Supporting Information for

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

C. Daniel Varnado, Jr., Evelyn L. Rosen, Mary S. Collins, Vincent M. Lynch and Christopher W. Bielawski*

Department of Chemistry & Biochemistry, The University of Texas, Austin, Texas 78712

E-mail: bielawski@cm.utexas.edu

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Syntheses and Discussion of 19 and 20.

(5)(PCy₃)Cl₂Ru=CHPh (19). A 6 mL glass vial equipped with a stir bar was charged with [5H][BF₄] (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, (PCy₃)₂Cl₂Ru=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 SiO₂, eluent 10:1 v/v hexanes/ethyl acetate). The column was washed with the aforementioned solvent ratio until unreacted $\mathbf{6}$ 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. ¹H NMR (500 MHz, CD₂Cl₂, -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, 1H), 2H), 4.22–4.16 (m, 5H), 4.09 (s, 3H), 2.73 (s, 3H), 2.08–0.75 (m, 30H). ¹³C NMR (125 MHz, CD_2Cl_2 , -80 °C): 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. ³¹P NMR (200 MHz, CD₂Cl₂, -80 °C): δ 35.86. HRMS: [M⁺-Cl] Calcd. for C38H54N2PClFeRu: 762.2106; Found 762.2098. Anal. Calcd (%) for C38H53Cl2FeN2PRu: C, 57.29; H, 6.71; N, 3.52. Found: C, 57.43; H, 6.78; N, 3.67.

¹ For comparison, the corresponding ¹H NMR (benzylidene) and ³¹P NMR signals were recorded at 20.00 ppm (d, J = 5.10) and 35.22 ppm, respectively, at room temperature.

(5)(SIMes)Cl₂Ru=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)₂Cl₂Ru=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 SiO₂, 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). ¹H NMR (600 MHz, CD₂Cl₂): δ 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). ¹³C NMR (125 MHz, CD₂Cl₂): δ 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 C₄₁H₄₆N₄Cl₂FeRu: 822.1492; Found: 822.1493. Anal. Calcd (%) for C₄₁H₄₆N₄Cl₂FeRu•0.25(C₆H₁₄): 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) $(PCy_3)_2Cl_2Ru=CHPh$ (6) (0.30 equiv), toluene, ambient temperature, 10 min. (*ii*) (a) NaHMDS (1.0 equiv), toluene, ambient temperature, 5 min. (b) (SIMes)(pyridine)_2Cl_2Ru=CHPh (0.50 equiv), toluene, ambient temperature, 1 h.

We attempted the synthesis of a complex of the type (FcDAC)(PCy₃)Cl₂Ru=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.² 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 ¹H NMR spectrum of **19** was observed at 19.61 ppm (d, J = 4.5) in addition to a salient signal in the ³¹P NMR spectrum at 35.86 ppm (CD₂Cl₂).¹ Although **19** was found to have limited

² (a) M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.*, 1999, 40, 2247–2250; (b) J. P. Morgan, R. H. Grubbs, *Org. Lett.*, 2000, 2, 3153–3155; (c) J. Huang, E. D. Stevens, S. P. Nolan, J. L. Peterson, *J. Am. Chem. Soc.*, 1999, 121, 2674–2678; (d) W. A. Hermann, C. Köcher, *Angew. Chem. Int. Ed. Engl.*, 1997, 36, 2162–2187; (e) A. K. Chatterjee, J. P. Morgan, M. Scholl, R. H. Grubbs, *J. Am. Chem. Soc.*, 2000, 122, 3783–3784; For selected examples with imidazol-2-ylidenes, see: (f) A. Fürstner, O. R. Thiel, L. Ackermann, H. J. Schanz, S. P. Nolan, *J. Org. Chem.*, 2000, 65, 2204–2207; (g) A. Briot, M. Bujard, V. Gouverneur, S. P. Nolan, C. Mioskowski, *Org. Lett.*, 2000, 2, 1517–1519.

stability in solution and decomposed over a period of hours at ambient temperature, even in the absence of O_2 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)_a(NHC)_bCl₂Ru=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).3[,]4^{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).4^c 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 $(159.05(15)-166.9(4)^{\circ}).3^{4a,c-e,f}$

³ (a) T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem., Int. Ed.*, 1998, **37**, 2490–2493 (b) J. C. Conrad, G. P. A. Yap, D. E. Fogg, *Organometallics*, 2003, **22**, 1986–1988; (c) W. Zhang, C. Bai, X. Lu, R. He, *J. Organomet. Chem.*, 2007, **692**, 3563–3567; (d) N. Ledoux, B. Allaert, A. Linden, P. Van Der Voort, F. Verpoort, *Organometallics*, 2007, **26**, 1052–1056.

