Supporting Information for

Synthesis and Study of Olefin Metathesis Catalysts Supported by Redox-Switchable Diaminocarbene[3]ferrocenophanes

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Syntheses and Discussion of 19 and 20.

(5)(PCy$_3$)$_2$Cl$_2$Ru=CHPh (19). A 6 mL glass vial equipped with a stir bar was charged with [5H][BF$_4$] (12) (56.1 mg, 0.164 mmol), NaHMDS (30.3 mg, 0.165 mmol) and toluene (4 mL), and then sealed with a Teflon lined cap. The reaction mixture was stirred for 5 min at ambient temperature. Subsequently, (PCy$_3$)$_2$Cl$_2$Ru=CHPh (6) (40.5 mg, 0.0492 mmol) was added and the vial was re-sealed with a Teflon lined cap. The solution was stirred at ambient temperature for 10 min. The resulting brown mixture was then loaded directly onto a chromatography column (media SiO$_2$, eluent 10:1 v/v hexanes/ethyl acetate). The column was washed with the aforementioned solvent ratio until unreacted 6 eluted as a bright purple solution. The column was then washed with ethyl acetate and the product eluted as a lime green solution. Evaporation of the solvent under reduced pressure yielded a lime green solid. A solution of hexanes/ethyl acetate (20:1 v/v, 10 mL) was then added which caused precipitation of a pale green powder which was collected by vacuum filtration to give the desired compound (22.4 mg, 57% yield). The compound was found to decompose in solution over a period of hours at room temperature; thus, NMR spectra were recorded at −80 °C. $^1$H NMR (500 MHz, CD$_2$Cl$_2$, −80 °C): $^1$δ 19.61 (d, 1H, $J = 4.5$), 9.04 (s, 1H), 7.74 (s, 1H), 7.59 (t, 1H, $J = 7.0$), 7.36 (br s, 2H), 4.40 (s, 1H), 4.30 (s, 2H), 4.22–4.16 (m, 5H), 4.09 (s, 3H), 2.73 (s, 3H), 2.08–0.75 (m, 30H). $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$, −80 °C): $^1$δ 299.7, 223.6 (d, $J = 76.6$), 151.2, 130.8, 129.3, 128.7, 128.1, 127.8, 98.3, 97.21, 97.18, 71.7, 71.0, 70.4, 70.3, 66.5, 66.4, 66.3, 65.5, 49.8, 45.5, 31.2 (br), 28.3, 27.1 (br), 26.0. $^{31}$P NMR (200 MHz, CD$_2$Cl$_2$, −80 °C): $^1$δ 35.86. HRMS: [$M^+\text{-Cl}$] Calcd. for C$_{38}$H$_{54}$N$_2$PClFeRu: 762.2106; Found 762.2098. Anal. Calcd (%) for C$_{38}$H$_{53}$Cl$_2$FeN$_2$PRu: C, 57.29; H, 6.71; N, 3.52. Found: C, 57.43; H, 6.78; N, 3.67.

