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First Examples of Heteroleptic Dipyrrin/η^5-Pentamethylcyclopentadienyl Rhodium/Iridium(III) Complexes and Their Catalytic Activity

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Heteroleptic pentamethylcyclopentadienyl rhodium/iridium(III) complexes imparting dipyrrins as co-ligands with the general formulations [(η^5-C_5Me_5)MCl(L)] [(M = Rh(III) or Ir(III); L = 5-(4-cyanophenyl)dipyrromethene, cydpm; 5-(4-nitrophenyl)dipyrromethene, ndpm; and 5-(4-benzyloxyphenyl)dipyrromethene, bdpm] have been synthesized. Reactivity of the complexes [(η^5-C_5Me_5)MCl(L)] (M = Rh(III), Ir(III); L = ndpm and cydpm) with various species, viz., sodium azide (NaN_3), ammonium thiocyanate (NH_4SCN), triphenylphosphine (PPh_3), 4,4′-bipyridine (bpy), and bis(diphenylphosphino)hexane (dpph), has been examined. Resulting complexes have been characterized by elemental analyses and spectral and electrochemical studies. Molecular structures of the representative complexes [(η^5-C_5Me_5)RhCl(cydpm)], [(η^5-C_5Me_5)RhCl(ndpm)], [(η^5-C_5Me_5)Rh-(PPh_3)(cydpm)]SO_3CF_3, and [(η^5-C_5Me_5)Ir(PPh_3)(ndpm)]SO_3CF_3 have been determined crystallographically. The complexes [(η^5-C_5Me_5)MCl(L)] [(M = Rh(III) or Ir(III) and L = cydpm, ndpm, or bdpm) effectively catalyze reduction of terephthalaldehyde to 4-hydroxymethybenzaldehyde in the presence of HCOOH/CH_3COONa in water under aerobic conditions. Among these complexes the rhodium complex [(η^5-C_5Me_5)RhCl(ndpm)] is most effective in this regard.

Introduction

Enormous current interest has arisen in the coordination chemistry of dipyrrinato ligands owing to their ease of synthesis, intense optical absorptions, and propensity to form stable neutral complexes with a variety of metal ions.[1] Taking advantage of these properties, a number of charge-neutral complexes and supramolecular clusters based on dipyrrins have been synthesized.[2] Much of the interest in dipyrrin compounds derives from their rich optical properties. Compounds that incorporate dipyrrins are often deeply colored and can display photoluminescence.[1,3] In this regard, highly conjugated *meso*-substituted dipyrrins, which can be easily synthesized from aldehydes via condensation with pyrrole followed by oxidation, have attracted a great deal of attention.[4] An extensive π-skeleton of the substituted phenyl ring as *meso*-substituents and two conjugated rigid pyrrole rings in dipyrrins enable them to behave as a better bidentate nitrogen donor ligand like 2,2′-bipyridine or 1,10-phenanthroline. Further, one can fine-tune properties of the dipyrrins by incorporating electron-withdrawing/donating substituents, which have a pronounced effect on the electrochemical and optical properties.[5] Electron-donating groups increase electron density on the ligand and redox processes occur at more negative potentials, while the opposite effect occurs when electron-withdrawing groups are employed. While there are a number of examples of dipyrrin complexes with boron, main group metals, or first-row transition metals,[1,3,6] there is just one report dealing with rhodium dipyrrinato complexes and not even a single report dealing with iridium dipyrrinato complexes.[7] Further, rhodium/iridium(III) complexes containing both the dipyrrin and η^5-pentamethyl cyclopentadienyl groups have not yet been reported.

Furthermore, the dimeric chloro-bridged complexes [{(η^5-C_5Me_5)M(μ-Cl)Cl}$_2$] (M = Rh or Ir) have proved to be indispensable starting materials in organometallic chemistry.[8]

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The complexes undergo a rich variety of chemistry via intermediacy of the chloro bridge cleavage reactions, leading to the formation of a series of interesting neutral and cationic mononuclear complexes.[9] Because of their potential applications in many areas, half-sandwich η^5-pentamethylcyclopentadienyl rhodium/iridium(III) complexes have widely been investigated in the past few years.[10] Rhodium/iridium complexes are also being explored for their medicinal properties as potential anticancer agents.[11]

The heteroleptic dipyrrin complexes described to date result from the formation of complexes based on the Fe(II), Zn(II), Pd(II), Hg(II), Rh(I), Cr(III), Co(III), and Cu(II) metal center.[1,2,12] With an objective of expanding the chemistry of dipyrrins we have synthesized and characterized a series of new neutral and cationic heteroleptic pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes based on *meso*-substituted dipyrrins. These represent the first examples of rhodium/iridium(III) complexes containing both the dipyrrin and η^5-pentamethylcyclopentadienyl groups. In this paper we describe reproducible synthesis, spectral and structural characterization, reactivity, and catalytic activity of some heteroleptic rhodium/iridium(III) complexes $[(\eta^5\text{-}C_5Me_5)MCl(L)]$ [(M = Rh(III) or Ir(III) and L = cydpm, ndpm, or bdpm) based on dipyrrinato ligands. Also, we present herein the synthesis and characterization of some bis(diphenylphosphino)hexane (dpph)-, 4,4′-bipyridine (bpy)-, and azido-bridged dinuclear complexes based on dipyrrin/η^5-pentamethylcyclopentadienyl ligands.

Experimental Section

Reagents. All the experiments were conducted under a nitrogen atmosphere. The solvents were purified rigorously by standard procedures prior to their use.[13] Hydrated rhodium(III) chloride, hydrated iridium(III) chloride, pentamethylcyclopentadiene, silver trifluoromethanesulfonate, triphenylphosphine, bis(diphenylphosphino)hexane, sodium azide, ammonium thiocyanate, 4,4′-bipyridine, 2,3-dicloro-5,6-dicyano-1,4-benzoquinone (DDQ), 4-cyanobenzaldehyde, 4-bezyloxybenzaldehyde, 4-nitrobenzaldehyde, and pyrrole (all Aldrich) were used as received without further purifications. The precursor complexes $[\{(\eta^5\text{-}C_5Me_5)M(\mu\text{-}Cl)Cl\}_2]$[14] (M = Rh or Ir) and the ligands 5-(4-cyanophenyl)dipyrromethane,[15a] 5-(4-nitrophenyl)dipyrromethane,[15b] and 5-(4-benzyloxyphenyl)dipyrromethane[15c] were prepared and purified by reported literature procedures.

General Methods. Elemental analyses for C, H, and N were performed on an Exeter Analytical Inc. model CE-440 elemental analyzer. IR spectra were acquired on a Varian 3300 FT-IR spectrometer in the region 4000−400 cm^{-1}. ^1H NMR spectra were obtained on a JEOL AL 300 FT-NMR spectrometer at rt using $CDCl_3$ as a solvent and TMS as an internal reference. Electronic and emission spectra were recorded on Shimadzu UV-1700 series and LS-45 (Perkin-Elmer) luminescence spectrophotometers, respectively. FAB mass spectra were obtained on a JEOL SX 102/Da-600 mass spectrometer. Cyclic voltammetric measurements were performed on a CHI 620c electrochemical analyzer. A glassy carbon working electrode, a platinum wire auxiliary electrode, and Ag/Ag^+ reference electrode were used in a standard three-electrode configuration. Tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte, and the solution concentration was ca. 10^{-3} M.

Synthesis of $[(\eta^5\text{-}C_5Me_5)RhCl(cydpm)]$ (1). DDQ (0.228 g, 1.0 mmol) dissolved in benzene (150 mL) was added slowly (over an hour) with stirring to a solution of 5-(4-cyanophenyl)dipyrromethane (0.247 g, 1.0 mmol) in $CHCl_3$ (150 mL) cooled in an ice bath. After TLC examination revealed complete consumption of the starting material, solvent was evaporated and the resulting dark residue was redissolved in $CHCl_3$/MeOH (75 mL; 1:1 v/v). Triethylamine (0.75 mL) was added to this solution followed by addition of $[\{(\eta^5\text{-}C_5Me_5)Rh(\mu\text{-}Cl)Cl\}_2]$ (0.309 g, 0.50 mmol) dissolved in dichloromethane (5 mL). The dark reaction mixture thus obtained was heated at reflux temperature overnight and then evaporated to dryness under vacuum to produce a black solid. The crude product was charged on a flash column (20 × 3 cm, SiO_2; CH_2Cl_2/hexane). A second, bright orange band was collected and evaporated to dryness to afford $[(\eta^5\text{-}C_5Me_5)RhCl(4\text{-cydpm})]$. Yield: 0.268 g, 55%. Anal. Calcd for $C_{26}H_{25}ClN_3Rh$: C, 60.34; H, 4.87; N, 8.12. Found: C, 60.02; H, 4.75: N, 8.20. IR (KBr pellet, cm^{-1}): 2224, 1533, 1449, 1402, 1374, 1336, 1248, 1203, 1077, 1022, 987, 891, 820, 711, 531, 474. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 1.51 (s, 15H), 6.50 (d, 2H, J = 3.6 Hz), 6.54 (d, 2H, J = 3.9 Hz), 7.52 (d, 2H, J = 7.2 Hz), 7.73 (d, 2H, J = 8.1 Hz), 7.82 (s, 2H). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.5 (C-CH_3), 94.8 (C_5Me_5), 112.4 ($C{\equiv}N$), 118.5, 119.7, 131.2, 132.2, 134.9, 142.7, 143.6, 153.9. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 512 (2.36×10^4), 436 (1.17×10^4), 306 (1.00×10^4), 263 (1.17×10^4), 237 (3.12×10^4).

