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PAPER

Rhodium complexes bearing tetradentate diamine-bis(phenolate) ligands†

Xiang Y. Liu,[a] Kapil S. Lokare,*[b] Somesh K. Ganesh,[a] Jason M. Gonzales,[c] Jonas Oxgaard,[c] William A. Goddard III*[c] and Roy A. Periana*[b]

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Using tetradentate, dianionic ligands, several new rhodium complexes have been prepared. Some of these diamine-bis(phenolate) compounds, are active for C–H activation of benzene. These complexes are air and thermally stable. All four complexes were characterized by X-ray diffraction.

Introduction

First reported in 2000,[1] the family of *trans*-(κ^2-acac-O,O)$_2$Ir(R)(L) (acac = acetylacetonato, R = hydrocarbyl, L = dative ligand) O-donor complexes have been shown to be capable of activating C–H bonds and catalyze the selective, *anti*-Markovnikov hydroarylation of unactivated olefins with arenes.[2] These complexes are relatively simple to synthesize and remarkably, likely due to unique properties imparted by O-donor ligands, solutions are thermally stable to air and basic as well as acidic media. Mechanistic studies show that these *trans* bis-acac-O,O Ir(III) complexes are catalyst precursors and that the active catalysts are generated by loss of L, followed by rate determining *trans* to *cis* isomerization to generate coordinatively unsaturated, five-coordinate pseudo square pyramidal complexes with the four O's of the two acac-O,O ligands in a meridional geometry that places the R group *cis* to an open site.[3] In an effort to design more active catalysts with similar reactivity and stability we sought to explore related metal complexes with tetradentate O-donor ligands that were already locked into meridional geometry. Recently, tetradentate diamine-bis(phenols) {NN′O$_2$} that enforce a meridional geometry with Ti and Zr have emerged as alternative ligands in developing new catalysts for polymerization of α-olefins[4] and as sulfoxidation catalysts with V.[5] In order to test whether replacing the bis-acac-O,O motifs with these ligand could lead to more efficient C–H activation and olefin arylation chemistry we synthesized several new rhodium complexes, Rh(NN′O$_2$)(R)(L). In this contribution we report the synthesis, structure, and reactivity of these new complexes towards arenes.

[a]*Loker Hydrocarbon Institute, Department of Chemistry, University of Southern California, Los Angeles, California, USA, 90089*
[b]*The Scripps Research Institute, Scripps Florida, Jupiter, Florida, USA, 33458. E-mail: rperiana@scripps.edu; Fax: 1-561-228-3064; Tel: 1-561-228-2457*
[c]*Materials and Process Simulation Center, California Institute of Technology, Pasadena, California, USA, 91125. E-mail: wag@wag.caltech.edu*

† Electronic supplementary information (ESI) available: Additional data. CCDC reference numbers 788725–788728. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00997k

Results and discussion

The ligands $H_2N^{py}N'O_2^{tBu}$ (**1a**), $H_2N^{NMe2}N'O_2^{Me}$ (**1b**), and $H_2N^{py}N'O_2^{Me}$ (**1c**) were synthesized in a single-step Mannich condensation reaction using the general procedure developed by Kol and coworkers.[6] The reaction of $H_2NN'O_2$ ligands with the commercially available $RhCl_3{\cdot}(H_2O)_x$ afforded the chloro complexes **2a**, **2b**, **2c** as yellow-orange microcrystalline solids in moderate yields as shown in Fig. 1. These complexes were readily crystallized from a mixture of CH_3OH–$CHCl_3$ (1 : 1) at −30 °C, which were then analyzed by X-ray crystallography (see supporting information for the metric parameters for complexes **2a–2c**†). The geometry around the Rh center for all three complexes can be described as a distorted octahedral and the ORTEP drawing of the molecular structures of **2a**, **2b**, and **2c** are presented in Fig. 2. As can be seen the tetradentate NN′O$_2$ spectator ligands enforce a meridional geometry in these complexes that afford the

