. The optimized Fe-M distances (Table 2) are close to each other and to the values obtained experimentally (Table S1). The calculated Mayer bond orders61-62 are around 0.2 and are similar to the values obtained for other palladium complexes that show Fe-Pd interactions.31-32, 35, 45

Each of the analyzed compounds showed several molecular orbitals that indicate bonding interactions between iron and nickel or palladium (Figure 5 for selected orbitals and see the supporting information for more MOs for all three complexes, Figures S48, S50, and S52). Some of these orbitals are lying relatively deep, especially for the palladium complexes, for example, HOMO-16 and HOMO-25 for [fc(NPPh₃)₂PdMe]⁺ and HOMO-13 for [fc(NPEt₃)₂PdMe]⁺. Interestingly, the palladium complexes also contain π type iron-metal interactions, however, both the bonding and antibonding components are occupied (Figures S50 and S52).

Table 2. Computational parameters for [fc(NPPh₃)₂NiPh]⁺, [fc(NPPh₃)₂PdMe]⁺, and [fc(NPEt₃)₂PdMe]⁺.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Pd (PPh₃)</th>
<th>Pd (PEt₃)</th>
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<tr>
<td>Fe-M (Å)</td>
<td>2.81</td>
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<td>2.84</td>
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<td>Fe-M Mayer Bond Order</td>
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<td>0.27</td>
<td>0.27</td>
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<tr>
<td>Mulliken Charges</td>
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<tr>
<td>Fe</td>
<td>-0.15</td>
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<tr>
<td>M</td>
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<tr>
<td>M</td>
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<tr>
<td>Wiberg bond index</td>
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<td>0.10</td>
</tr>
<tr>
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<tr>
<td>Fe</td>
<td>0.14</td>
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### Conclusions
The preparation of ferrocene-bis(phosphinimine) nickel and palladium alkyl complexes, via halide abstraction, was described. The ferrocene ligands are bound in a $\kappa^3$ fashion featuring iron-nickel and iron-palladium interactions. Electrochemically, only irreversible redox processes were observed for the palladium species. Chemically, [fc(NPPh$_3$)$_2$NiPh][BPh$_4$] and [fc(NPEt$_3$)$_2$PdMe][BPh$_4$] were redox inactive, while [fc(NPPh$_3$)$_2$PdMe][BPh$_4$] underwent an irreversible oxidation resulting in the loss of the alkyl group. Attempts at disrupting the iron-palladium interactions using weak nucleophiles, such as acetonitrile and olefins, were unsuccessful. Although DFT calculations indicate that these interactions are relatively weak, they are important to the overall electronic stabilization of each metal complex, especially in the case of palladium. Based on the results of this study, the ferrocene-bis(phosphinimine) nickel and palladium alkyl complexes discussed herein are not viable for applications in redox-switchable olefin polymerization.

### EXPERIMENTAL SECTION

**General considerations.** All reactions were performed using standard Schlenk techniques or in an MBraun drybox (<1 ppm O$_2$/H$_2$O) unless noted otherwise. All glassware, cannulas, and Celite were stored in an oven at $> 425$ K before being brought into the drybox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs$^{68}$ and transferred to the glovebox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. NMR spectra were recorded at ambient temperature on Bruker AV-300, AV-500, and DRX-500 spectrometers unless otherwise noted. Proton and carbon chemical shifts are given relative to residual solvent peaks. Phosphorus, boron, and fluorine chemical shifts are given relative to external standards, H$_3$PO$_4$, Et$_2$O·BF$_3$, and 1% Freon-113 in C$_6$D$_6$, respectively. Compounds (PPh$_3$)$_2$NiClPh,$^{69}$ (COD)PdCl(Me) (COD = 1,5-cyclooctadiene),$^{25}$ fc(NPPh$_3$)$_2$,$^{43}$ fc(NPPh$_3$)$_2$,$^{43}$ fc(NPPh$_3$)$_2$,$^{43}$ fc(NPPh$_3$)$_2$,$^{43}$ fc(NPPh$_3$)$_2$,$^{43}$ fc(NPPh$_3$)$_2$,$^{43}$ fc(NPPh$_3$)$_2$,$^{43}$ fc(NPPh$_3$)$_2$,$^{43}$ fc(NPPh$_3$)$_2$,$^{43}$ and f$^{[66]}$Fc$[^{[66]}$BaF$^{[66]}$ were prepared using literature procedures and, unless otherwise noted, all reagents were acquired from commercial sources and used as received. Elemental analysis of compounds [fc(NPPh$_3$)$_2$NiPh][BPh$_4$], [fc(NPPh$_3$)$_2$PdMe][BPh$_4$], [fc(NPPh$_3$)$_2$PdMe][BPh$_4$], [fc(NPPh$_3$)$_2$PdMe][BPh$_4$], and [fc(NPPh$_3$)$_2$PdMe][BPh$_4$] was performed on an Exeter Analytical, Inc. CE-440 Elemental Analyzer. Elemental analysis of [fc(NPPh$_3$)$_2$Pd(THF)][BPh$_4$], [fc(NPPh$_3$)$_2$PdMe][BPh$_4$], and [fc(NPPh$_3$)$_2$PdCl(Me)] was carried out by Midwest Microlab, LLC, Indianapolis, IN.