Synthesis of $[(\eta^5\text{-}C_5Me_5)RhCl(ndpm)]$ (2). This complex was prepared following the above procedure adopted for **1**, except that 5-(4-nitrophenyl)dipyrromethane (0.268 g, 1.0 mmol) was used in place of 5-(4-cyanophenyl)dipyrromethane. Yield: 0.298 g, 58%. Anal. Calcd for $C_{25}H_{25}ClN_3O_2Rh$: C, 55.86, H, 4.69; N, 7.82. Found: C, 56.15; H, 4.78: N, 7.70. IR (KBr pellets, cm^{-1}): 1545, 1374, 1342, 1248, 1199, 1102, 1021, 987, 892, 823, 771, 724, 477. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 1.52 (s, 15H), 6.50 (d, 2H, J = 4.8 Hz), 6.54 (d, 2H, J = 4.5 Hz), 7.58 (d, 2H, J = 9.0 Hz), 7.83 (s, 2H), 8.29 (d, 2H, J = 8.4 Hz). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.6 (C-CH_3), 94.8 (C_5Me_5), 119.8, 122.6, 132.2, 134.9, 143.2, 144.6, 147.9, 154.0. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 512 (2.33×10^4), 435 (1.18×10^4), 305 (1.39×10^4), 269 (1.84×10^4), 228 (2.35×10^4).

Synthesis of $[(\eta^5\text{-}C_5Me_5)RhCl(bdpm)]$ (3). This complex was prepared following the above procedure for **1**, except that 5-(4-benzyloxyphenyl)dipyrromethane (0.328 g, 1.0 mmol) was used in place of 5-(4-cyanophenyl)dipyrromethane. Yield: 0.298 g, 50%. Anal. Calcd for $C_{32}H_{32}N_2OClRh$: C, 64.17; H, 5.38; N, 4.68. Found: C, 64.46; H, 5.48; N, 4.60. IR (KBr pellet, cm^{-1}): 1602, 1525, 1445, 1374, 1335, 1289, 1247, 1174, 1021, 987, 886, 816, 733, 641. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 1.48 (s, 15H), 5.14 (s, 2H), 6.48 (d, 2H, J = 4.8 Hz), 6.73 (d, 2H, J = 3.9 Hz), 7.15 (d, 2H, J = 9.0 Hz), 7.34−7.47 (m, 7H), 7.73 (s, 2H). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.5 (C-CH_3), 70.1, 94.5 (C_5Me_5),

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113.6, 118.8, 127.5, 128.1, 128.6, 130.7, 131.8, 132.7, 136.0, 136.8, 146.5, 152.8, 159.2. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 507 (2.40×10^4), 432 (1.05×10^4), 355 (1.11×10^4), 268 (7.14×10^3), 230 (3.49×10^4).

Synthesis of [(η^5-C_5Me_5)IrCl(cydpm)] (4). This complex was prepared following the above procedure adopted for **1**, except that [{(η^5-C_5Me_5)Ir(μ-Cl)Cl}$_2$] (0.309 g, 0.50 mmol) was used in place of [{(η^5-C_5Me_5)Rh(μ-Cl)Cl}$_2$]. Yield: 0.298 g, 54%. Anal. Calcd for $C_{26}H_{25}N_3ClIr$: C, 51.43; H, 4.15; N, 6.92. Found: C, 51.74; H, 4.20; N, 6.85. IR (KBr pellet, cm^{-1}): 2224, 1537, 1452, 1376, 1339, 1248, 1202, 1025, 990, 893, 820, 766, 714, 473. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.51 (s, 15H), 6.39 (d, 2H, J = 4.5 Hz), 6.47 (d, 2H, J = 4.2 Hz), 7.53 (d, 2H, J = 8.1 Hz), 7.50 (d, 2H, J = 6.6 Hz), 7.74 (s, 2H). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.4 (C-CH_3), 86.7 (C_5Me_5), 112.4 ($C\equiv$N), 117.7, 118.6, 129.1, 131.2, 132.4, 142.4, 144.2, 154.1. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 504 (1.86×10^4), 457 (2.10×10^4), 303 (1.38×10^4), 268 (1.36×10^4), 233 (2.08×10^4).

Synthesis of [(η^5-C_5Me_5)IrCl(ndpm)] (5). This complex was prepared following the above procedure adopted for **1**, except that [{(η^5-C_5Me_5)Ir(μ-Cl)Cl}$_2$] (0.309 g, 0.50 mmol) was used in place of [{(η^5-C_5Me_5)Rh(μ-Cl)Cl}$_2$] and 5-(4-nitrophenyl)dipyrromethane (0.268 g, 1.0 mmol) in place of 5-(4-cyanophenyl)dipyrromethane. Yield: 0.298 g, 55%. Anal. Calcd for $C_{25}H_{25}ClO_2N_3Ir$: C, 47.88; H, 4.02; N, 6.70. Found: C, 47.88; H, 4.10: N, 6.60. IR (KBr pellets, cm^{-1}): 1546, 1455, 1377, 1343, 1249, 1202, 1102, 1024, 990, 893, 823, 723, 477. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.52 (s, 15H), 6.39 (d, 2H, J = 4.2 Hz), 6.48 (d, 2H, J = 3.9 Hz), 7.59 (d, 2H, J = 8.4 Hz), 7.70 (s, 2H), 8.30 (d, 2H, J = 8.4 Hz). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.4 (C-CH_3), 86.8 (C_5Me_5), 118.7, 122.6, 131.2, 132.3, 143.8, 144.2, 147.9, 154.3. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 502 (2.02×10^4), 459 (2.11×10^4), 302 (1.83×10^4), 271 (2.27×10^4), 229 (2.25×10^4).

Synthesis of [(η^5-C_5Me_5)Rh(SCN)(cydpm)] (6). Complex **1** (0.515 g, 1.0 mmol) was treated with NH_4SCN (0.076 g, 1.0 mmol) in dry acetone (20 mL), and the suspension was stirred at room temperature for 3 h. It was concentrated to dryness under vacuum, and the residue was extracted with dichloromethane (10 mL) and filtered to remove solid ammonium chloride. The filtrate was concentrated to ~2 mL, and an excess of hexane was added to assist precipitation. The orange-colored product thus obtained was washed with diethyl ether and dried under vacuum. Yield: 0.412 g, 77%. Anal. Calcd for $C_{27}H_{25}N_4SRh$: C, 60.00; H, 4.66; N, 10.37. Found: C, 60.38; H, 4.52 ; N, 10. 28. IR (KBr pellet, cm^{-1}): 2229, 2099, 1545, 1441, 1376, 1341, 1250, 1024, 991, 812, 772, 723, 673, 476. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.55 (s, 15H), 6.52 (d, 2H, J = 3.9 Hz), 6.58 (d, 2H, J = 3.9 Hz), 7.54 (d, 2H, J = 8.1 Hz), 7.71 (s, 2H), 7.74 (d, 2H, J = 8.1 Hz). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.3 (C-CH_3), 96.6 (C_5Me_5), 112.6, 118.9, 120.0, 131.2, 132.7, 134.7, 142.5, 143.9, 152.9. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 504 (2.31×10^4), 427 (7.14×10^3), 357 (6.78×10^3), 308 (9.15×10^3), 259 (1.49×10^4), 234 (2.91×10^4).

Synthesis of [(η^5-C_5Me_5)Rh(PPh_3)(cydpm)]SO_3CF_3 (7). Compound **1** (0.515 g, 1.0 mmol) was treated with $AgSO_3CF_3$ (0.257 g, 1 mmol) in dry acetone (30 mL) and stirred for 2 h at rt. It was filtered through Celite to remove silver chloride. Triphenylphosphine (0.262 g, 1 mmol) was added to the filtrate and stirred at rt for 4 h. The solvent was removed *in vacuo* and residue extracted with dichloromethane (5 mL) and filtered. An excess of hexane was added to the filtrate to assist precipitation. A yellow-colored precipitate thus obtained was separated by filtration, washed with diethyl ether, and dried under vacuum. Yield: 0.606 g, 70%. Anal. Calcd for $C_{45}H_{40}N_3SF_3O_3PRh$: C, 60.47; H, 4.51; N, 4.70. Found: C, 60.11; H, 4.51: N, 4.81. IR (KBr pellet, cm^{-1}): 2230, 1625, 1555, 1436, 1379, 1341, 1270, 1141, 1097, 1031, 990, 891, 812, 750, 696, 634, 516. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.39 (s, 15H), 6.35 (d, 2H, J = 3.6 Hz), 6.52 (d, 2H, J = 4.5 Hz), 7.14 (s, 2H), 7.33−7.70 (m, 17H), 7.77 (d, 2H, J = 8.1 Hz) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.7 (C-CH_3), 102.3 (C-CH_3), 113.1, 118.5, 121.1, 127.5, 128.1, 129.1, 129.2, 130.5, 130.8, 131.4, 132.5, 133.4, 134.1, 134.6, 141.9, 144.2, 154.0. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 501 (2.30×10^4), 339 (6.03×10^3), 316 (6.88×10^3), 267 (1.18×10^4), 233 (2.87×10^4).

