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Notes

Reactions of Pyridyl Side-Chain-Functionalized Cyclopentadienes with Metal Carbonyl: Intramolecular C−H Activation of Pyridine

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Summary: Thermal treatment of the pyridyl side-chain-functionalized cyclopentadienes with Fe(CO)$_5$ and Ru$_3$(CO)$_{12}$ gave different intramolecular C−H activated products, in addition to the normal dinuclear metal complexes. Reactions of the dinuclear metal complexes with I$_2$ also gave different metal iodide complexes.

Introduction

The chemistry of cyclopentadienyl metal complexes containing a donor-functionalized side chain has been receiving much attention.[1] For the pyridyl side-chain-functionalized cyclopentadienyl ligands, the nitrogen atom can act as a good two-electron donor site and can coordinate to a variety of metals, and intramolecular coordination to a Lewis acidic metal center or construction of oligonuclear metal complexes should be easily achieved with them.[1a,2] In this contribution we report the reactions of pyridyl side-chain-functionalized cyclopentadienes with Fe(CO)$_5$ and Ru$_3$(CO)$_{12}$, which gave different intramolecular C−H activated products, in addition to the normal bis(cyclopentadienyl) dinuclear metal complexes. The reactions of the dinuclear metal complexes with I$_2$ were also found to give different metal iodide complexes.

Results and Discussion

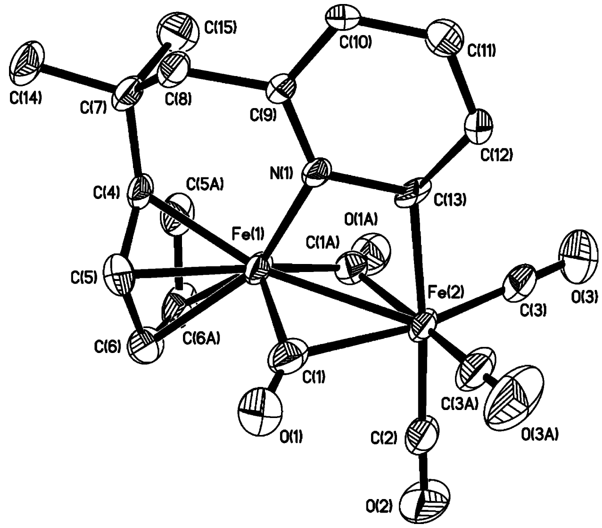
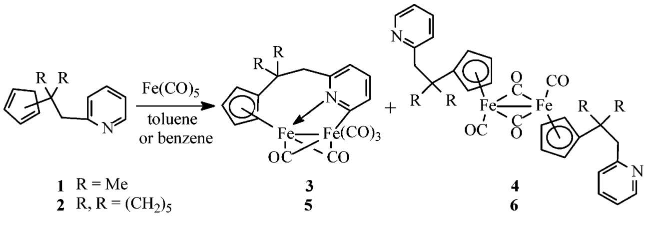


Figure 1. ORTEP diagram of **3**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [deg]: Fe(1)−Fe(2) 2.577(2), Fe(1)−C(1) 1.861(7), Fe(1)−N(1) 1.955(6), Fe(2)−C(1) 2.153(7), Fe(2)−C(13) 1.980(7), N(1)−Fe(1)−Fe(2) 72.34(16), C(13)−Fe(2)−Fe(1) 71.30(19), C(13)−N(1)−Fe(1) 106.4(5), N(1)−C(13)−Fe(2) 106.5(5).

Scheme 1



Upon thermal treatment of ligand **1** with Fe(CO)$_5$ in refluxing toluene, the intramolecular C−H activated product **3** (1%) and the diiron complex **4** (37%) were obtained (Scheme 1). The ^{1}H NMR spectrum of **3** shows three groups of peaks for the pyridyl protons at 6.81, 6.64, and 6.46 ppm, two triplets for the cyclopentadienyl protons at 5.19 and 3.72 ppm, and one singlet for the methylene and methyl protons at 2.53 and 1.26 ppm, respectively. The IR spectrum of **3** shows three terminal and two bridging carbonyl absorptions at 2042, 1973, 1938, and 1839, 1775 cm^{-1}. X-ray diffraction analysis shows that in **3** one iron atom is coordinated with an η^5-cyclopentadienyl and an intramolecular nitrogen atom of the pyridyl; the other iron atom is bonded to the α-C of the pyridyl and coordinated with three carbonyls (Figure 1). Complex **3** is the first example of a cyclometalated complex of iron containing a heterocyclic donor atom, although cyclometalated derivatives of ruthenium and