**[fc(NPPh$_3$)$_2$NiPh][BPh$_4$].** A solution of fc(NPPh$_3$)$_2$ (316.9 mg, 0.413 mmol) and (PPh$_3$)$_2$NiClPh (261.5 mg, 0.375 mmol) in 10 mL of methylene chloride was added to a suspension of NaBPh$_4$ (128.6 mg, 0.375 mmol) in 5 mL of methylene chloride at 0 °C. The reaction mixture was stirred for 1 h at 0 °C followed by a filtration through a Celite plug. Volatile substances were removed under a reduced pressure and the remaining solids
were washed with diethyl ether (5 × 10 mL). The remaining solids were dissolved in 3 mL of methylene chloride, layered with 9 mL of diethyl ether, and stored for several hours at -35 °C. Decanting of the solution and washing with cold diethyl ether yielded the product as a red crystalline material. Recrystallization from methylene chloride/diethyl ether (1:3 vol %) layering at ambient temperature and washing with diethyl ether yielded analytically pure product (406.1 mg, 82.4%). X-ray quality crystals were obtained from methylene chloride/diethyl ether (1:3 vol %) layering at ambient temperature. Crystals of [fc(NPPh3)2Pd(THF)][BF4]2 always contain 1.5 molecules of methylene chloride per molecule of compound as supported by NMR spectroscopic data.1H NMR (CDCl3, 500 MHz, 298 K): δ (ppm) 1.61 (s, 4H, CH2), 3.53 (s, 4H, OCH2), 3.63 (t, 4H, Cp-H), 5.39 (t, 4H, Cp-H), 7.66 (m, 12H, o-Ph), 7.75 (m, 18H, m-Ph, p-Ph). 13C NMR (CDCl3, 126 MHz, 298 K): δ (ppm) 25.9 (s, CH2), 69.1 (s, OCH2), 73.2 (d, Cp-C), 83.8 (C, Cp-C), 106.9 (d, Cp-C), 123.9 (d, PPh), 130.8 (d, PPh), 133.3 (d, PPh), 135.4 (d, PPh). 31P NMR (CDCl3, 161 MHz, 298 K): δ (ppm) -0.4 (s). 19F NMR spectrum (CD2Cl2, 203 MHz, 298 K) of [fc(NPPh3)2Pd(THF)][BF4]2: δ (ppm) -152.0 (br s), -152.1 (br s). 31P{1H} NMR (CDCl3, 203 MHz, 298 K): δ (ppm) 37.4 (s). Anal. Calcd: [fc(NPPh3)2Pd(THF)]·(BF4)2: C 51.20; H, 3.97; N, 2.28.