$^1$ For comparison, the corresponding $^1$H NMR (benzylidene) and $^{31}$P NMR signals were recorded at 20.00 ppm (d, $J = 5.10$) and 35.22 ppm, respectively, at room temperature.
(5)(SIMes)Cl$_2$Ru=CHPh (20). A 6 mL glass vial equipped with a stir bar was charged with 12 (43.8 mg, 0.128 mmol), NaHMDS (23.2 mg, 0.127 mmol) and toluene (4 mL), and then sealed with a Teflon lined cap. The reaction mixture was stirred for 5 min at ambient temperature. (SIMes)(pyridine)$_2$Cl$_2$Ru=CHPh (46.5 mg, 0.064 mmol) was added and the vial was re-sealed with a Teflon lined cap. The solution was stirred at ambient temperature for 1 h and then concentrated under reduced pressure to afford a brown solid. The solid was then purified using column chromatography (media SiO$_2$, eluent 3:1 v/v hexanes/ethyl acetate). Removal of the solvent by evaporation under reduced pressure yielded the product as a lime green solid (26.5 mg, 50% yield). $^1$H NMR (600 MHz, CD$_2$Cl$_2$): $\delta$ 19.04 (s, 1H), 7.45 (tt, $J = 7.3, 1.1, 1H$), 7.16 (t, $J = 7.8, 2H$), 7.01 (br s, 2H), 6.94 (br s, 1H), 6.19 (br s, 1H), 4.23–3.74 (br m, 12H), 3.08 (s, 3H), 2.82 (br s, 3H), 2.68 (br s, 3H), 2.45 (br s, 3H), 2.36 (s, 3H), 2.30 (s, 3H), 2.19 (s, 3H), 1.74 (br s, 3H). $^{13}$C NMR (125 MHz, CD$_2$Cl$_2$): $\delta$ 303.4, 226.4, 219.6, 150.1, 138.7, 138.5, 138.3, 137.6, 137.1, 136.9, 136.6, 135.5, 130.2, 129.1, 128.9, 128.7, 128.6, 128.5, 127.5, 126.4, 98.1, 96.8, 71.4, 70.8, 69.7, 66.3, 66.2, 66.1, 64.9, 51.2, 50.5, 49.3, 43.7, 20.65, 20.59, 19.0, 18.8, 18.1, 17.2. HRMS: [M$^+$] Calcd. for C$_{41}$H$_{46}$N$_4$Cl$_2$FeRu: 822.1492; Found: 822.1493. Anal. Calcd (%) for C$_{41}$H$_{46}$N$_4$Cl$_2$FeRu•0.25(C$_6$H$_{14}$): C, 60.47; H, 5.91; N, 6.64. Found: C, 60.69; H, 5.91; N, 6.38.
Scheme S1. Synthesis of Ru complexes containing 5. (i) (a) NaHMDS (1.0 equiv), toluene, ambient temperature, 5 min. (b) (PCy$_3$)$_2$Cl$_2$Ru=CHPh (6) (0.30 equiv), toluene, ambient temperature, 10 min. (ii) (a) NaHMDS (1.0 equiv), toluene, ambient temperature, 5 min. (b) (SIMes)(pyridine)$_2$Cl$_2$Ru=CHPh (0.50 equiv), toluene, ambient temperature, 1 h.

We attempted the synthesis of a complex of the type (FcDAC)(PCy$_3$)$_2$Cl$_2$Ru=CHPh, as the analogous SIMes containing complex 7 is well known to display high catalytic activities in a broad range of olefin metathesis reactions and is moderately stable in solution. As summarized in Scheme S1, treating a toluene solution of 12 with NaHMDS to form FcDAC 5 in situ followed by the addition of 6 afforded the expected complex 19 which was sufficiently stable to be isolated using column chromatography. The diagnostic low field benzylidene signal observed in the $^1$H NMR spectrum of 19 was observed at 19.61 ppm (d, $J = 4.5$) in addition to a salient signal in the $^{31}$P NMR spectrum at 35.86 ppm (CD$_2$Cl$_2$). Although 19 was found to have limited

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stability in solution and decomposed over a period of hours at ambient temperature, even in the absence of O₂ and water, the complex was stable in the solid state when stored at –30 °C.

Phosphine-free Ru complexes containing 5 were also investigated. Complexes of the type (NHC)₂Cl₂Ru=CHPh³ and (NHC)₉(NHC)₈Cl₂Ru=CHPh⁴ often exhibit high catalytic activities at elevated temperatures and are typically stable due to the strong σ-donicity of their NHC ligands. The addition of (SIMes)(pyridine)₂Cl₂Ru=CHPh to a toluene solution of 5 (generated in situ from 12) resulted in the formation of mixed FcDAC-NHC Ru complex 20, which was isolated in 50% yield after purification via column chromatography. To compare the solid-state structure of 20 to other Ru complexes and to determine if any isomerization had occurred during its synthesis or isolation (as was observed for 18; see main text), X-ray quality crystals were grown by slow evaporation of a concentrated hexanes solution of the complex (Figure S1). The Ru–C_carbene bond distances for previously reported bis-carbene Ru complexes span a relatively large range depending on the nature of the carbene ligands (2.052(9)–2.153(9) Å).³⁴/a,c-e,f The Ru–C_FcDAC and Ru–C_SIMes bond distances measured in the solid state structure of 20 (2.117(3) and 2.121(3) Å) were within the expected range and nearly identical to those reported for a mixed ADC–SIMes Ru complex (ADC = N,N’-dimesityl-N,N’-dimethylformamidin-2-ylidene) (Ru–C_ADC 2.112(3) Å; Ru–C_SIMes 2.132(3) Å).⁴c Additionally, the C1–Ru–C3 bond angle measured in the solid state structure of 20 (162.9(1)°) was comparable to that reported for related bis-carbene complexes (159.05(15)–166.9(4)°).³⁴/a,c-e,f