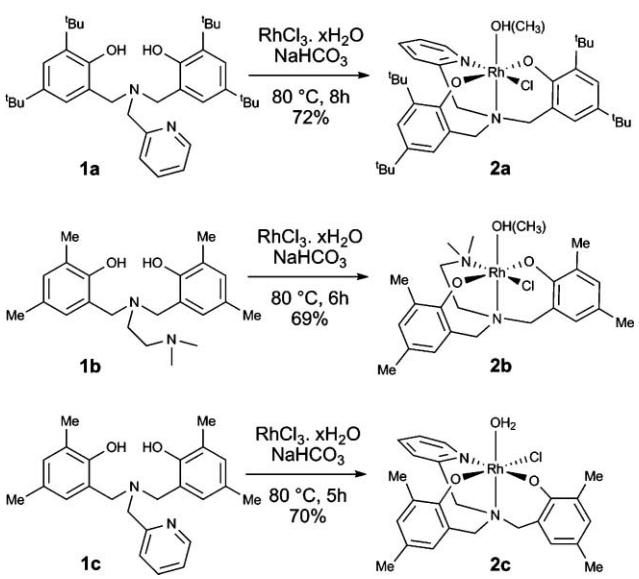

Fig. 1 Synthesis of the complexes **2a–2c**.

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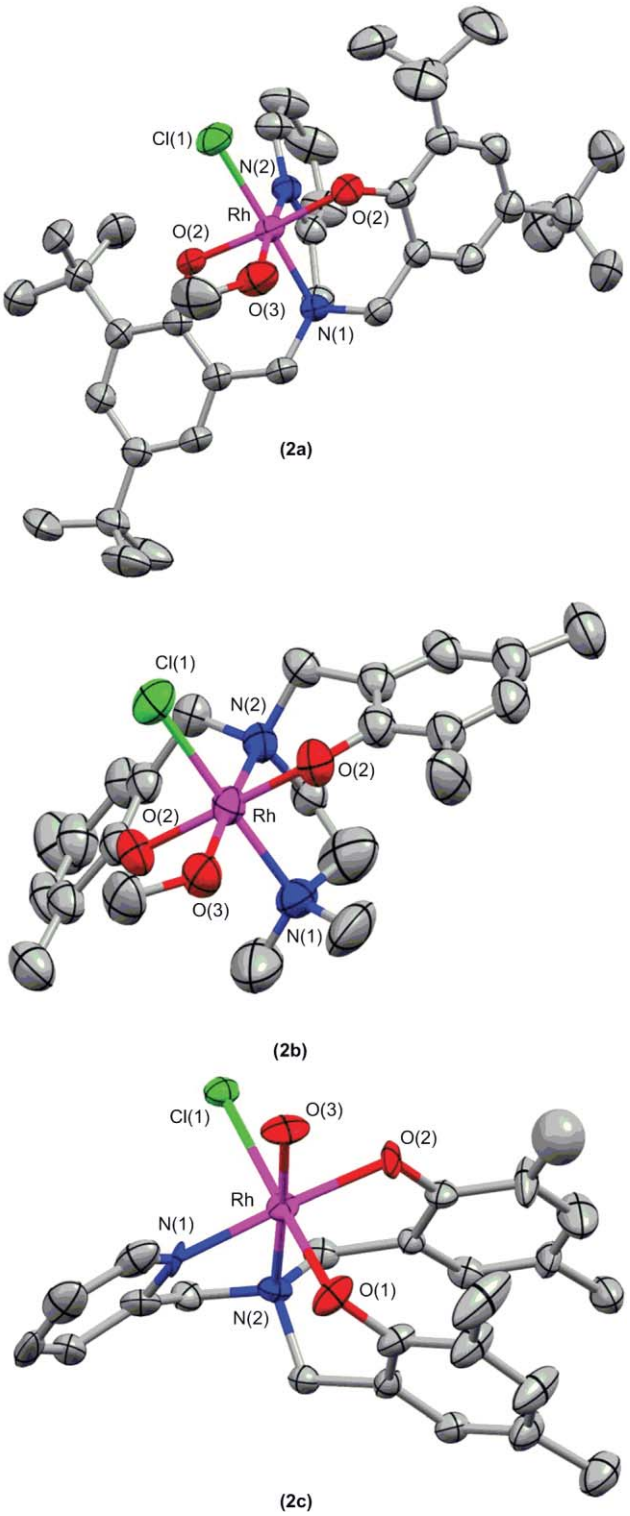

Fig. 2 ORTEP representation (50% probability level) of the molecular structure of complexes **2a–2c**. Solvent molecules as well as hydrogen atoms were omitted for clarity.

required *cis*-geometry for the other two sites where reaction could occur.