⁴ (a) T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Wilhelm, M. Scholl, T.-L. Choi, S. Ding, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.*, 2003, **125**, 2546–2558; (b) T. Vorfalt, S. Leuthäusser, H. Plenio, *Angew. Chem., Int. Ed.* 2009, **48**, 5191–5194; (c) E. L. Rosen, D. H. Sung, Z. Chen, V. M. Lynch, C. W. Bielawski, *Organometallics*, 2010, **29**, 250–256; (d) V. Sashuk, L. H. Peeck, H. Plenio, *Chem. Eur. J.*, 2010, **16**, 3983–3993; (e) X. Bantreil, R. A. M. Randall, A. M. Z. Slawin, S. P. Nolan, *Organometallics*, 2010, **29**, 3007–3011; (f) L. H. Peeck, H. Plenio, *Organometallics*, 2010, **29**, 2761–2766.



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); C11–Ru–C12, 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 PCy_3 .^{3d,4c} Heating a solution of **20** in benzene (15 mg in 0.8 mL of C_6D_6) in the presence of a 10-fold molar excess of PCy_3 at 100 °C 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], CD_2Cl_2 or toluene- d_8 , 30 or 80 °C. (*ii*) 1 mol% [Ru], CD_2Cl_2 or toluene- d_8 , 30 or 80 °C.

Table S1. Summary of catalytic activities displayed by 19 in ROMP and RCM reactions. ^a						
Entry	Substrate	Solvent	Temperature (°C)	Reaction Time (h)	Conversion (%)	
1	COD	CD_2Cl_2	30	1	58	
2	COD	CD_2Cl_2	30	24	93	
3	COD	toluene-d ₈	80	0.5	100	
4	DDM	CD_2Cl_2	30	1	10	
5	DDM	CD_2Cl_2	30	24	30	
6	DDM	toluene-d ₈	80	1	37	
7	DDM	toluene-d ₈	80	24	45	

^{*a*} [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 $E_{pa} = 0.71$ and 0.86 V versus

⁵ T. Ritter, A. Hejl, A. G. Wenzel, T. W. Funk, R. H. Grubbs, *Organometallics*, 2006, 25, 5740–5745.

SCE, which indicated that reversible control over catalytic activity would be precluded. Complex **20** exhibited two reversible⁶ 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-PPh₃ complex **9** (i.e., (PPh₃)₂Cl₂Ru=(3-phenylindenylid-1-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.

Compound	$E_{\rm pa}$ or $E_{1/2}$ (V) b
19	$0.71 \text{ (ir)},^{c} 0.86 \text{ (ir)}^{c}$
20	$0.57 (r),^{d} 0.98 (r)^{d}$

Table S2. Summary of electrochemical properties of complexes 19 and 20.^{*a*}

^{*a*} Conditions: CH₂Cl₂ solution containing 1 mM analyte and 0.1 M [Bu₄N][PF₆] 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.

⁸ I. Noviandri, K. N. Brown, D. S. Fleming, P. T. Gulyas, P. A. Lay, A. F. Masters, L. Phillips, *J. Phys. Chem. B*, 1999, **103**, 6713–6722.

containing ferrocene derivatives as a diagnostic ferrocenium ligand-to-metal-charge-transfer (LMCT) transitions occur at approximately 620 nm upon oxidation.⁹ We selected 2,3-dichloro-5,6-dicyanoquinone (DDQ) ($E_{1/2} = 0.58$ V versus SCE in CH₂Cl₂/[Et₄N][ClO₄]) as a one electron oxidant for **20** as numerous reports have characterized analogous oxidation products of Fc and Fc-substituted derivatives.¹⁰ An equimolar solution of **20** and DDQ was studied by UV/vis spectroscopy, which revealed diagnostic absorptions attributed to a DDQ^{•-} species at $\lambda_{max} = 586$, 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.¹¹ 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 $\times 10^{-4}$ M) in CH₂Cl₂.

⁹ (a) A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd edn., Elsevier, Amsterdam, 1984; (b) R. Prins, *J. Chem. Soc.*, *Chem. Commun.*, 1970, 280b–281.