Figure S1. ORTEP diagram of 20 showing ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Key atom distances (Å) and angles (°): Ru–C1, 2.117(3); Ru–C2, 1.846(3); Ru–C3, 2.121(3); C1–Ru–C3, 162.9(1); Cl1–Ru–Cl2, 171.92(2); N1–C1–N2, 120.0(2); N3–C3–N4, 106.7(2).

After the synthesis and characterization of 19 and 20, a preliminary investigation of their catalytic activities was conducted. An exchange experiment was first employed to determine which ligand preferentially dissociated in 20, which can be studied by heating a solution of the complex in the presence of excess PCy₃. Heating a solution of 20 in benzene (15 mg in 0.8 mL of C₆D₆) in the presence of a 10-fold molar excess of PCy₃ at 100 ºC for 3 h resulted in a color change from lime green to brownish-red, which was consistent with the formation of 6 (note: complex 19 is green). ¹H and ³¹P NMR spectroscopic analysis of the crude revealed new signals at δ 19.62 and 30.54 ppm, which were nearly identical to those NMR signals observed for an independent solution of 6 recorded in the same solvent (19.63 and 30.53 ppm). This experiment revealed that the FcDAC ligand dissociates in preference to SIMes. As such, complex 20 would yield the same catalytically-active intermediate as commercially-available catalysts 6 or 7, and so its activity was not further studied, although the electrochemical properties of 20 were still measured (see below). The activity of complex 19 was evaluated in two representative olefin metathesis reactions (see Scheme S2).
Scheme S2. Olefin metathesis reactions studied using 19 as the catalyst. (i) 0.1 mol% [Ru], CD₂Cl₂ or toluene-₆₈, 30 or 80 °C. (ii) 1 mol% [Ru], CD₂Cl₂ or toluene-₆₈, 30 or 80 °C.

Table S1. Summary of catalytic activities displayed by 19 in ROMP and RCM reactions. 

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Solvent</th>
<th>Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>Conversion (%)</th>
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<td>CD₂Cl₂</td>
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<td>1</td>
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</tr>
<tr>
<td>3</td>
<td>COD</td>
<td>toluene-₆₈</td>
<td>80</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>DDM</td>
<td>CD₂Cl₂</td>
<td>30</td>
<td>1</td>
<td>10</td>
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<tr>
<td>5</td>
<td>DDM</td>
<td>CD₂Cl₂</td>
<td>30</td>
<td>24</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>DDM</td>
<td>toluene-₆₈</td>
<td>80</td>
<td>1</td>
<td>37</td>
</tr>
<tr>
<td>7</td>
<td>DDM</td>
<td>toluene-₆₈</td>
<td>80</td>
<td>24</td>
<td>45</td>
</tr>
</tbody>
</table>

* [COD]₀ = 0.5 M; [DDM]₀ = 0.1 M; [19]₀ = 0.1 mol%. Conversions were determined by ¹H NMR spectroscopy. See text for additional details.

Under the standardized conditions reported by Grubbs and co-workers,⁵ 19 showed relatively low catalytic activity in representative ring-opening metathesis polymerization (ROMP) of cis,cis-1,5-cyclooctadiene (COD) and the ring-closing metathesis (RCM) of diethyl diallylmalonate (DDM). Significantly enhanced catalytic activities were observed at elevated temperatures as 19 gave complete conversion of COD to poly(1,4-butadiene) in 30 min at 80 °C. The highest conversion measured using 19 to catalyze the RCM of DDM was 45%.