Synthesis of [(η^5-C_5Me_5)Rh(N_3)(ndpm)] (8). This complex was prepared following the above procedure for **6**, except that NaN_3 was used in place of NH_4SCN, using complex **2** (0.535 g, 1.0 mmol). Yield: 0.403 g, 75%. Anal. Calcd for $C_{25}H_{25}N_6O_2Rh$: C, 55.16; H, 4.63; N, 15.44. Found: C, 55.42; H, 4.50: N, 15.52. IR (KBr pellet, cm^{-1}): 2017, 1545, 1523, 1340, 1247, 1199, 1105, 1023, 992, 796, 718, 478. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.54 (s, 15H), 6.55 (d, 2H, J = 4.8 Hz), 6.58 (d, 2H, J = 4.2 Hz), 7.60 (d, J = 8.4), 7.85 (s, 2H), 8.30 (d, 2H, J = 8.4 Hz). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.3 (C-CH_3), 94.6 (C_5Me_5), 119.8, 122.5, 122.8, 132.2, 135.0, 143.2, 144.6, 147.9, 152.4. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 504 (2.35×10^4), 353 (1.13×10^4), 301 (1.71×10^4), 271 (2.25×10^4), 230 (2.49×10^4).

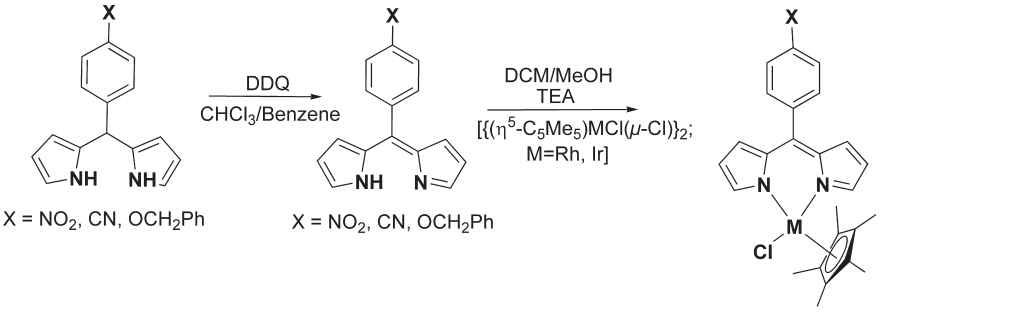
Synthesis of [(η^5-C_5Me_5)Rh(SCN)(ndpm)] (9). This complex was prepared following the procedure adopted for **6**, using complex **2** (0.535 g, 1.0 mmol) in place of **1**. Yield: 0.454 g, 74%. Anal. Calcd for $C_{26}H_{25}N_4O_2SRh$: C, 55.72; H, 4.50; N, 10.00. Found: C, 56.03; H, 4.58: N, 9.95. IR (KBr pellet, cm^{-1}): 2094, 1542, 1342, 1246, 1024, 988, 891, 821, 720, 476. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.56 (s, 15H), 6.55 (d, 2H, J = 3.9 Hz), 6.60 (d, 2H, J = 4.8 Hz), 7.61 (d, J = 8.1) 7.73 (s, 2H), 8.31 (d, 2H, J = 8.7 Hz) ppm. ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.3 (C-CH_3), 96.6 (C_5Me_5), 118.7, 122.3, 122.5, 131.2, 134.9, 143.2, 144.6, 147.9, 153.0. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 505 (2.35×10^4), 359 (8.23×10^3), 306 (1.19×10^4), 262 (1.94×10^4), 230 (1.83×10^4).

Synthesis of [(η^5-C_5Me_5)Rh(PPh_3)(ndpm)]SO_3CF_3 (10). It was prepared following the method employed for **7** starting from complex **2** (0.535 g, 1.0 mmol). Yield: 0.637 g, 72%. Anal. Calcd for $C_{44}H_{40}N_3O_5F_3PSRh$: C, 57.84; H, 4.41; N, 4.60. Found: C, 57.46; H, 4.32; N, 4.71. IR (KBr pellet, cm^{-1}): 1553, 1521, 1436, 1378, 1344, 1267, 1150, 1095, 1030, 990, 892, 821, 747, 697, 637, 572, 522. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.40 (s, 15H), 6.36 (d, 2H, J = 3.6 Hz), 6.53 (d, 2H, J = 4.5 Hz), 7.16 (s, 2H), 7.37−7.57 (m, 17H), 8.34 (d, 2H, J = 8.7). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.7 (C-CH_3), 102.4 (C_5Me_5), 121.2, 122.9, 123.0, 127.6, 128.2, 129.2, 130.7, 131.0, 133.4, 134.1, 134.5, 143.7, 154.1. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 501 (2.37×10^4), 349 (7.69×10^3), 305 (9.24×10^3), 262 (1.99×10^4), 229 (2.37×10^4).

Synthesis of [(η^5-C_5Me_5)Ir(PPh_3)(ndpm)]SO_3CF_3 (11). It was prepared following the method employed for **7** starting from complex **5** (0.535 g, 1.0 mmol). Yield: 0.637 g, 74%. Anal. Calcd for $C_{44}H_{40}N_3SF_3O_5PIr$: C, 52.69; H, 4.02; N, 4.19. Found: C, 53.03; H, 4.12: N, 4.25. IR (KBr pellet, cm^{-1}): 1633, 1576, 1348, 1265, 1143, 1096, 1028, 992, 819, 747, 695, 636, 519. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.42 (s, 15H), 6.34 (d, 2H, J = 4.5 Hz), 6.41 (d, 2H, J = 4.5 Hz), 7.22 (s, 2H), 7.38−7.60 (m, 17H), 8.34 (t, 2H). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.3 (C-CH_3), 96.4 (C_5Me_5), 120.4, 122.9, 123.0, 127.2, 127.9, 129.2, 130.6, 131.1, 131.6, 133.6, 143.2, 144.1, 148.3, 155.0. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 500 (2.14×10^4), 427 (6.03×10^3), 302 (1.16×10^4), 266 (1.65×10^4), 230 (2.47×10^4).

Synthesis of [{(η^5-C_5Me_5)Ir(ndpm)}$_2$(μ-dpph)]$(SO_3CF_3)_2$ (12). Complex **12** was prepared following the above procedure starting from complex **5** (0.535 g, 1.0 mmol) and dpph (0.192 g, 0.50 mmol). Yield: 0.521 g, 64%. Anal. Calcd for $C_{82}H_{82}N_6O_{10}F_6P_2S_2Ir_2$: C, 50.87; H, 4.27; N, 4.34. Found: C, 51.05; H, 4.35; N, 4.23. IR (KBr pellet, cm^{-1}): 1556, 1520, 1381, 1346, 1265, 1150, 1102, 1031, 994, 895, 823, 746, 719, 636, 517. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.54 (s, 30H), 2.17−2.35 (m, 12H), 6.32 (d, 4H, J = 3.9 Hz), 6.49 (d, 4H, J = 3.9 Hz), 7.06−7.49 (m, 28H), 8.26 (t, 4H). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.4 (C-CH_3), 24.3, 25.5, 31.5, 96.3(C_5Me_5), 120.7, 123.0, 123.1, 127.4, 128.1, 129.2, 131.0, 133.4, 134.0, 134.5, 143.4,

Scheme 1



M=Rh(III), X= CN(**1**)**55%**,
X= NO_2(**2**)**58%**, X=OCH_2Ph(**3**)**50%**
M=Ir(III), X=CN (**4**)**54%**, X=NO_2(**5**)**55%**

144.1, 148.3, 155.1. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 496 (2.15×10^4), 430 (6.18×10^3), 302 (1.10×10^4), 268 (1.56×10^4), 226 (2.55×10^4).

Synthesis of [{(η^5-C_5Me_5)Ir(ndpm)}$_2$(μ-bpy)](SO_3CF_3)$_2$ (13). Complex **13** was prepared following the above procedure starting from complex **5** (0.535 g, 1.0 mmol) and 4,4′-bpy (0.078 g, 0.50 mmol). Yield: 0.472 g, 65%. Anal. Calcd for $C_{62}H_{58}N_8O_{10}F_6S_2Ir_2$: C, 45.47; H, 3.57; N, 6.84. Found: C, 45.16; H, 3.43; N, 6.95. IR (KBr pellet, cm^{-1}): 1649, 1553, 1520, 1380, 1344, 1253, 1151, 1030, 994, 822, 721, 635. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.56 (s, 30H), 6.53 (d, 4H, J = 4.5 Hz), 6.69 (d, 4H, J = 3.6 Hz), 7.57 (m, 4H), 8.02 (s, 4H), 8.12 (d, 4H, J = 6.3 Hz) 8.28 (t, 4H), 8.53 (d, 4H, J = 6.0 Hz). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.5 (C-CH_3), 89.5 (C_5Me_5), 120.7, 122.6, 122.9, 125.2, 130.9, 131.4, 132.6, 143.2, 144.7, 145.2, 148.2, 152.0, 153.1. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 496 (2.10×10^4), 427 (6.03×10^3), 302 (1.06×10^4), 267 (1.5×10^4), 227 (2.45×10^4).