¹⁰ (a) J. S. Miller, P. J. Krusic, D. A. Dixon, W. M. Reif, J. H. Zhang, E. C. Anderson, A. J. Epstein, *J. Am. Chem. Soc.*, 1986, **108**, 4459–4466; (b) V. J. Murphy, D. O'Hare, *Inorg. Chem.*, 1994, **33**, 1833–1841; (c) H. M. A. Salman, M. R. Mahmoud, M. H. M. Abou-El-Wafa, U. M. Rabie, R. H. Crabtree, *Inorg. Chem. Commun.*, 2004, 7, 1209–1212; (d) S. K. Pal, K. Alagesan, A. G. Samuelson, J. Pebler, *J. Organomet. Chem.*, 1999, **575**, 108–118.

 ¹¹ (a) S. Hartmann, R. F. Winter, B. M. Brunner, B. Sarkar, A. Knödler, Hartenbach, I. Eur. J. Inorg. Chem., 2003, 876–891; (b) N. Das, A. M. Arif, P. Stang, *Inorg. Chem.*, 2005, 44, 5798–5804; (c) W. Kaim, T. Sixt, M. Weber, J. Fiedler, J. Organomet. Chem., 2001, 637, 167–171; (d) H. B. Gray, Y. S. Sohn, D. N. Hendrickson, J. Am. Chem. Soc., 1971, 93, 3603–3612.

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 CH₂Cl₂, 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.¹² 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).¹² 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.

¹² T. Kojima, D. Noguchi, T. Nakayama, Y. Inagaki, Y. Shiota, K. Yoshizawa, K. Ohkubo and S. Fukuzumi *Inorg. Chem.*, 2008, **47**, 886–895.

Cyclic Voltammetry



Figure S3. CV of 9 in CH₂Cl₂ with 0.1 M [Bu₄N][PF₆] and Fc* internal standard.



Figure S4. CV of [5H][BF₄] (12) in CH₂Cl₂ with 0.1 M [Bu₄N][PF₆] and Fc* internal standard.



Figure S5. CV of 13 in CH_2Cl_2 with 0.1 M [Bu₄N][PF₆] and Fc* internal standard.



Figure S6. CV of 15 in CH_2Cl_2 with 0.1 M [Bu₄N][PF₆] and Fc^{*} internal standard.



Figure S7. CV of 19 in CH₂Cl₂ with 0.1 M [Bu₄N][PF₆] and Fc* internal standard.



Figure S8. CV of 20 in CH₂Cl₂ with 0.1 M [Bu₄N][PF₆] and Fc* internal standard.



Figure S9. Scan rate dependency study for complex **20** in CH₂Cl₂ with 0.1 M [Bu₄N][PF₆] 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 ΔE_p data.

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

Scan Rate (mVs ⁻¹)	$E_{1/2}$ (V) (Fe ^{11/111} , Ru ^{11/111})
10	0.58, 0.99
50	0.60, 1.02
100	0.60, 1.02
500	0.60, 1.02
1000	0.60, 1.02
2000	0.60, 1.03

^{*a*} Conditions: CH₂Cl₂ as solvent, [**20**] = 1 mM, 0.1 M [Bu₄N][PF₆] as electrolyte, versus silver wire.

EPR Spectra



Figure S10. X-band EPR spectrum of **18** (1 mM) treated with DDQ (1 mM) in CH₂Cl₂ 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_2Cl_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 (l = 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 (l = 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 (l = 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 1.40.¹³ Data reduction for **18** were performed using DENZO-SMN.¹⁴ For all crystals, the structure was solved by direct methods using SIR97¹⁵ and refined by full-matrix least-squares on F² with anisotropic displacement parameters for the non-H atoms using SHELXL-97.¹⁶

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

¹³ CrystalClear 1.40 (2008). Rigaku Americas Corporation, The Woodlands, TX.

¹⁴ DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.

¹⁵ SIR97. (1999). A program for crystal structure solution. A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. J. Spagna, *Appl. Cryst.* **32**, 115–119.