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10.1021/om050684p CCC: $33.50

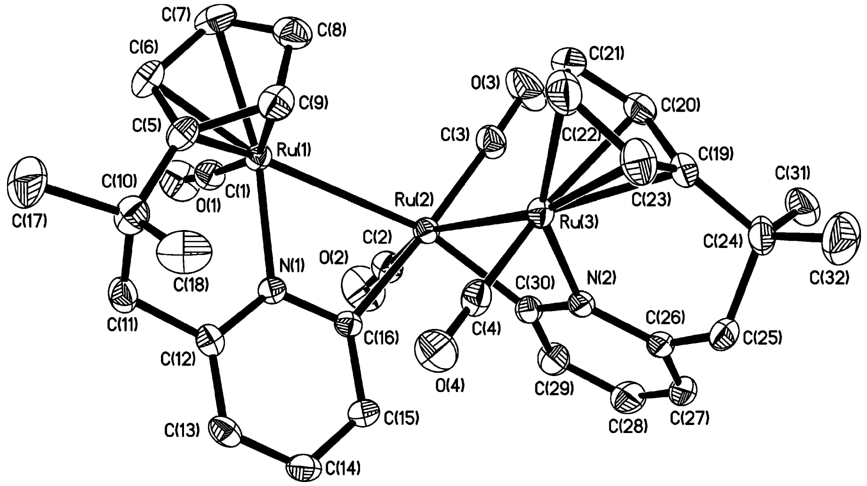
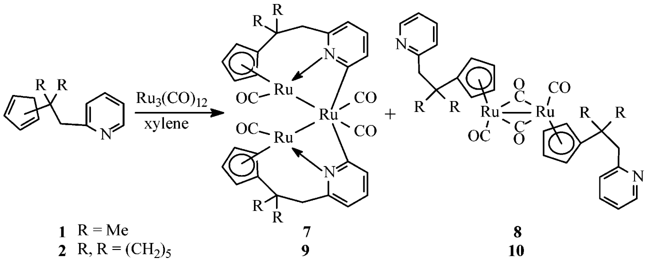
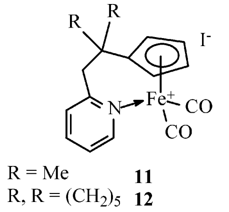


Figure 2. ORTEP diagram of **7**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [deg]: Ru(1)−Ru(2) 3.0131(10), Ru(2)−Ru(3) 2.9998(9), Ru(1)−N(1) 2.086(3), Ru(2)−C(30) 2.063(4), Ru(2)−C(16) 2.099(4), Ru(3)−N(2) 2.077(3), N(1)−Ru(1)−Ru(2) 66.19(9), C(30)−Ru(2)−Ru(3) 67.13(13), C(16)−Ru(2)−Ru(1) 67.10(11), Ru(3)−Ru(2)−Ru(1) 99.96(3), N(2)−Ru(3)−Ru(2) 65.73(10), C(16)−N(1)−Ru(1) 114.8(3), C(30)−N(2)−Ru(3) 114.6(3), N(1)−C(16)−Ru(2) 111.8(3), N(2)−C(30)−Ru(2) 112.5(3).

Scheme 2



Scheme 3



osmium are relatively well-known.[3] Similarly, reaction of ligand **2** with $Fe(CO)_5$ gave the C−H activated product **5** (5%) and the diiron complex **6** (52%).