The structures for **2a**, **2b**, and **2c** in the solid state are consistent with solution NMR data with a *trans*-O,O for **2a**, with *trans*-bond angles O(1)–Rh(1)–O(2), O(3)–Rh(1)–N(2), and Cl(1)–Rh(1)–N(1) of 176.08(9), 174.89(11), and 178.26(8) respectively, *trans*-O,O for **2b**, with *trans*-bond angles O(1)–Rh(1)–O(2), O(3)–Rh(1)–N(1), and Cl(1)–Rh(1)–N(2) of 170.68(13), 176.73(14), and 178.75(13) respectively, and *cis*-O,O for **2c** with *trans*-bond angles O(1)–Rh(1)–Cl(1), O(3)–Rh(1)–N(2), and O(2)–Rh(1)–N(1) of 174.26(17), 177.1(2), and 175.4(2) respectively.

The selective *trans*-O,O in **2a** and *cis*-O,O in **2c** may be attributed to the subtle steric bulk between the two *tert*-butyl substituents in **2a**. Similar selectivity in geometry is consistent with the observations made by Mountford and coworkers for the corresponding $Zr(N^{py}N'O_2{}^{tBu})Cl_2$ {*trans*-O,O}, and $Zr(N^{py}N'O_2{}^{Me})Cl_2$ {*cis*-O,O}.[7] However, it is not *a priori* obvious why complex **2b** also favours *trans*-O,O. Consequently, we turned to DFT calculations (B3LYP/LACVP** using Jaguar 6.5 program suite, see supporting information for more information†). DFT calculations on the complexes *cis*/*trans*-**2a** indicate that the *trans*-**2a** (0.0 kcal mol^{-1}) is favored over *cis*-**2a** (3.4 kcal mol^{-1}). Similarly, *trans*-**2b** (0.0 kcal mol^{-1}) is favored over *cis*-**2b** (2.8 kcal mol^{-1}) and *cis*-**2c** (0.0 kcal mol^{-1}) is favored over *trans*-**2c** (1.5 kcal mol^{-1}). Since the *cis*-*trans* isomers are only separated by a couple kcal mol^{-1} in solution, if the barrier to rearrange is manageable, both would be accessible during catalysis.

Moreover, as expected, the calculations suggest that the methyl analogues **2b** and **2c** do not show any preferences on the basis of sterics in either *cis* or *trans*-O,O coordination. However, *trans*-**2c** exhibits substantial angle strain in the Rh–N–CH_2–C═N–Rh metallacycle, as the coordination of the two phenolates *trans* to each other "push" the metallacycle into a planar configuration. This is not a problem in *trans*-**2b**, with a more flexible side arm as compared to complex **2c**.

Thus, we can conclude that electronically, the *trans*-O,O coordination is favored by 3 kcal mol^{-1}. Making the N–C–C–N bridge more rigid increases the energy of the *trans*-O,O coordination, causing *cis*-**2c** to be favored, while the introduction of sterics on the phenolates increases the energy of the *cis*-O,O coordination, thus favoring the *trans*-O,O coordination in **2a**.

The Rh–N(1) distances vary from 2.019(7) to 2.040(2) Å in this set of compounds. While, the Rh–N(2) distances vary over much of this range for this series, 1.958(6) to 2.095(4) Å. In addition, the Rh–O distances vary together and are the same within error in complexes **2a–2c**. The Rh–Cl distances are particularly sensitive to changes in ligands on Rh and, vary from 2.3475(13) to 2.3757(9) Å.

We were particularly interested in preparing Rh–Ar derivatives because of their importance as catalysts for C–H activation. Consequently, reaction of **2c** with Ph_2Hg in CH_2Cl_2–CH_3OH (2 : 1) at room temperature afforded complex **3** as a yellow-orange powder in 60% yield. PhLi, Ph_2Zn and PhMgBr afforded complex reaction mixtures. Crystallization from CH_2Cl_2–hexane (1 : 1) yielded microcrystals of **3**, which were analyzed by X-ray crystallography. The ORTEP drawing of the molecular structure of **3** is presented in Fig. 3. The solution NMR data and the solid state structure for **3** closely resembles **2c**, with the only notable difference being the expected replacement of the chloride with a phenyl group. The *trans*-bond angles O(1)–Rh(1)–N(2), O(2)–Rh(1)–C(25), and O(3)–Rh(1)–N(1) are 175.6(3), 173.2(3), and 177.2(3) respectively. The Rh(1)–C(25)