¹⁶ Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

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: $F_{COTT} = kF_C/[1 + (1.02(19)x10^{-7})*F_C^2 1^3/(sin2q)]^{0.25}$ 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).¹⁷

¹⁷ International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

	12	13	15	18	20
CCDC No.	938913	938914	9389145	938916	938917
empirical formula	$C_{13}H_{15}BF_4FeN_2$	C21H26ClFeIrN2	C ₁₅ H ₁₄ ClFeIrN ₂ O ₂	C52H45Cl2FeN2PRu	C41H46Cl2FeN4Ru
formula weight	341.93	589.94	537.78	956.69	822.64
morphology and growth method ^a	Yellow prisms Vd pentane into CH ₂ Cl ₂	Yellow prisms Slow evap. of hexanes	Yellow prisms Vd pentane into chloroform	Orange plates Vd hexanes into benzene	Green plates Slow evap. of hexanes
crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
space group	Pbca	I2/a	P-1	P21/n	P21/n
<i>a</i> , Å	10.1257(10)	22.976(4)	7.8524(16)	16.7743(11)	14.5623(9)
b, Å	13.5984(14)	6.4866(10)	12.170(2)	15.8924(9)	19.3183(12)
<i>c,</i> Å	20.253(2)	26.186(5)	17.782(4)	17.3028(12)	13.9662(8)
α, deg	90.00	90.00	98.77(3)	90.00	90.00
β, deg	90.00	94.263(3)	91.41(3)	108.242(2)	112.9070(10)
γ, deg	90.00	90.00	108.35(3)	90.00	90.00
<i>V</i> , Å ³	2788.7(5)	3891.9(12)	1589.63(6)	4363.5(5)	3619.1(4)
<i>Т</i> , К	233(2)	233(2)	120(2)	153(2)	100(2)
Z	8	8	4	4	4
$D_{\text{calc}}, \text{Mg/m}^3$	1.629	2.014	2.248	1.456	1.510
cryst size (mm)	0.13 x 0.15 x 0.20	0.04 x 0.10 x 0.25	0.04 x 0.08 x 0.14	0.04 x 0.11 x 0.12	0.05 x 0.12 x 0.16
reflections collected	27892	19094	28399	18025	58124
independent reflections	3187	4427	7264	9982	8165
$R_1, wR_2 \{I > 2\sigma(I)\}^b$	0.0408, 0.0994	0.0182, 0.0431	0.0348, 0.0841	0.0573, 0.0794	0.0388, 0.0868
goodness of fit	0.986	1.092	1.023	0.987	1.057

Table S4. Summary of Crystal Data, Intensity Collection, & Refinement Parameters for [5H][BF₄] (12), 13, 15, 18, and 20.

^{*a*} Vd = vapor diffusion. ^{*b*} R₁ = S(|F₀| - F_c|)/S|F₀|}; $wR_2 = {Sw(|F_0|^2 - |F_c|^2)^2/Sw(|F_0|)^4}^{1/2}$ where w is the weight given each reflection.



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DV0703_FcNHMe2_2

Archive directory: /home/staff31/vnmrsys/data Sample directory: DV0703_FcNHMe2_2_20130703_01

Pulse Sequence: s2pul Solvent: c6d6 Temp. 25.0 C / 298.1 K File: PROTON_01 INOVA-500 "mmrfred"

Relax. delay 2.000 sec Pulse 30.0 degrees Acq. time 2.555 sec Width 6410.3 Hz 128 repetitions OBSERVE H1, 399.6757434 MHz DATA PROCESSING FT size 32768 Total time 9 min, 44 sec





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DV0703_FcNHMe2_2

Archive directory: /home/staff31/vnmrsys/data Sample directory: DV0703_FcNHMe2_2_20130703_01

Pulse Sequence: s2pul Solvent: c6d6 Temp. 25.0 C / 298.1 K File: PROTON_01 INOVA-500 "mmrfred"

Relax. delay 2.000 sec Pulse 30.0 degrees Acq. time 2.556 sec Vidth 6410.3 Hz 128 repetitions OBSERVE H1, 399.6757434 MHz DATA PROCESSING FT size 32768 Total time 9 min, 44 sec







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S29



S30

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PULSE SEQUENCE	OBSERVE	F19, 282.4142991	DATA PROCESSING		DV061410H
Relax. delay 2.000 sec	:		Line broadening 1.0 Hz		
Pulse 20.8 degrees			FT size 131072		Pulse Sequence: s2pul
Acq. time 0.978 sec			Total time 3 minutes		Solvent: DMS0
Width 65466.4 Hz					Ambient temperature
58 repetitions					UNITYplus-300 "nmr2"
	:				