When ligand **1** reacted with $Ru_3(CO)_{12}$ in refluxing xylene, the intramolecular C−H activated product **7** (7%) and the diruthenium complex **8** (24%) were obtained (Scheme 2). The ^1H NMR spectrum of **7** shows five groups of peaks for the pyridyl protons at 7.44, 7.17, 6.86−6.75, 6.68, and 6.17 ppm, seven groups of peaks for the cyclopentadienyl protons at 5.46, 5.31, 5.27, 5.18, 4.47, 4.44, and 4.33 ppm, four groups of peaks for the methylene protons at 2.73, 2.68, 2.62, and 2.57 ppm, and one singlet for the methyl protons at 1.54 ppm, indicating that complex **7** contains two ligands in a molecule. The IR spectrum of **7** shows only four terminal carbonyl absorptions at 2004, 1950, 1933, and 1910 cm^{-1}. X-ray diffraction analysis shows that complex **7** contains a $Ru(CO)Ru(CO)_2Ru(CO)$ unit, coordinated with two ligands (Figure 2). The Ru(1) and Ru(3) are coordinated each with an η^5-cyclopentadienyl, an intramolecular nitrogen atom of the pyridyl, and a carbonyl. The Ru(2) is bonded with two α-C of the pyridyls and coordinated with two carbonyls. There are many examples of ruthenium clusters with orthometalated pyridyl ligands.[3−5] The Ru−Ru distances [3.0131(10), 2.9998(9) Å] in **7** are much longer, while the Ru−C(pyridyl) [2.099(4), 2.063(4) Å] and Ru−N [2.086(3), 2.077(3) Å] distances are generally shorter than those in these complexes (2.715−2.921, 2.04−2.19, and 2.07−2.14 Å, respectively).[4,5] Similarly, reaction of ligand **2** with $Ru_3(CO)_{12}$ gave the C−H activated product **9** (6%) and the diruthenium complex **10** (31%).

When the dinuclear metal complexes **4**, **6**, **8**, and **10** reacted with I_2, different metal iodide complexes **11**−**14** were obtained (Scheme 3). Complexes **11** and **12** are the intramolecular nitrogen-coordinated ionic complexes (Figure 3), while complexes **13** and **14** are the intramolecular nitrogen-coordinated Ru−I complexes (Figure 4).

Experimental Section

General Considerations. ^1H NMR spectra were recorded on a Bruker AV300 or Bruker AC-P200, while IR spectra were recorded as KBr disks on a Nicolet 5DX FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. Ligands **1** and **2** were prepared according to literature methods.[2a]

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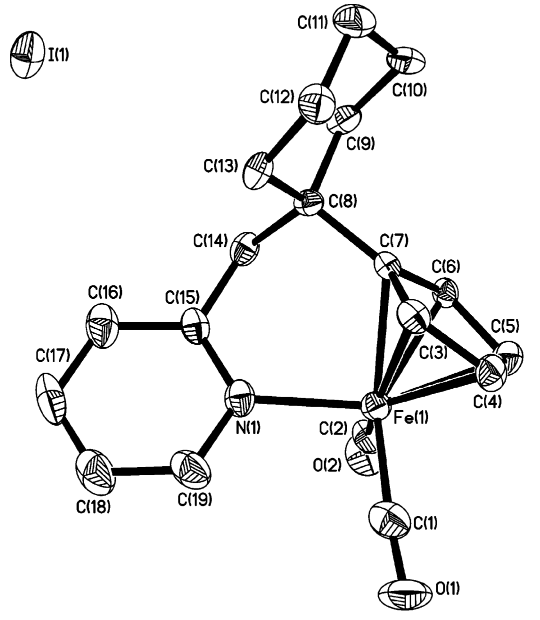

Figure 3. ORTEP diagram of **12**. Thermal ellipsoids are shown at the 30% level.

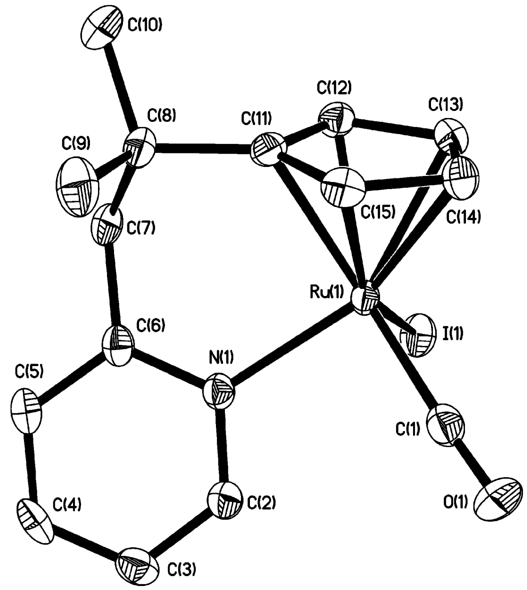

Figure 4. ORTEP diagram of **13**. Thermal ellipsoids are shown at the 30% level.