The electrochemical properties of 19 and 20 were studied by CV (Table S2; Figures S6 and S7, respectively). Complex 19 exhibited two irreversible oxidations at E<sub>pa</sub> = 0.71 and 0.86 V versus

SCE, which indicated that reversible control over catalytic activity would be precluded. Complex 20 exhibited two reversible\(^6\) oxidations that were well-resolved with the first oxidation event occurring at a lower potential \(E_{1/2} = 0.57\) V versus SCE) than that measured for 18 or 19 under otherwise identical conditions. These observations suggested to us that the presence of two strongly donating carbene ligands increased the overall electron density in the complex and stabilized the corresponding oxidation product. Consistent with this trend, the bis-PPh\(_3\) complex 9 (i.e., \((\text{PPh}_3)_2\text{Cl}_2\text{Ru}=(3\text{-phenylindenylid}-1\text{-ene})\)) underwent oxidation at \(E_{1/2} = 0.84\) V versus SCE,\(^7\) which is a potential higher than that measured for complexes containing one or two NHCs.

**Table S2.** Summary of electrochemical properties of complexes 19 and 20.\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_{pa}) or (E_{1/2}) (V)(^b)</th>
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</thead>
<tbody>
<tr>
<td>19</td>
<td>0.71 (ir),(^c) 0.86 (ir)(^c)</td>
</tr>
<tr>
<td>20</td>
<td>0.57 (r),(^d) 0.98 (r)(^d)</td>
</tr>
</tbody>
</table>

\(^a\) Conditions: CH\(_2\)Cl\(_2\) solution containing 1 mM analyte and 0.1 M [Bu\(_4\)N][PF\(_6\)] as supporting electrolyte. Abbreviations; ir = irreversible; r = reversible.\(^b\) Values are reported relative to SCE through the addition of Fc\(^*\) as an internal standard adjusted to –0.057 V.\(^8\)\(^c\) Anodic peak potential \(E_{pa}\).\(^d\) Half wave potential \(E_{1/2}\).

In light of the well-resolved redox-processes observed for 20, subsequent attention was directed toward studying the electrochemical properties of this complex in more detail to discern the Fe and Ru oxidation processes. To do so, we employed UV/vis spectroscopy which is a useful technique for the characterization of the electrochemical properties of compounds

\(^6\) The reversibility of the redox couples was confirmed by a scan rate dependency study; see Figure S9.
\(^7\) See main text and Figure S3.
containing ferrocene derivatives as a diagnostic ferrocenium ligand-to-metal-charge-transfer (LMCT) transitions occur at approximately 620 nm upon oxidation. We selected 2,3-dichloro-5,6-dicyanoquinone (DDQ) \( (E_{1/2} = 0.58 \text{ V versus SCE in CH}_2\text{Cl}_2/[\text{Et}_4\text{N}][\text{ClO}_4]) \) as a one electron oxidant for 20 as numerous reports have characterized analogous oxidation products of Fc and Fc-substituted derivatives. An equimolar solution of 20 and DDQ was studied by UV/vis spectroscopy, which revealed diagnostic absorptions attributed to a DDQ•– species at \( \lambda_{\text{max}} = 586, 542, 455, 430, \) and 346 nm (Figure S2). Collectively, these results suggested to us that DDQ underwent reduction; however, the strong absorbance in the expected region for ferrocenium transitions prevented assignment of the corresponding oxidation process to a Fe versus Ru center. Upon the addition of two equivalents of DDQ, no increase in absorbance attributed to DDQ•– was observed which suggested to us that only oxidation of one metal center had occurred.