Synthesis of [{(η^5-C_5Me_5)Rh(cydpm)}$_2$(μ-N_3)]Cl (14). A suspension of the complex **1** (0.515 g, 1.0 mmol) and sodium azide, NaN_3 (0.033 g, 0.5 mmol), were stirred in dry acetone for 3 h at room temperature. The solvent was removed *in vacuo* and the residue extracted with dichloromethane (10 mL) and filtered to remove solid sodium chloride. The filtrate was concentrated to ~2 mL, and an excess of hexane was added to assist precipitation. The orange-colored product separated, which was filtered, washed with diethyl ether, and dried under vacuum. Yield: 0.425 g 73%. Anal. Calcd for $C_{52}H_{50}ClN_9Rh_2$: C, 59.93; H, 4.84; N, 12.10. Found: C, 59.60; H, 4.71; N, 12.20. IR (KBr pellet, cm^{-1}): 2226, 2016, 1615, 1545, 1446, 1375, 1338, 1248, 1023, 989, 891, 813, 769, 719, 474. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 1.53 (s, 30H), 6.50−6.58 (m, 8H), 7.52 (m, 4H), 7.73 (d, 4H, J = 7.2 Hz), 7.84 (s, 4H). ^{13}C NMR (75.45 MHz, $CDCl_3$, δ ppm): 8.5 (C-CH_3), 96.5 (C_5Me_5), 112.5, 118.7, 119.7, 131.3, 132.3, 134.6, 142.4, 143.8, 152.2. UV−vis (CH_2Cl_2, λ_{max} nm, ε): 493 (2.38×10^4), 430 (8.22×10^3), 303 (1.43×10^3), 266 (2.78×10^4), 225 (3.46×10^4).

Catalytic Experiments. A solution of 1.0 equiv of terephthaldehyde, HCOOH (13 mmol), CH_3COONa (13 mmol), and 1 mol % of the catalyst (few drops of acetonitrile were added for dissolution of catalyst) in water (5.5 mL) was stirred at 50 °C under aerobic conditions. After full conversion had been achieved the reaction was filtered through silica and $MgSO_4$, washed (20% EtOAc/80% hexane), and concentrated under vacuum to give the reduction product. The residue was purified by flash column chromatography.

Crystallographic Studies. Crystals suitable for single-crystal X-ray diffraction analyses for **1**, **2**, **7**, and **11** were grown from dichloromethane and diethyl ether at room temperature using the diffusion technique. Preliminary data on the space group and unit cell dimensions as well as intensity data for **7** and **11** were collected on an Oxford Diffraction X CAUBER-S, while for **1** and **2** on a Bruker SMART APEX diffractometer using graphite-monochromatized Mo Kα radiation. The structure was solved by direct methods and refined using SHELX 97.[16] The non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms attached to carbon were included as a fixed contribution and were geometrically calculated and refined using the SHELX riding model.

Complex 1. Formula = $C_{26}H_{25}ClN_3Rh$, M_r = 517.86, monoclinic space group $C2/c$, a = 16.047(4) Å, b = 16.610(4) Å, c = 19.215(4) Å, α = 90.00°, β = 99.38°, γ = 90.00°, V = 5053(2) Å^3, Z = 8, D_c (Mg m^{-3}) = 1.454, μ = 0.749, T(K) = 293(2), λ = 0.71073 Å, R(all) = 0.0380, $R[I > 2\sigma(I)]$ = 0.0322, wR2 = 0.0784, wR2 $[I > 2\sigma(I)]$ = 0.0760, GooF = 1.121.

Complex 2. Formula = $C_{25}H_{25}ClN_3O_2Rh$, M_r = 537.85, orthorhombic space group *Pbca*, a = 13.2123(11) Å, b = 16.6245(14)v, c = 23.926(2) Å, β = 90.00, V = 5255.3(8) Å^3, Z = 8, D_c (Mg m^{-3}) = 1.530, μ = 0.964, T(K) = 293(2), λ = 0.71073 Å, R(all) = 0.0440, $R[I > 2\sigma(I)]$ = 0.0385, wR2 = 0.1013, wR2 $[I > 2\sigma(I)]$ = 0.0969, GooF = 1.017.

Complex 7. Formula = $C_{45}H_{40}N_3SF_3O_3PRh$, M_r = 893.77, orthorhombic space group *Pnma*, a = 15.3601(14) Å, b = 13.4016(11) Å, c = 19.6671(12) Å, V = 4048.5(6) Å^3, Z = 4, D_c (Mg m^{-3}) = 1.474, μ = 0.572, T(K) = 150(2), λ = 0.71073 Å, R(all) = 0.0734, $R[I > 2\sigma(I)]$ = 0.0634, wR2 = 0.1421, wR2 $[I > 2\sigma(I)]$ = 0.1391, GooF = 1.235.

Complex 11. Formula = $C_{22}H_{16}N_4RuS_2$, M_r = 501.60, orthorhombic space group $P2_12_12_1$, a = 13.0911(11) Å, b = 14.3862(13) Å, c = 21.2380(18) Å, V = 3999.8(6) Å^3, Z = 4, D_c (Mg m^{-3}) = 1.666, μ = 3.495, T(K) = 293(2), λ = 0.71073 Å, R(all) = 0.0403, $R[I > 2\sigma(I)]$ = 0.0336, wR2 = 0.0719, wR2 $[I > 2\sigma(I)]$ = 0.0684, GooF = 0.977.

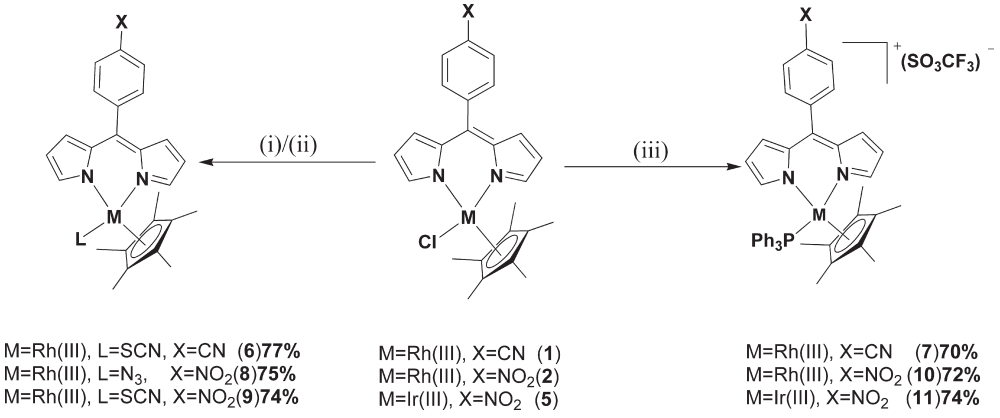
Results and Discussion

Synthesis of the Complexes. The dipyrromethanes employed in this work were synthesized following the literature procedures,[15] and the dipyrrins were obtained by oxidation of the corrresponding dipyrromethane using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in a chloroform/benzene solution. Resulting dipyrrins were not isolated, but used

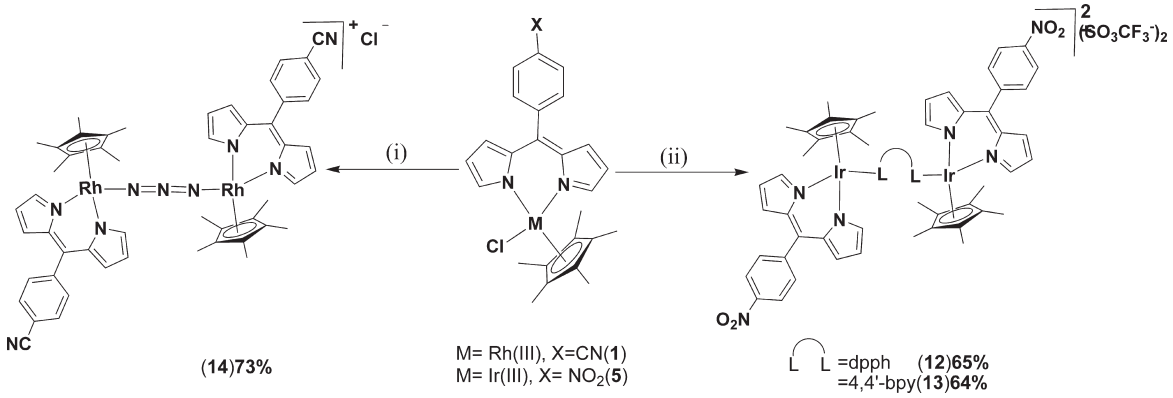
(16) (a) Mackay, S.; Dong, W.; Edwards, C.; Henderson, A.; Gilmox, C.; Stewart, N.; Shankland, K.; Donald, A. *MAXUS*; University of Glasgow: Scotland, 1999. (b) Sheldrick, G. M. *SHELX-97: Programme for refinement of crystal structures*; University of Gottingen: Gottingen, Germany, 1997. (c) PLATON. Spek, A. L. *Acta Crystallogr. A* **1990**, *46*, C31.

(15) (a) Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323–7344. (b) Littler, B. J.; Miller, M. A.; Hung, C. H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391–1396. (c) Lee, C. H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427–11440.