Reaction of 1 with $Fe(CO)_5$. A solution of 4.96 g (24.92 mmol) of ligand **1** and 5.00 mL (37.19 mmol) of $Fe(CO)_5$ in 30 mL of toluene was refluxed for 7 h. The solvent was removed under reduced pressure, and the residue was placed in an Al_2O_3 column. Elution with CH_2Cl_2/petroleum ether developed a red band and with acetone developed another red band. The first red band gave 0.095 g (1%) of **3** as red crystals, and the second red band yielded 2.875 g (37%) of **4** as dark red crystals. **3**: mp 203 °C (dec). Anal. Calcd for $C_{19}H_{15}Fe_2NO_5$: C, 50.82; H, 3.37; N, 3.12. Found: C, 50.68; H, 3.34, N, 3.30. ^1H NMR ($CDCl_3$) δ: 6.81 (t, 1H, C_5H_3N), 6.64 (d, $J = 7.57$ Hz, 1H, C_5H_3N), 6.46 (d, $J = 7.49$ Hz, 1H, C_5H_3N), 5.19 (t, 2H, C_5H_4), 3.72 (t, 2H, C_5H_4), 2.53 (s, 2H, CH_2), 1.26 (s, 6H, Me_2C). IR (ν_{CO}, cm^{-1}): 2042(s), 1973(s), 1938(m), 1839(m), 1775(s). **4**: mp 133−134 °C. Anal. Calcd for $C_{32}H_{32}Fe_2N_2O_4$: C, 61.96; H, 5.20; N, 4.52. Found: C, 61.88; H, 4.92, N, 4.55. ^1H NMR ($CDCl_3$) δ: 8.46 (d, $J = 4.68$ Hz, 2H, C_5H_4N), 7.46 (t, 2H, C_5H_4N), 7.07 (t, 2H, C_5H_4N), 6.81 (d, $J = 7.81$ Hz, 2H, C_5H_4N), 4.72 (t, 4H, C_5H_4), 4.10 (t, 4H, C_5H_4), 2.98 (s, 4H, CH_2), 1.41 (s, 12H, Me_2C). IR (ν_{CO}, cm^{-1}): 1934(s), 1898(m), 1763(s), 1728(m).

Reaction of 2 with $Fe(CO)_5$. Using a procedure similar to that described above, reaction of **2** with $Fe(CO)_5$ gave **5** and **6** in 5% and 52% yields, respectively. **5**: mp 200 °C (dec). Anal. Calcd for $C_{22}H_{19}Fe_2NO_5$: C, 54.03; H, 3.92; N, 2.86. Found: C, 54.09; H, 3.76, N, 2.91. ^1H NMR ($CDCl_3$) δ: 6.82 (t, 1H, C_5H_3N), 6.64 (d, $J = 7.33$ Hz, 1H, C_5H_3N), 6.49 (d, $J = 7.59$ Hz, 1H, C_5H_3N), 5.20 (s, 2H, C_5H_4), 3.72 (s, 2H, C_5H_4), 2.58 (s, 2H, CH_2), 1.77−1.41-(m, 10H, $(CH_2)_5C$). IR (ν_{CO}, cm^{-1}): 2042(s), 1985(s), 1970(s), 1878(m), 1787(s). **6**: mp 162−163 °C. Anal. Calcd for $C_{38}H_{40}Fe_2N_2O_4$: C, 65.15; H, 5.76; N, 4.00. Found: C, 65.02; H, 5.68, N, 4.16. ^1H NMR ($CDCl_3$) δ: 8.38 (d, $J = 4.68$ Hz, 2H, C_5H_4N), 7.36 (t, 2H, C_5H_4N), 7.00 (t, 2H, C_5H_4N), 6.56 (d, $J = 7.76$ Hz, 2H, C_5H_4N), 4.55 (t, 4H, C_5H_4), 4.02 (t, 4H, C_5H_4), 3.08 (s, 4H, CH_2), 1.90−1.40 (m, 20H, $(CH_2)_5C$). IR (ν_{CO}, cm^{-1}): 1942(s), 1914(m), 1775(s), 1752(m).