![Figure S2. UV/vis absorption spectra of 20 (1.2 × 10⁻⁴ M) treated with DDQ (1.2 × 10⁻⁴ M or 2.4 × 10⁻⁴ M) in CH₂Cl₂.](image)

To identify the metal center undergoing oxidation in the aforementioned process, the EPR spectra for 20 treated with DDQ were recorded. When 20 and DDQ were combined (in a 1:1 molar ratio) in CH$_2$Cl$_2$, the resulting EPR spectrum showed two major features at $g = 4.29$ and 2.01 (Figure S13). Given the high intensity and relative sharpness of the signal at $g = 2.01$, this peak was assigned to an organic-centered radical arising from DDQ•−. The weaker, broad signal observed at $g = 4.29$ was consistent with an Fe$^{III}$-centered radical. The Fe$^{III}$ signal was comparable to a previously reported Ru$^{II}$ complex incorporating a ferrocene-substituted pyridylamine ligand, where one electron oxidation using [Ru(bpy)$_3$]$^{3+}$ resulted in an EPR signal at $g = 4.22$, that was attributed to an Fe based process. These data indicated that the oxidation of the Fe center occurred at a lower energy than that of the Ru center. However, when 20 was oxidized using excess DDQ (four equivalents), in addition to the expected signals at $g = 4.29$ and 2.01 a broad, low intensity signal was observed at $g = 1.96$ (overlapping with the signal at $g = 2.01$) which was consistent with the formation of a Ru$^{III}$ species (Figure S14). As a control experiment, an analogous sample was prepared using 6 (which contains only Ru) and DDQ (Figure S15). One strong signal was observed, attributed to DDQ•−, found at $g = 2.01$, in addition to a broad signal attributed to Ru$^{III}$, occurring at $g = 2.03$ (overlapping with the former). Collectively, these results indicated that the oxidation of the Fe center occurred more readily than the oxidation of the Ru center, although DDQ appeared to oxidize both Fe and Ru in this particular complex when present in large excess relative to 20.

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Cyclic Voltammetry

Figure S3. CV of 9 in CH$_2$Cl$_2$ with 0.1 M [Bu$_4$N][PF$_6$] and Fe* internal standard.

Figure S4. CV of [5H][BF$_4$] (12) in CH$_2$Cl$_2$ with 0.1 M [Bu$_4$N][PF$_6$] and Fe* internal standard.
Figure S5. CV of 13 in CH₂Cl₂ with 0.1 M \([\text{Bu₄N}][\text{PF}_6]\) and Fe⁺ internal standard.

Figure S6. CV of 15 in CH₂Cl₂ with 0.1 M \([\text{Bu₄N}][\text{PF}_6]\) and Fe⁺ internal standard.
**Figure S7.** CV of 19 in CH$_2$Cl$_2$ with 0.1 M [Bu$_4$N][PF$_6$] and Fe* internal standard.

**Figure S8.** CV of 20 in CH$_2$Cl$_2$ with 0.1 M [Bu$_4$N][PF$_6$] and Fe* internal standard.
Figure S9. Scan rate dependency study for complex 20 in CH$_2$Cl$_2$ with 0.1 M [Bu$_4$N][PF$_6$] versus silver wire reference. From inner-most to outer-most CV, scan rate: 10 mVs$^{-1}$, 50 mVs$^{-1}$, 100 mVs$^{-1}$, 500 mVs$^{-1}$, 1000 mVs$^{-1}$, and 2000 mVs$^{-1}$. See Table S3 for a summary of the corresponding $E_{1/2}$ and $\Delta E_p$ data.

Table S3. Summary of electrochemical properties for the scan rate dependency study of 20$^a$

<table>
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<th>$E_{1/2}$ (V) (Fe$^{II/III}$, Ru$^{II/III}$)</th>
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<tr>
<td>10</td>
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</tr>
<tr>
<td>50</td>
<td>0.60, 1.02</td>
</tr>
<tr>
<td>100</td>
<td>0.60, 1.02</td>
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<tr>
<td>500</td>
<td>0.60, 1.02</td>
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<tr>
<td>1000</td>
<td>0.60, 1.02</td>
</tr>
<tr>
<td>2000</td>
<td>0.60, 1.03</td>
</tr>
</tbody>
</table>

$^a$ Conditions: CH$_2$Cl$_2$ as solvent, [20] = 1 mM, 0.1 M [Bu$_4$N][PF$_6$] as electrolyte, versus silver wire.
EPR Spectra

Figure S10. X-band EPR spectrum of 18 (1 mM) treated with DDQ (1 mM) in CH$_2$Cl$_2$ recorded at 110 K. Frequency: 9.438 GHz.