Scheme 2. Synthesis of Mononuclear Complexes (i) NaN_3/Acetone, (ii) NH_4SCN/Acetone, and (iii) $AgSO_3CF_3/PPh_3$/Acetone



Scheme 3. Synthesis of Binuclear Complexes (i) NaN_3/Acetone and (ii) $AgSO_3CF_3$/L-L/Acetone



in situ to generate the desired metal complexes.[17−20] Syntheses of the neutral heteroleptic metal complexes [(η^5-C_5Me_5)RhCl(cydpm)] (**1**), [(η^5-C_5Me_5)RhCl(ndpm)] (**2**), [(η^5-C_5Me_5)RhCl(bdpm)] (**3**), [(η^5-C_5Me_5)IrCl(cydpm)] (**4**), and [(η^5-C_5Me_5)IrCl(ndpm)] (**5**) were achieved by treatment of a solution of the chloro-bridged dimeric precursor complexes [{(η^5-C_5Me_5)M(μ-Cl)Cl}$_2$] (M = Rh or Ir) in dichloromethane in the presence of triethylamine to a solution containing respective dipyrrins. A simple scheme showing the syntheses of neutral heteroleptic metal complexes is depicted in Scheme 1. The complexes were formed under refluxing conditions, after which the products were purified by column chromatography over silica. In general, the complexes obtained are bright orange-red compounds that appeared lustrous green upon removal of the solvent. Complexes **1**−**5** are air-stable solids, and these do not show any signs of decomposition in solution upon exposure to air for several days. These are soluble in polar organic solvents such as chloroform, methanol, ethanol, dichloromethane, acetonitrile, dimethylformamide, and dimethylsulfoxide and insoluble in ether, benzene, and hexane.

Reactivities of the complexes [(η^5-C_5Me_5)RhCl(4-cydpm)] (**1**), [(η^5-C_5Me_5)RhCl(ndpm)] (**2**), and [(η^5-C_5Me_5)IrCl(ndpm)] (**5**) were examined with some nitrogen and phosphorus donor ligands. It was observed that the reactions of **1** and **2** with N_3^- or SCN^- in acetone afforded neutral complexes [(η^5-C_5Me_5)Rh(SCN)(cydpm)] (**6**), [(η^5-C_5Me_5)Rh(N_3)(ndpm)] (**8**), and [(η^5-C_5Me_5)Rh(SCN)(ndpm)] (**9**), wherein Cl^- was replaced by N_3^- or SCN^-. On the other hand, reactions of **1**, **2**, and **5** with PPh_3 or exobidantate ligands dpph and 4,4′-bipyridine in the presence of $AgSO_3CF_3$ afforded cationic mononuclear complexes [(η^5-C_5Me_5)Rh(PPh_3)(cydpm)]SO_3CF_3 (**7**), [(η^5-C_5Me_5)Rh(PPh_3)(ndpm)]SO_3CF_3 (**10**), and [(η^5-C_5Me_5)Ir(PPh_3)(ndpm)SO_3CF_3 (**11**) and dinuclear complexes [{(η^5-C_5Me_5)Ir(ndpm)}$_2$(μ-dpph](SO$_3$CF$_3$)$_2$ (**12**) and [{(η^5-C_5Me_5)Ir(ndpm)}$_2$(μ-bpy)](SO$_3$CF$_3$)$_2$ (**13**).

Further, it was observed that the reaction of **1** with NaN_3 afforded the binuclear complex [{(η^5-C_5Me_5)Rh(cydpm)}$_2$-(μ-N_3)]Cl (**14**). A simple scheme showing the synthesis of derivatives of **1**, **2**, and **5** is depicted in Schemes 2 and 3.

Characterization. The complexes were characterized by elemental analyses, FAB-MS, IR, NMR (^{1}H and ^{13}C), and electronic spectral and electrochemical studies. Analytical data of the complexes (recorded in the Experimental Section) supported the proposed formulations. Information about composition of the binuclear complexes **12** and **14** was also obtained from FAB-MS spectral studies, and resulting spectra along with their assignments are shown in Figures 1 and 2. Fragmentation patterns of these complexes provided valuable information about the relative stability of the various moieties bonded to Ir(III)/Rh(III). Complex **12** in its FAB mass spectrum displayed peaks at m/z 1787(1786.46, 66.67%), 1046(1046.35, 37.50%), and 592(592.16, 100.00%), assignable to [$M^+ - SO_3CF_3$], [$M^+ - (SO_3CF_3 +$ IrCp*(ndpm)], and [$M^+ - (SO_3CF_3 +$ IrCp*(ndpm) + dpph)],

(17) Brückner, C.; Zhang, Y.; Rettig, S. J.; Dolphin, D. *Inorg. Chim. Acta* **1997**, *263*, 279–286.
(18) Brückner, C.; Karunaratne, V.; Rettig, S. J.; Dolphin, D. *Can. J. Chem.* **1996**, *74*, 2182–2193.
(19) Cohen, S. M.; Halper, S. R. *Inorg. Chim. Acta* **2002**, *341*, 12–16.
(20) Halper, S. R.; Cohen, S. M. *Chem.—Eur. J.* **2003**, *9*, 4661–4669.

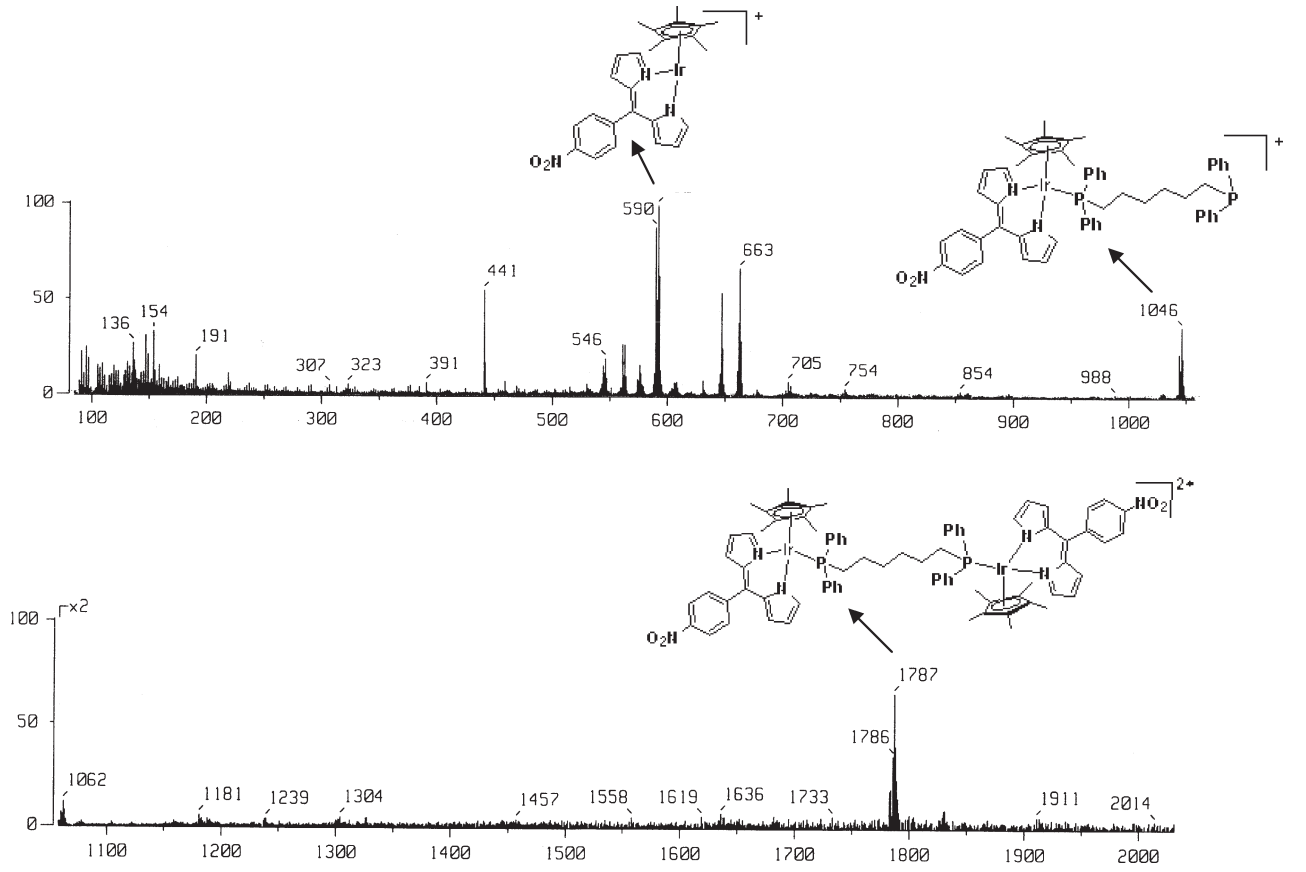


Figure 1. FAB mass spectrum of complex **12**.