Reactions of 1 and 2 with $Ru_3(CO)_{12}$. Using a procedure similar to that described above, reactions of **1** and **2** with $Ru_3(CO)_{12}$ under refluxing xylene for 12 h gave **7**, **8**, and **9**, **10** in 7%, 24%, and 6%, 31% yields, respectively. **7**: mp 133 °C (dec). Anal. Calcd for $C_{32}H_{30}N_2O_4Ru_3$: C, 47.46; H, 3.73; N, 3.46. Found: C, 47.50; H, 3.71, N, 3.45. ^1H NMR ($CDCl_3$) δ: 7.44 (d, $J = 7.50$ Hz, 1H, C_5H_3N), 7.17 (t, 1H, C_5H_3N), 6.86−6.75 (m, 2H, C_5H_3N), 6.68 (d, $J = 7.50$ Hz, 1H, C_5H_3N), 6.17 (d, $J = 7.50$ Hz, 1H, C_5H_3N), 5.46 (s, 1H, C_5H_4), 5.31 (s, 1H, C_5H_4), 5.27 (s, 1H, C_5H_4), 5.18 (s, 1H, C_5H_4), 4.47 (s, 1H, C_5H_4), 4.44 (s, 1H, C_5H_4), 4.33 (m, 2H, C_5H_4), 2.73 (s), 2.68 (s), 2.62 (s), 2.57 (s) (total, 4H, CH_2), 1.54 (s, 12H, Me_2C). IR (ν_{CO}, cm^{-1}): 2004(s), 1950(s), 1933(s), 1910(m). **8**: mp 127−128 °C. Anal. Calcd for $C_{32}H_{32}N_2O_4Ru_2$: C, 54.08; H, 4.54; N, 3.94. Found: C, 54.03; H, 4.42, N, 4.01. ^1H NMR ($CDCl_3$) δ: 8.50 (d, $J = 3.00$ Hz, 2H, C_5H_4N), 7.53−7.48 (m, 2H, C_5H_4N), 7.13−7.09 (m, 2H, C_5H_4N), 6.85(d, $J = 8.40$ Hz, 2H, C_5H_4N), 5.12 (t, 4H, C_5H_4), 4.79 (t, 4H, C_5H_4), 2.98 (s, 4H, CH_2), 1.35 (s, 12H, Me_2C). IR (ν_{CO}, cm^{-1}): 1938(s), 1906(m), 1763(s), 1736-(m). **9**: mp 175 °C (dec). Anal. Calcd for $C_{38}H_{38}N_2O_4Ru_3$: C, 51.12; H, 4.29; N, 3.14. Found: C, 51.10; H, 4.33, N, 3.10. ^1H NMR ($CDCl_3$) δ: 7.45 (d, $J = 7.50$ Hz, 1H, C_5H_3N), 7.17 (t, 1H, C_5H_3N), 6.84 (d, $J = 7.50$ Hz, 1H, C_5H_3N), 6.78 (t, 1H, C_5H_3N), 6.68 (d, $J = 7.50$ Hz, 1H, C_5H_3N), 6.18 (d, $J = 6.00$ Hz, 1H, C_5H_3N), 5.47 (br s, 1H, C_5H_4), 5.31 (br s, 1H, C_5H_4), 5.27 (br s, 1H, C_5H_4), 5.18 (br s, 1H, C_5H_4), 4.47 (m, 1H, C_5H_4), 4.44 (m, 1H, C_5H_4), 4.33 (m, 2H, C_5H_4), 2.73 (s), 2.68 (s), 2.62 (s), 2.57 (s) (total, 4H, CH_2), 2.05−1.92 (m, 2H, $(CH_2)_5$), 1.70−1.00 (m, 18H, $(CH_2)_5$). IR (ν_{CO}, cm^{-1}): 1999(s), 1956(s), 1936(s), 1909(s). **10**: mp 202−203 °C. Anal. Calcd for $C_{38}H_{40}N_2O_4Ru_2$: C, 57.57; H, 5.09; N, 3.54. Found: C, 57.89; H, 4.99, N, 3.60. ^1H NMR ($CDCl_3$) δ: 8.43 (d, 2H, $J = 4.80$ Hz, C_5H_4N), 7.44−7.39 (m, 2H, C_5H_4N), 7.06−7.02 (m, 2H, C_5H_4N), 6.63(d, 2H, $J = 7.80$ Hz, C_5H_4N), 4.94 (t, 4H, C_5H_4), 4.70 (t, 4H, C_5H_4), 3.08 (s, 4H, CH_2), 1.95−1.26 (m, 20H, $(CH_2)_5$). IR (ν_{CO}, cm^{-1}): 1958(s), 1930(w), 1767(s), 1728(w).