Figure S11. X-band EPR spectrum of 18 (0.67 mM) treated with DDQ (1.33 mM) in CH$_2$Cl$_2$ recorded at 110 K. Frequency: 9.438 GHz.
Figure S12. X-band EPR spectrum of 18 (1 mM) reacted with DDQ (6.6 mM) in toluene recorded at 110 K. Frequency: 9.445 GHz.

Figure S13. X-band EPR spectrum of 20 (1 mM) treated with DDQ (1 mM) in CH₂Cl₂ recorded at 110 K. Frequency: 9.438 GHz.
**Figure S14.** X-band EPR spectrum of 20 (1 mM) treated with DDQ (4 mM) in CH₂Cl₂ recorded at 110 K. Frequency: 9.438 GHz.

**Figure S15.** X-band EPR spectrum of 6 (1 mM) treated with DDQ (1 mM) in CH₂Cl₂ recorded at 110 K. Frequency: 9.439 GHz.
X-Ray Crystallography

**Figure S16.** ORTEP diagram of 12 showing ellipsoids at 50% probability. Hydrogen atoms and BF$_4^-$ counterion have been omitted for clarity. Key atom distances (Å) and angles (°): N1–C1, 1.310(4); N2–C1, 1.314(4); Fe–C1, 3.272; N1–C1–N2, 129.4(3).

**X-Ray Crystallography: Experimental Details.**

The data for 12 and 13 were collected on a Rigaku SCX-Mini diffractometer with a Mercury CCD using a graphite monochromator with MoKa radiation (λ = 0.71073Å) at 223 K using a Rigaku Tech50 low temperature device. The data for 13 and 15 were collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with MoKa radiation (λ = 0.71073Å) at 100 K using a Rigaku XStream low temperature device. The data for 18 were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKa radiation (λ = 0.71073Å) at 153 K using an Oxford Cryostream low temperature device.

Details of crystal data, data collection and structure refinement are summarized in Table S4. Data reduction for 12, 13, 15, and 20 were performed using Rigaku Americas Corporation’s Crystal Clear version 1.40. Data reduction for 18 were performed using DENZO-SMN. For all crystals, the structure was solved by direct methods using SIR97 and refined by full-matrix least-squares on F$^2$ with anisotropic displacement parameters for the non-H atoms using SHELXL-97.

For 12, 13, 15, and 18, the hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). For 18, most hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atom on C1a was observed in a ΔF map and refined with an

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isotropic displacement parameter. The data for 12, 15, and 18 were checked for secondary extinction effects but no correction was necessary. The data for 13 were corrected for secondary extinction taking the form: $F_{\text{corr}} = kF_c/[1 + (1.02(19)\times10^{-7}) \times F_c^2 \times l^3/(\sin^2q)]^{0.25}$ where k is the overall scale factor. The tetrafluoroborate anion for 12 was disordered about two orientations. The disorder was modeled by assigning the variable x to the site occupancy factors for one component of the disorder consisting of atoms, B1, F1, F2, F3 and F4. The variable (1-x) was assigned to the atoms of the alternate component consisting of atoms, B1a, F1a, F2a, F3a and F4a. A common isotropic displacement parameter was refined for the fluorine atoms and a second isotropic displacement parameter was refined for B1 and B1a. While refining x, the geometry of the two anions was restrained to be approximately equal. In this way, the site occupancy factor for atoms, B1, F1, F2, F3 and F4 refined to 60(2)%. The atoms of the anion were refined anisotropically with their displacement parameters restrained to be approximately isotropic. Geometric restraints were applied throughout the refinement process. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).\textsuperscript{17}

Table S4. Summary of Crystal Data, Intensity Collection, & Refinement Parameters for \([5H][BF_4]\) (12), 13, 15, 18, and 20.