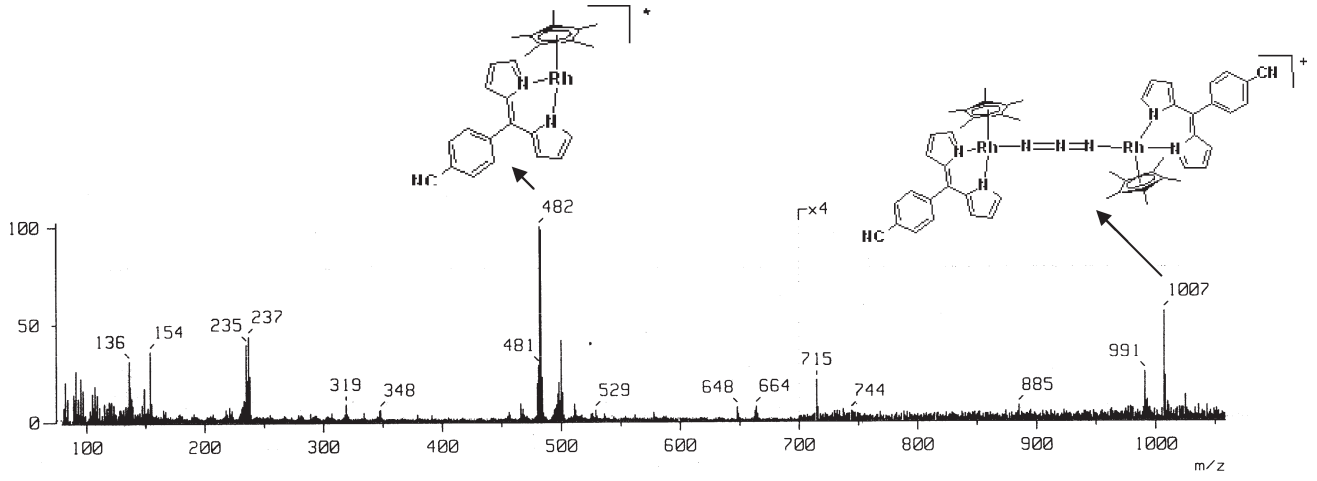


Figure 2. FAB mass spectrum of complex **14**.

respectively, while complex **14** exhibited prominent peaks at *m*/*z* 1007(1006.23, 57.00%) and 482(482.11, 100.00%). The presence of molecular ion peaks at *m*/*z* 1787(1786.46) and 1007(1006.23) in the FAB-MS of **12** and **14**, respectively, strongly supported formation of the binuclear complexes.

^{1}H and ^{13}C NMR spectral data of the complexes are in good agreement with their respective formulations. To facilitate assignment of various resonances, ^{1}H−^{1}H COSY experiments were performed, and the resulting spectrum for complex **2** is shown in Figure 3. Upon complexation with the metal center, the dipyrrin protons exhibited an appreciable downfield shift as compared to that in the respective dipyrromethanes. In general, α-pyrrolic protons (∼δ 6.76) displayed a significant deshielding (∼δ 7.83), and the β-protons in **1**, **2**, **4**, and **5**, where the *meso*-susbstituent contains an electron-withdrawing group (−CN or NO_2) appeared as two doublets (closely spaced). On the other hand, in complex **3**, in which *meso*-susbstituent contains an electron-releasing group (−OCH_2Ph), these appeared as two well-resolved doublets (Figure S1). In the iridium complexes **4** and **5** separation between the doublets is somewhat larger as compared to that in the rhodium complexes **1** and **2**. For example, the ^{1}H NMR spectra of complex **2** exhibited

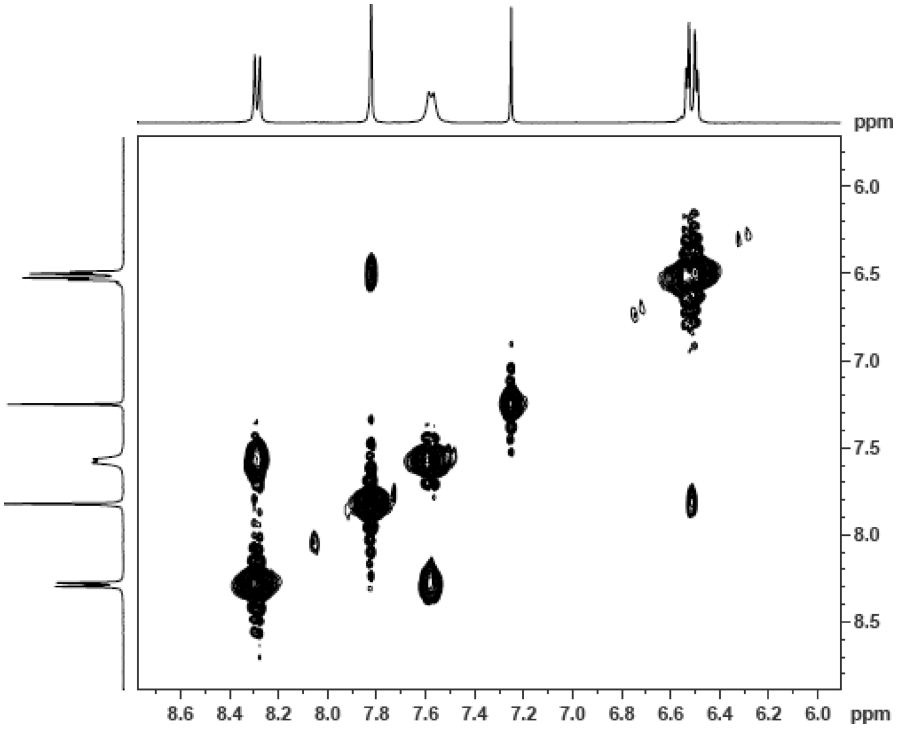


Figure 3. $^{1}H-^{1}H$ COSY spectrum of complex **2** in $CDCl_3$.

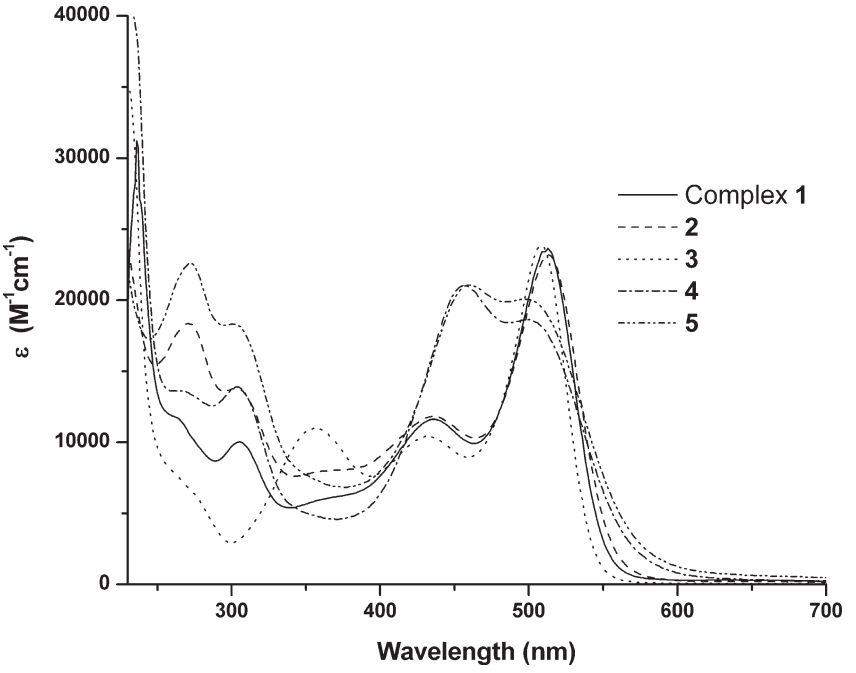


Figure 4. UV−visible spectra of complexes **1**−**5** in dichloromethane.

resonances at 6.50(d, 2H, $J = 4.8$ Hz), 6.54(d, 2H, $J = 4.5$ Hz), 7.58(d, 2H, $J = 9.0$ Hz), 7.83(s, 2H), and 8.29(d, 2H, $J = 8.4$ Hz) ppm assignable to pyrrolic and phenyl protons of the dipyrrin (ndpm). This region of the spectrum integrated for 10 protons, as expected for the coordinated ndpm ligand. The protons due to pentamethylcyclopentadienyl resonated at δ 1.52(s, 15H) ppm. The position and integrated intensity of various signals conformed well to the proposed formulation of the complex. Similar trends have been observed in the ^{1}H NMR spectra of other complexes. In the $^{13}C\{^{1}H\}$ NMR spectra of complex **2**, the ndpm carbons resonated at 119.8, 122.6, 132.2, 134.9, 143.2, 144.6, 147.9, and 154.0, whereas pentamethylcyclopentadienyl[21] carbons resonated at 8.55(C-CH_3) and 94.78(C_5Me_5) ppm. In general, it is observed that the number of signals in the ^{13}C NMR spectra of the complexes was not in agreement with the number of expected signals. This discrepancy may be attributed to the resonance of various types of carbons at the same position.

(21) Herberich, G. E.; Ganter, B. *Inorg. Chem. Commun.* **2001**, *4*, 100–103.