Reactions of 4 and 6 with I_2. A solution of 0.837 g (1.35 mmol) of **4** and 0.344 g (1.35 mmol) of I_2 in 20 mL of CH_2Cl_2 was stirred for 12 h at room temperature. The solution was washed with saturated $Na_2S_2O_3$ solution and water in turn and dried over anhydrate Na_2SO_4. After removal of solvent under reduced pressure, the residue was placed in an Al_2O_3 column. Elution with acetone developed a yellow band, which gave 0.300 g (25%) of **11** as yellow crystals. Similarly, reaction of **6** with I_2 gave **12** in 28% yield. **11**: mp 155 °C (dec). Anal. Calcd for $C_{16}H_{16}FeINO_2$: C, 43.97; H, 3.69, N, 3.21. Found: C, 43.92; H, 3.78; N, 3.18. ^1H NMR ($CDCl_3$) δ: 8.60 (br s, 1H, C_5H_4N), 7.88 (m, 1H, C_5H_4N), 7.63 (m, 1H, C_5H_4N), 7.28 (br s, 1H, C_5H_4N), 6.10 (s, 2H, C_5H_4), 4.88 (s, 2H, C_5H_4), 3.32 (s, 2H, CH_2), 1.33 (s, 6H, Me_2C). IR (ν_{CO}, cm^{-1}): 2050(s), 2018(s). **12**: mp 165 °C (dec). Anal. Calcd for $C_{19}H_{20}$-

Table 1. Crystal Data and Summary of X-ray Data Collection for 3, 7, 12, and 13

	3	7	12	13
formula	$C_{19}H_{15}Fe_2NO_5$	$C_{32.5}H_{31}ClN_2O_4Ru_3$	$C_{19}H_{20}FeINO_2$	$C_{15}H_{16}INORu$
fw	449.02	852.25	477.11	454.26
T, K	293(2)	293(2)	293(2)	293(2)
radiation (λ), Å	Mo Kα	Mo Kα	Mo Kα	Mo Kα
cryst syst	orthorhombic	triclinic	orthorhombic	triclinic
space group	*Pnma*	$P\bar{1}$	$P2(1)2(1)2(1)$	$P\bar{1}$
a, Å	10.477(7)	9.315(3)	7.987(2)	8.471(4)
b, Å	9.756(6)	12.751(5)	14.590(4)	9.095(5)
c, Å	18.071(11)	14.097(5)	16.197(5)	11.059(6)
α, deg	90	96.156(5)	90	84.051(9)
β, deg	90	108.847(6)	90	87.122(9)
γ, deg	90	92.507(6)	90	62.536(7)
V, Å^3	1847(2)	1570.1(10)	1887.4(10)	751.9(7)
Z	4	2	4	2
D_{calc}, g·cm^{-3}	1.615	1.803	1.679	2.006
μ, mm^{-1}	1.600	1.549	2.445	3.087
$F(000)$	912	842	944	436
cryst size, mm	0.14 × 0.12 × 0.06	0.24 × 0.22 × 0.18	0.22 × 0.14 × 0.14	0.32 × 0.26 × 0.20
2θ range, deg	4.50−53.18	3.22−52.86	3.76−50.02	5.06−50.02
no. of reflns collected	10 057	9229	9763	3869
no. of indep reflns/R_{int}	2025/0.0813	6396/0.0182	3325/0.0455	2619/0.0178
no. of params	169	401	217	174
goodness-of-fit on F^2	1.108	1.066	1.076	1.088
R_1, wR_2 [$I > 2\sigma(I)$]	0.0629, 0.1284	0.0315, 0.0711	0.0406, 0.0966	0.0234, 0.0546
R_1, wR_2 (all data)	0.1023, 0.1443	0.0506, 0.0862	0.0673, 0.1058	0.0331, 0.0587