**[fc(NPPh3)2PdMe][BF4]2.** A solution of [fc(NPPh3)2] (293.0 mg, 0.398 mmol) and (COD)PdCl(Me) (101.3 mg, 0.382 mmol) in 6 mL of methylene chloride was added to a suspension of NaBPh4 (88.5 mg, 0.258 mmol) in 3 mL of methylene chloride. Decanting of the solution and washing with cold THF yielded the product as an orange crystalline material (319.6 mg, 67.0%). X-ray quality crystals were obtained from methylene chloride/diethyl ether per molecule of compound as supported by NMR data.1H NMR (CDCl3, 500 MHz, 298 K): δ (ppm) -0.13 (s, 4H, CH2), 3.12 (s, 4H, CH2), 4.58 (s, 4H, CH2), 6.86 (t, 4H, B-(p-Ph)), 7.01 (t, 8H, B-(m-Ph), 7.31 (br s, 8H, B-(o-Ph)), 7.73 (m, 12H, P-(m-Ph), 7.67 (t, 6H, B-(p-Ph)), 7.13 (m, 12H, P-(m-Ph)). 13C NMR (CDCl3, 126 MHz, 298 K): δ (ppm) -4.7 (t, PD-CH3), 68.2 (d, C-P), 72.6 (s, C-P), 88.3 (d, C-P), 122.2 (s, B-P), 126.1 (q, BP), 126.9 (d, P-P), 129.5 (d, P-P), 133.8 (d, P-P), 134.0 (d, PD-P), 136.5 (q, BP), 164.6 (q, JCNCA = 49.6 Hz, B-CH3). 11B NMR (CDCl3, 161 MHz, 298 K): δ (ppm) -5.9 (s). 31P{1H} NMR (CDCl3, 203 MHz, 298 K): δ (ppm) 30.2 (s). Anal. Calcd: [fc(NPPh3)2PdMe][BF4]2. (C3H5F3N2O-Pd) C, 72.10; H, 5.57; N, 2.24. Found: C, 72.13; H, 5.61; N, 2.29.

**[fc(NPPh3)2PdCl(Me)][BF4]2.** To a suspension of AgBF4 (54.4 mg, 0.279 mmol) in 2 mL of methylene chloride was added [fc(NPPh3)2PdCl(Me)] (116.3 mg, 0.093 mmol) in 5 mL of methylene chloride at ambient temperature. The reaction solution was stirred for 10 min at ambient temperature before being filtered through a Celite plug. The filtrate was concentrated to 2 mL followed by the addition of a few drop of THF, layering with 2 mL of diethyl ether, and stored overnight at -35 °C. Decanting of the solution and washing with cold diethyl ether yielded the product as dark golden plates (79.9 mg, 73.2%). X-ray quality crystals were obtained from a methylene chloride/THF (1:2 vol %) layering at ambient temperature. Crystals of [fc(NPPh3)2Pd(THF)][BF4]2 always contain 1.5 molecules of methylene chloride per molecule of compound as supported by NMR spectroscopic data.1H NMR (CDCl3, 500 MHz, 298 K): δ (ppm) 1.61 (m, 4H, CH2), 3.53 (m, 4H, OCH2), 3.63 (t, 4H, Cp-H), 5.39 (t, 4H, Cp-H), 7.66 (m, 12H, o-Ph), 7.75 (m, 18H, m-Ph, p-Ph). 13C NMR (CDCl3, 126 MHz, 298 K): δ (ppm) 25.9 (s, CH2), 69.1 (s, OCH2), 73.2 (d, Cp-C), 83.8 (C, Cp-C), 106.9 (d, Cp-C), 123.9 (d, PPh), 130.8 (d, PPh), 133.3 (d, PPh), 135.4 (d, PPh). 31P NMR (CDCl3, 161 MHz, 298 K): δ (ppm) -0.4 (s). 19F NMR spectrum (CD2Cl2, 203 MHz, 298 K) of [fc(NPPh3)2Pd(THF)][BF4]2: δ (ppm) -152.0 (br s), -152.1 (br s). 31P{1H} NMR (CDCl3, 203 MHz, 298 K): δ (ppm) 37.4 (s). Anal. Calcd: [fc(NPPh3)2Pd(THF)]·(BF4)2: C 51.20; H, 3.97; N, 2.28.