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C	2	2
С	3	3



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110 100	9.0	80	70	6.0	50	40		ppm_
PULSE SEQUENCE OBSERVE C13	3, 75.4700206	DATA PROCESSING					DV010210BC	
Relax. delay 2.000 sec DECOUPLE H	1, 300.1409259	Line broadening 1.0 Hz						
Pulse 36.0 degrees Power 40 d	3	FT size 131072					Pulse Sequence: szpi	u 1
Acq. time 1.777 sec continuous	ly on	Total time 78 minutes					Solvent: CDC13	
Width 22637.2 Hz : WALTZ-16 md	odulated						Ambient temperature	
1248 repetitions Single prec	ision data						UNITYplus-300 "nmr2	2"

S36


















- 0 1	r3-	har	comb
- 10 - 1	1.0-	NP1	CONID

exp4 Carbon

SAM	PLE		SPECIAL
date Nov	/ 17 2009	temp	p 27.0
solvent	cd2c12	gaii	n 40
file	exp	Sp1:	n 20
ACQUIS	ITION	hst	0.008
sw	65789.5	pw91	0 7.800
at	2.000	alfe	a 10.000
np	263158		FLAGS
fb	17000	11	n
bs	64	in	n
55	32	dp	v
d1	2.000	hs	nň
nt	15000		PROCESSING
ct	15000	1b	1.00
TRANSM	TTER	fn	not used
tn	C13		DISPLAY
sfra	150.837	SD	-754.2
tof	14738.0	WD	61076.8
towr	58	rf1	11914.2
nw	2.600	rfn	8113.4
DECOUR	PLER	rn.	113.6
dn becood.	н1	16	23.1
dof		. 10	PLOT
dm	~~~~	we.	250
dmm	333		250
down	46	40	106976
dmf	15997	*b	100370
um i	10001		ode nh
		- e i	















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<pre>** *** * 1** * 1** * 000 **** * 2001 **** * 2001 **** * 2002 **** * 2002 **** * 2003 **** * 100 **** * 2003 **** * 100 **** * 2003 **** * 2003 ***** * 2003 **** * 2003 ****</pre>	;	500 MHz nmr0					
expl starl date 389 5 2000 fri 2021 dra 491.88 Acquisition way tri 2.080 dra 10092 tri 2.080 dra 10002 tri 2	•	elr3_me_FcG2 temp = -80c	H ₃ C ^Ń C ^Ń CH ₃				
SAMELE solution P3 of C2 dr M SAR ref 2013 100 804 dor 307 rf 2031 dam 3052 rf 2031 temp - 80.0 rf 2		exp1 s2pul	CI				
		SAMPLE DEC. & VT date Sep 30 2009 dfrq 499.868 solvent cd2C12 dn H1 file exp dpwr 37 ACQUISITION dof 0 sfrq 202.343 dmm W at 2.000 dmf 10582 np fl 10582 sw 40465.4 dres 1.0 fl fl fl fl sw 40465.4 dres 1.0 fl fl fl fl fl 22000 homo n nt fl fl fl sw 40465.4 dres 1.0 fl fl fl fl fl 2000 homo n mt fl	CI PCy3	35.863			
		and a second and a second s	and the second	and a second	؇ _ۿ ؇ۄٳ؊؞؋ۺٷڮٷ؇ٷٷۅۑٷ؞	᠁᠁᠁᠁ᡧᡗ᠃ᢞᠰᢛᡐᡇᡭᡐᢣ᠌	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~

ppm

elr3_meFcSimes

exp1	Proton

SAMPL	SPECIAL				
date Oct	13 2009	tem	D		27.0
solvent	cd2c12	001	'n		30
file	exp	spin	n		20
ACOUISI	TON	hst	-		0.008
SW	16447.4	pw9	0		11.600
at	4.000	alf	i		10.000
np	131580		. FL	AGS	
fb	4000	11			n
bs	32	in			'n
d1	2.000	dp			÷
nt	128	hs			nn
ct	128		PROC	ESST	NG
TRANSMIT	TER	1b	1 1.00	2001	0.10
tn	H1	fn			262144
sfra	599 758	•••	DIS		202244
tof	3868 4	60	010		-299 9
1040	61	a p			200.0
cpwi nu	1 0 2 0	wp eff 1			1956 5
pw DECOUDI	1.330	-6-			1350.5
de DECOUPL	.EK OIO	гтр			100 4
an	613	rp			132.4
001	0	Ip			17.5
dm	nnn		Р	L01	
dmm	°.	wc			250
dpwr	37	sc			0
dmf	35088	vs			311
		th			12
		ai	cdc	nh	















150

100

ppm














S73