$FeINO_2$: C, 47.83; H, 4.23, N, 2.94. Found: C, 47.68; H, 4.36; N, 2.80. ^1H NMR ($CDCl_3$) δ: 8.73 (br s, 1H, C_5H_4N), 7.80 (m, 1H, C_5H_4N), 7.51 (m, 1H, C_5H_4N), 7.22 (br s, 1H, C_5H_4N), 5.92 (s, 2H, C_5H_4), 4.91 (s, 2H, C_5H_4), 3.21 (s, 2H, CH_2), 1.56−1.18 (m, 10H, $(CH_2)_5C$). IR (ν_{CO}, cm^{-1}): 2044(s), 1983(m).

Reactions of 8 and 10 with I_2. Using a procedure similar to that described above, reactions of **8** and **10** with I_2 gave **13** and **14** in 59% and 31% yields, respectively. **13**: mp 180 °C (dec). Anal. Calcd for $C_{15}H_{16}INORu$: C, 39.57; H, 3.54, N, 3.08. Found: C, 39.90; H, 3.70; N, 3.04. ^1H NMR ($CDCl_3$) δ: 9.27 (br s, 1H, C_5H_4N), 7.60 (t, 1H, C_5H_4N), 7.24 (d, J = 7.50 Hz, 1H, C_5H_4N), 7.01 (t, 1H, C_5H_4N), 5.38 (s, 1H, C_5H_4), 5.05 (s, 1H, C_5H_4), 4.55 (s, 1H, C_5H_4), 4.46 (s, 1H, C_5H_4), 3.15 (d, J = 14.4 Hz, 1H, CH_2), 2.84 (d, J = 14.4 Hz, 1H, CH_2), 1.38 (s, 3H, Me_2C), 1.00 (s, 3H, Me_2C). IR (ν_{CO}, cm^{-1}): 1931(s). **14**: mp 183−184 °C. Anal. Calcd for $C_{18}H_{20}INORu$: C, 43.64; H, 4.07, N, 2.83. Found: C, 43.50; H, 4.05; N, 2.74. ^1H NMR ($CDCl_3$) δ: 9.22 (br s, 1H, C_5H_4N), 7.60 (t, 1H, C_5H_4N), 7.31 (d, J = 7.50 Hz, 1H, C_5H_4N), 7.01 (t, 1H, C_5H_4N), 5.44 (s, 1H, C_5H_4), 4.94 (s, 1H, C_5H_4), 4.60 (s, 1H, C_5H_4), 4.53 (s, 1H, C_5H_4), 3.19 (d, J = 14.1 Hz, 1H, CH_2), 2.98 (d, J = 14.1 Hz, 1H, CH_2), 1.57−1.23 (m, 10H, $(CH_2)_5C$). IR (ν_{CO}, cm^{-1}): 1938(s).

Crystallographic Studies. Crystals of complexes **3**, **4**, **7**, **8**, **12**, and **13** suitable for X-ray diffraction were investigated with a Bruker SMART 1000 diffractometer, using graphite-monochromated Mo Kα radiation ($\omega-2\theta$ scans, λ = 0.71073 Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were done using the SHELXL-97 program system. The crystal data and summary of the X-ray data collection for complexes **3**, **7**, **12**, and **13** are presented in Table 1.

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Supporting Information Available: X-ray structural information for complexes **3**, **4**, **7**, **8**, **12**, and **13**, including the ORTEP figures of **4** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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