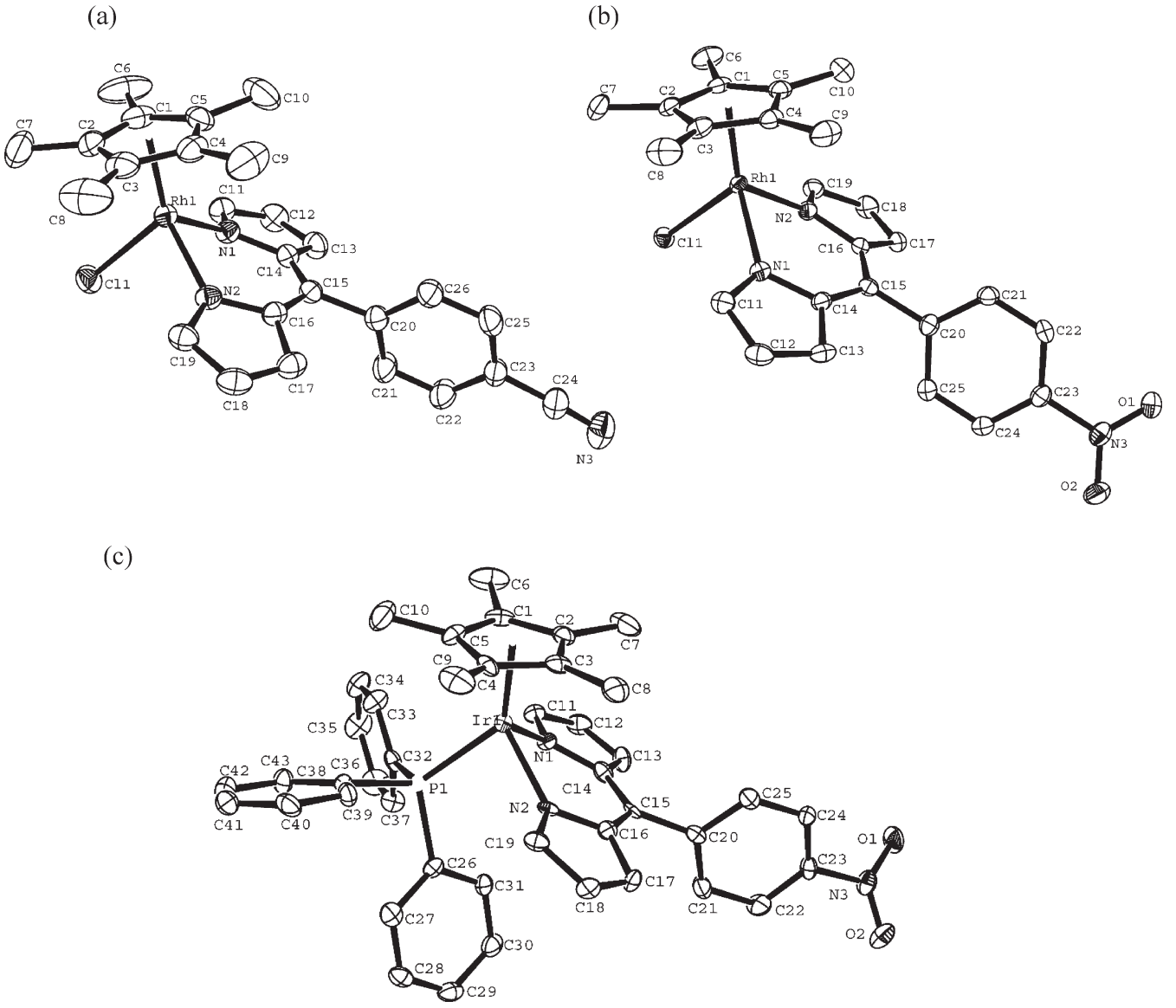


Figure 5. ORTEP views of **1**, **2**, and **11** at 30% probability. Hydrogen atoms and the trifluoromethanesulfonate anion are omitted for clarity.

Comparative electronic spectra of the mononuclear complexes **1**−**5** in dichloromethane are depicted in Figure 4. Electronic spectra of complexes **1**−**5** showed moderately intense bands in the region ~512, 435, 304, 269, and 228 nm (see Experimental Section). By analogy with the earlier reports the intense low-energy bands (512/435 nm) have been assigned to highly conjugated dipyrrin-based $S_0 \rightarrow S_1$ ($\pi \rightarrow \pi^*$) transitions[22] along with metal-dipyrrin charge transfer transitions in the visible region.[17,20,22c] The higher energy bands may be ascribed to the dipyrrin-based $\pi \rightarrow \pi^*$/n $\rightarrow \pi^*$ transitions.[17,20,22] In complex **3**, the bands at 355 nm exhibited a red shift in comparison to the complexes **1**, **2**, **4**, and **5** (~304 nm). This shift may be attributed to the presence of a benzyloxy chromophore. The pentamethylcyclopentadienyl (Cp*) mainly shows low-intensity $\pi \rightarrow \pi^*$ transition bands in the UV region overlapping with dipyrrin-based $\pi \rightarrow \pi^*$/n $\rightarrow \pi^*$ transitions.[23] The absorption bands for the iridium complexes are blue-shifted in comparison to their rhodium counterparts; this may be attributed to the greater sepration between t_{2g} and eg sets of orbitals in Ir(III). Emission experiments on the complexes were carried out in DCM with 1.0 mM solutions at rt. Upon excitation at their respective lowest energy bands, these complexes did not exhibit any emission.

Molecular Structures. Molecular structures of the representative complexes **1**, **2**, **7**, and **11** have been determined crystallographically. Details about the data collection, solution, and refinement are summarized in the Experimental Section. Molecular structures with atom-numbering schemes are shown in Figure 5, and important geometrical parameters are gathered in Table S1.

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(23) (a) Chandra, M.; Sahay, A. N.; Mobin, S. M.; Pandey, D. S. *J. Organomet. Chem.* **2002**, *658*, 43–49. (b) Singh, S. K.; Chandra, M.; Dubey, S. K.; Pandey, D. S. *Eur. J. Inorg. Chem.* **2006**, 3954–3961. (c) Singh, S. K.; Trivedi, M.; Chandra, M.; Pandey, D. S. *J. Organomet. Chem.* **2005**, *690*, 647–652.

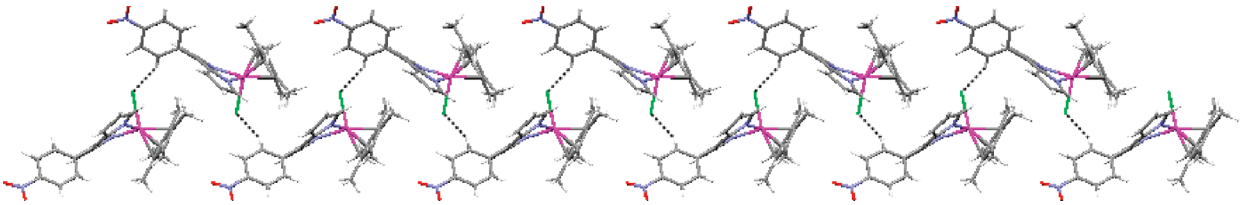

Figure 6. Linear chain resulting from C−H···Cl interaction along the *b*-axis in complex **2**.

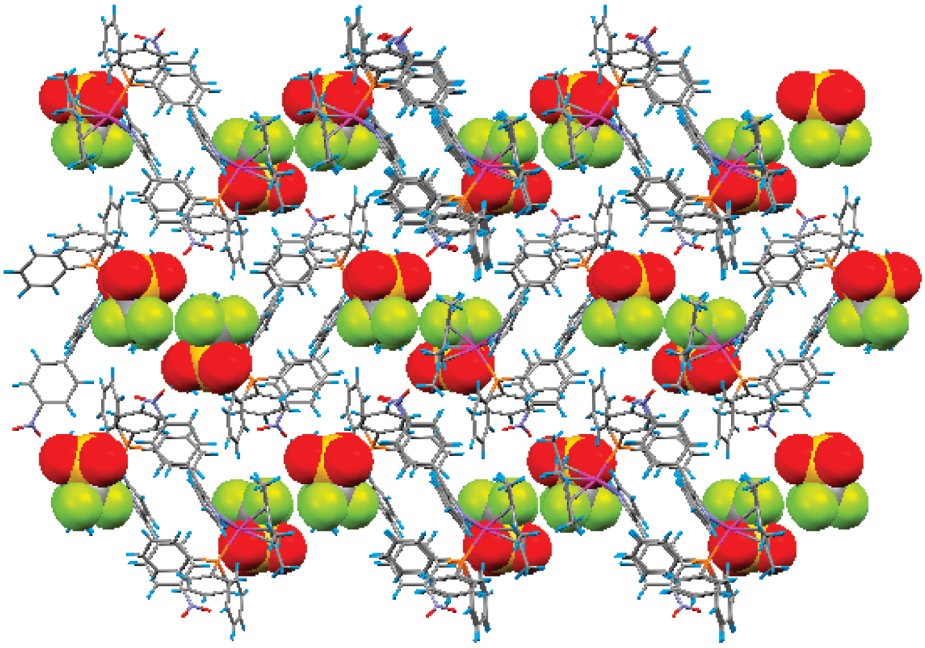

Figure 7. H-bonding interactions along the *a*-axis in complex **11**.