**[fc(NPPh3)2PdCl(Me)]**. To (COD)PdCl(Me) (80.2 mg, 0.303 mmol) in 3 mL of methylene chloride was added [fc(NPPh3)2PdCl(Me)] (123.3 mg, 0.275 mmol) in 4 mL of methylene chloride and the reaction mixture was stirred for 1 h at ambient temperature. The reaction mixture was filtered through Celite, volatile substances were removed under a reduced pressure. The remaining orange crystalline solids were dissolved in 2 mL of diethyl ether, layering with 2 mL of hexanes, and stored for 18 h at -35 °C. Decanting of the solution and washing with 2 mL of cold hexanes yielded the product as red crystals (295.1 mg, 90.9%). 1H NMR (CDCl3, 500 MHz, 298 K): δ (ppm) 1.13 (m, 18H, CH2CH2), 1.85 (m, 12H, CH2CH2), 3.66 (t, 4H, Cp-H), 3.74 (s, 4H, CH2CH2), 7.04 (s, 8H, B(3-Ph)), 7.21 (m, 12H, B-(2-Ph)), 7.53 (m, 12H, B-(1-Ph)), 4.99 (m, 2H, OCH2). 13C NMR (CDCl3, 126 MHz, 298 K): δ (ppm) 25.9 (s, CH2), 69.1 (s, OCH2), 73.2 (d, Cp-C), 83.8 (C Cp-C), 106.9 (d, Cp-C), 123.9 (d, PPh), 130.8 (d, PPh), 133.3 (d, PPh), 135.4 (d, PPh). 31P NMR (CDCl3, 161 MHz, 298 K): δ (ppm) -152.0 (br s), -152.1 (br s). 31P{1H} NMR (CDCl3, 203 MHz, 298 K): δ (ppm) 37.4 (s). Anal. Calcd: [fc(NPPh3)2Pd(THF)]·(BF4)2: C 51.20; H, 3.97; N, 2.28. To fc(NPPh3)2PdCl(Me) (156.5 mg, 0.258 mmol) in 8 mL of methylene chloride was added solid NaBPh4 (88.5 mg, 0.258 mmol) and the resulting suspension stirred for 30 min at ambient temperature. The reaction...
mixture was filtered through Celite followed by removal of volatile substances under reduced pressure. The remaining solids were dissolved in 2 mL of methylene chloride and layered with 6 mL of diethyl ether. Orange crystalline material forms after several hours at ambient temperature. Decanting of the solution and washing with diethyl ether yielded the product as an orange crystalline material (181.8 mg, 79.3%). X-ray quality crystals were obtained from methylene chloride/diethyl ether vapor diffusion. Crystals of [(NPEt3)2PdMe][BPh4] always contain a molecule of methylene chloride per molecule of compound as supported by NMR spectroscopic data. 1H NMR (CDCl3, 500 MHz, 298 K): δ (ppm) 0.91 (s, 3H, PD-CH3), 1.09 (m, 18H, (CH2)3), 1.82 (m, 12H, (CH2)6), 2.97 (t, 4H, Cp-H), 4.63 (t, 4H, Cp-H), 6.89 (t, 4H, B-(p-Ph)), 7.04 (t, 8H, B-(m-Ph)), 7.41 (br s, 8H, B-(o-Ph)). 13C NMR (CDCl3, 126 MHz, 298 K): δ (ppm) -11.1 (t, PD-CH3), 6.1 (d, CH2CH3), 18.1 (d, CH2CH3), 67.5 (d, Cp-C), 72.5 (s, Cp-C), 87.6 (d, Cp-C), 121.8 (s, BPH), 125.6 (q, BPh), 136.5 (q, BPH), 164.4 (q, JCH = 49.3 Hz, B-C). 11B NMR (CDCl3, 161 MHz, 298 K): δ (ppm) -5.7 (s). 31P{1H} NMR (CDCl3, 203 MHz, 298 K): δ (ppm) 57.3 (s). Anal. Calcd: C 72.5 (s). 31P{1H} NMR was sealed, taken out of the box and placed in an oil bath. The polymerization activity was monitored by 1H NMR spectroscopy. We thank the NSF, Grant 1362999 and CHE-1048804 for NMR spectroscopy.

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