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<th>13</th>
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<td>Yellow prisms Slow evap. of hexanes</td>
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<td>26.186(5)</td>
<td>17.782(4)</td>
<td>15.8924(9)</td>
<td>19.3183(12)</td>
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<tr>
<td>α, deg</td>
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<td>90.00</td>
<td>98.77(3)</td>
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<td>β, deg</td>
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<td>94.263(3)</td>
<td>91.41(3)</td>
<td>108.242(2)</td>
<td>112.9070(10)</td>
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<tr>
<td>γ, deg</td>
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<td>108.35(3)</td>
<td>90.00</td>
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<tr>
<td>V, Å(^3)</td>
<td>2788.7(5)</td>
<td>3891.9(12)</td>
<td>1589.63(6)</td>
<td>4363.5(5)</td>
<td>3619.1(4)</td>
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<tr>
<td>T, K</td>
<td>233(2)</td>
<td>233(2)</td>
<td>120(2)</td>
<td>153(2)</td>
<td>100(2)</td>
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<tr>
<td>Z</td>
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<td>D(_{\text{calc}}), Mg/m(^3)</td>
<td>1.629</td>
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<tr>
<td>crystal size (mm)</td>
<td>0.13 x 0.15 x 0.20</td>
<td>0.04 x 0.10 x 0.25</td>
<td>0.04 x 0.08 x 0.14</td>
<td>0.04 x 0.11 x 0.12</td>
<td>0.05 x 0.12 x 0.16</td>
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<tr>
<td>reflections collected</td>
<td>27892</td>
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<td>28399</td>
<td>18025</td>
<td>58124</td>
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<tr>
<td>independent reflections</td>
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<td>4427</td>
<td>7264</td>
<td>9982</td>
<td>8165</td>
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<tr>
<td>R(_1), wR(_2) ({</td>
<td>I</td>
<td>&gt; 2\sigma(I)})(^b)</td>
<td>0.0408, 0.0994</td>
<td>0.0182, 0.0431</td>
<td>0.0348, 0.0841</td>
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<tr>
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<td>1.092</td>
<td>1.023</td>
<td>0.987</td>
<td>1.057</td>
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\(^a\) Vd = vapor diffusion. \(^b\) R\(_1\) = S(|F\(_o\)| - |F\(_c\)|)/S|F\(_o\)|; wR\(_2\) = \(\{\text{Sw}(|F\(_o\)|^2 - |F\(_c\)|^2) / S\text{Sw}(|F\(_o\)|^4)\}^{1/2}\) where w is the weight given each reflection.
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PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 28.8 degrees
Acq. time 0.478 sec
Width 6588.4 Hz
60 repetitions

OBSERVE F15, 282.4142981

DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 minutes

UV61410N
Pulse Sequence: 1Jpul
Solvent: DMSO
Ambient temperature
UNITYplus-300 nmr2
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Pulse Sequence: s2p1
Solvent: cdc13
Temp. 25.0 °C / 298.1 K
File: PROTON_01
INOVA-500 "narrow"

Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
128 repetitions
OBSERVE H1, 399.6757281 MHz
DATA PROCESSING
FT size 32768
Total time 8 min, 44 sec

\[ \text{CH}_3 \]

\[ \text{Fe} \]

\[ \text{CH}_3 \]

\[ \text{C} - [\text{Ir(CO)}_2\text{Cl}] \]
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DOV754NHFeCDACrCO
Archive directory: /home/staff31/vmm/sys/data
Sample directory: DOV754NHFeCDACrCO_20130704_01

Pulse Sequence: 62pul
Solvent: cdc13
Temp. 25.0 C / 298.1 K
File: PROTON_01
INNOVA-500 "nonyred"

Relax. delay 2.000 sec
Pulse 30.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
128 repetitions
OBSERVE HL 399.6757281 MHz
DATA PROCESSING
FT size 32768
Total time 9 min, 44 sec

$\text{Fe} \begin{array}{c} \text{N} \\ \text{CH$_3$} \end{array} \text{C} \begin{array}{c} \text{[Ir(CO)$_2$Cl]} \\ \text{N} \\ \text{CH$_3$} \end{array}$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spectrum.png}
\caption{NMR spectrum of DOV754NHFeCDACrCO.}
\end{figure}
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<th>Sample</th>
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<th>Temperature</th>
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<th>Gain</th>
<th>Field</th>
<th>Sw</th>
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</tr>
</tbody>
</table>

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