A common structural feature of the rhodium complexes **1**, **2**, **7**, and iridium complex **11** is the arrangement of various groups about the metal centers rhodium and iridium. In these complexes the rhodium (**1**, **2**) metal center is coordinated to the dipyrrin nitrogen N(1) and N(2), chloro group Cl(1), and pentamethylcyclopentadienyl ring in a η^5-manner, while in **7** and **11** the rhodium (**7**) or iridium (**11**) metal center is coordinated through P(1) of the PPh_3 in place of Cl(1) [one of the phenyl rings of the coordinated PPh_3 ligand in **7** is highly disordered]. Considering the pentamethylcyclopentadienyl ring as a single coordination site, the overall coordination geometry about the rhodium or iridium metal center might be described as a piano-stool geometry. Average C−C distances in the pentamethylcyclopentadienyl rings are 1.410 and 1.431 Å in **1** and **2**. The rhodium to carbon distances are almost equal, with an average Rh−C distance of 2.148 in **1** and 2.161 Å in **2** and the rhodium metal center is displaced from the centroid of the pentamethylcyclopentadienyl ring by 1.785, 1.786, and 1.844 Å respectively in **1**, **2**, and **7**, which are comparable to the values reported in other rhodium complexes.[24] The metal to centroid of the pentamethylcyclopentadienyl ring distance in **7** is longer than that in its precursor complex **1**. The Rh−Cl bond distances are 2.3949(9) and 2.4091(8) Å in **1** and **2**, respectively, which are normal and comparable to those reported in other related systems.[24] The rhodium to pyrrolic nitrogen distances [Rh(1)−N(1), Rh(1)−N(2)] are 2.065(2), 2.068(2) Å in **1**, 2.082(3), 2.066(3) Å in **2**, and 2.089(4), 2.089(4) Å in **7**, which are comparable to Rh−N distances reported in the literature. The dipyrrinato bite angles N(1)−Rh(1)−N(2) are 85.02(9)°, 85.49(10)°, and 87.6(2)°, respectively in **1**, **2**, and **7**. The Rh−P distance in **7** is 2.335(2) Å, which is again comparable to the Rh−P distances in other rhodium complexes. As expected, the *meso*-phenyl substituents are twisted out of plane from the dipyrrin π-system by −75.4° in **1**, −113.8° in **2**, -90.8° in **7**, and −88.0° in **11**.

The iridium to pyrrolic nitrogen of dipyrrin distances in **11** [Ir(1)−N(1), Ir(1)−N(2)] are comarable and are 2.074(5) and 2.090(5) Å. The pentamethylcyclopentadienyl ring in this complex is almost planar, and iridium is displaced from the centroid of the pentamethylcyclopentadienyl ring by 1.843 Å. The metal to centroid of the pentamethylcyclopentadienyl ring distance in **11** is normal and comparable to the values reported in other iridium complexes.[24,25] The Ir−P distance in **11** is 2.3167(13) Å, which is again comparable to the Ir−P distances in other iridium complexes. The bond angle between iridium and N(1) and N(2) nitrogens of dipyrrin is 86.64(16)° (Table S1).

Crystal packing in complexes **1**, **2**, **7**, and **11** is stabilized by C−H···X type (X = Cl, F, N, O) intermolecular hydrogen bonding. The C−H···Cl (C(25)−H(25)···Cl(1) = 2.82 Å) interaction in complex **2** leads to linear structural motifs shown in Figure 6. The C−H···F, C−H···N, and C−H···O weak bonding interactions are present in complex **11**. A simple view

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Table 1. Electrochemical Data of the Complexes 1−5

complex	$E_{1/2}$, V (ΔE, mV)	$E_{p,a}$, V
1	0.83(74)	0.70
2	0.86(76)	0.72
3	0.78(78)	0.66
4	0.92(83)	0.75
5	0.94(71)	075

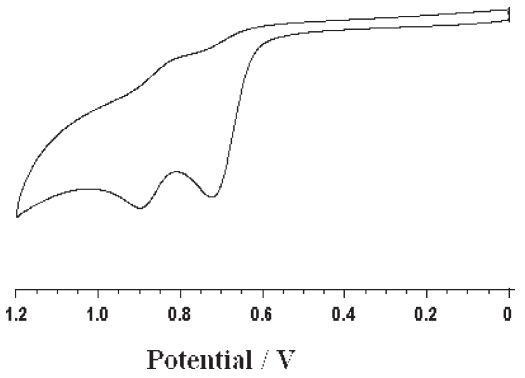
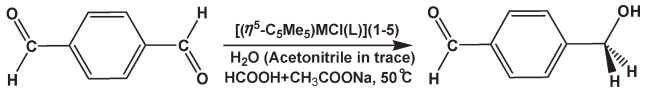


Figure 8. Cyclic voltammogram of complex **2** (vs Ag/Ag^+) in acetonitrile.

resulting from these interactions is shown in Figure 7. Matrixes for weak hydrogen bonding interactions in these complexes are shown in the Supporting Information Table S2.

Electrochemistry. The redox properties of compounds **1−5** were followed by cyclic voltammetry (CV) using 0.1 M *tert*-butylammoniumperchlorate (TBAP) in acetonitrile as supporting electrolyte. The potential of the Fc/Fc^+ couple under the experimental conditions was 0.10 V (80 mV) vs Ag/Ag^+. The electrochemical data are presented in Table 1. The cyclic voltammogram (CV) for compound **2** is depicted in Figure 8. The neutral complexes **1−5** exhibited one-electron reversible oxidation corresponding to the M(IV/III) (M = Rh, Ir) redox couple at the half-wave oxidation potential values ($E^{ox}_{1/2}$ in V vs Ag/Ag^+) in the range 0.78−0.94 V.[26] Although the i_{pa}/i_{pc} ratio is less than 1 for metal-based oxidation, it may be due to deposition of the electrogenerated species at the electrode surface. The complexes **1−3** showed that the oxidation potentials are affected by the electron-withdrawing/donating ability of the *meso*-substituents of the dipyrrinato ligands. Electron-donating groups (benzyloxy **3**) increase the electron density on the ligand and also on the rhodium center, which in turn leads to the redox process occurring at more negative potentials, while the opposite effect occurs when electron-withdrawing groups are used. The iridium complexes **4** and **5** exhibited more anodic redox potential compared to that in rhodium complexes **1−3**. All the complexes exhibited an additional oxidation wave with lower current intensity at a potential of ca. 0.66−0.75 V. This may be attributed to the oxidation of respective dipyrrins; this value falls within the range for dipyrrinato complexes.[1,27,28]

Scheme 4. Transfer Hydrogenation of Terephthalaldehyde with Catalysts 1−5 in Water and Aerobic Conditions[a]



Catalyst	% Conversion	T(h)	TOF[a](h^{-1})
none	< 20	10	< 2
1	> 99	1.5	66.7
2	> 99	1	100
3	> 99	2	50
4	> 99	3	33
5	> 99	3	33

[a] Based on > 99 % conversion.

[a] S/C ratio is 100.

Catalytic Studies. Transfer hydrogenation reactions of aldehyde were catalyzed by a number of half-sandwich Rh/Ir complexes. However, the reaction necessitated high temperature and inert atmosphere.[29] The selective reduction of terephthalaldehyde was carried out either with $NaBH_4$ or via catalytic hydrogenation using Pd/C catalysis or metallocenes; in all cases conversion yield is not good and also needs an organic solvent system.[30] To evaluate the selectivity and efficiency of complexes **1−5** as catalysts toward reduction of the diformyl group, terephthalaldehyde was used as a model substrate. Transfer hydrogenation was initiated by introducing formic acid−sodium acetate and terephthalaldehyde (1.0 mmol) in water (a few drops of acetonitrile was used to dissolve the catalyst) and air at 50 °C with 1% catalyst. All the complexes were found to catalyze transfer hydrogenation of terephthalaldehyde to produce 4-hydroxymethybenzaldehyde in aqueous solution (Scheme 4). It was observed that in all the cases only one formyl group of terephthalaldehyde was selectively reduced. Further, we found that the rhodium complexes **1** and **2** led to almost complete conversion of terephthalaldehyde into 4-hydroxymethylbenzaldehyde in 1 h. Analogous iridium complexes **4** and **5** were less active as compared to the rhodium complexes **1** and **2**, and using these, complete conversion of the substrate takes place in 2 h. However, complex **3** required 3 h for the same reduction and **3** is least effective in this regard. Among the rhodium complexes dipyrrin containing electron withdrawing *meso*-substituents (CN, NO_2) are more effective than its electron-releasing counterparts. This may be due to the inductive effect of the substituents on the metal center.

Conclusion

Through this work an attempt has been made to synthesize and characterize a series of heteroleptic piano-stool rhodium/iridium(III) complexes imparting dipyrrin as

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co-ligands. The complexes represent the first example of heteroleptic complexes of rhodium/iridium containing both dipyrrin and pentamethylcyclopentadienyl ligands. Furthermore, it has been shown that complexes **1**−**5** effectively catalyze the reduction of terephthalaldehyde, and among these, the rhodium complexes **1** and **2** are more effective transfer hydrogenating catalysts for use in water and air.

Acknowledgment. Thanks are due to the Council of Scientific and Industrial Research, New Delhi, India, for providing financial assistance through the scheme HRDG 01(2074)/06/EMR-II. We also thank the Head, SAIF, Central Drug Research Institute, Lucknow, for providing spectral facilities, and National Single Crystal X-ray Diffraction Laboratory, Indian Institute of Technology, Powai, Mumbai, for X-ray facilities. Special thanks are due to Prof. P. Mathur, Department of Chemistry, IIT, Mumbai, for encouragement.

Supporting Information Available: Figures S1−S16, full crystallographic data for the structure determination of **1**, **2**, **7**, and **11** in CIF format and tables S1−S2. This material is available free of charge via the Internet at http://pubs.acs.org.