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Table 1 Comparison of the bond lengths (Å) of different Rh(III)–C(phenyl) bonds in the crystal structures of **3** and analogous complexes

Complex	Rh–C(phenyl)	Ref.
$Rh(N^{py}N'O_2^{Me})(CH_3OH)(Ph)$ (**3**)	2.037(9)	This work
$Rh(acac\text{-}O,O)_2(CH_3OH)(Ph)$	1.970(3)	8
Rh(PNP)(Ph)(Br)	2.005(6)	9
$RhCp^*(C(O)(CH_2)_2SiMe_3)(PMe_3)(Ph)$	2.0636(12)	10
$RhCp^*(PMe_3)(Ph)(Br)$	2.054(9)	11
$RhCp^*(PMe_2Ph)(Ph)(Br)$	2.082(6)	12
$RhCp^*(PMePh_2)(Ph)(Br)$	2.065(5)	12
$RhCp^*(PPh_3)(Ph)(Br)$	2.08(1)	12
$[RhCp^*(PMe_3)(Ph)(CH_2Cl_2)][BAr'_4]$	2.026(8)	13

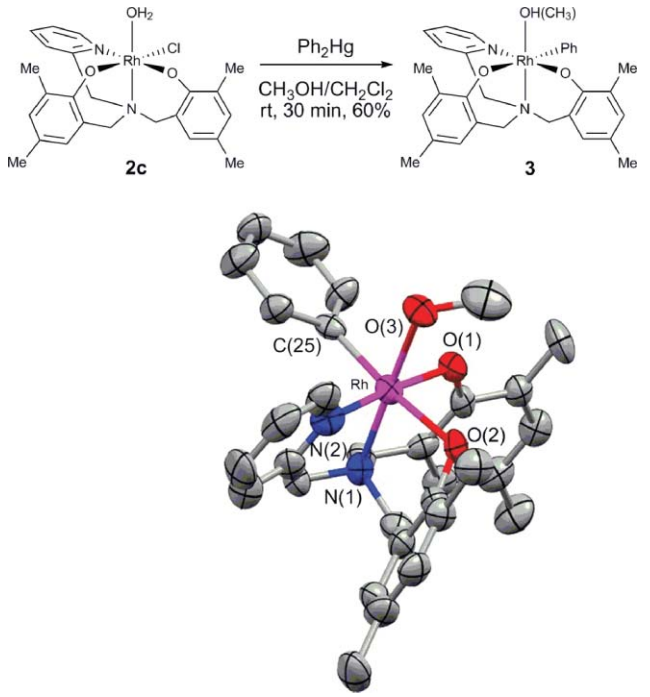

Fig. 3 Synthesis of complex **3** and ORTEP representation (50% probability level) of the molecular structure of complex **3**. Solvent molecules as well as hydrogen atoms were omitted for clarity.

bond length 2.037(9) is slightly longer than 1.970(3) to the analogous CH_3OH adduct $(acac\text{-}O,O)_2Rh(Ph)(CH_3OH)$ reported by our group.[8] This Rh–(phenyl) bond distance is intermediate to the distances reported for the other published Rh(III) complexes (Table 1).

As expected on the basis of analogues studies with the chloro acac-O,O Ir(III) complexes, $(acac\text{-}O,O)_2Ir(L)Cl$, the chloro complexes **2a–2c**, were found to be inactive for C–H activation and decompose at temperatures above 160 °C. However, the phenyl analogue of the chloro complex **2c**, complex **3**, was found to catalyze H/D scrambling of a C_6H_6/C_6D_6 mixture. Computational and experimental studies of the reaction mechanisms, activation barriers and efforts to design complexes for C–H activation with alternative ancillary ligands are in progress.

Conclusions

In summary we have reported a series of $Rh(NN'O_2)$ complexes. The $NN'O_2$ ligand framework is readily accessed and has proven useful in C–H activation reactions. A variety of rhodium complexes are synthesized with this tetradentate ancillary ligand. Unlike complex **3**, the isolated complexes **2a–2c** are inactive for C–H activation. It is hoped that these complexes and derivatives may provide a new, general class of reactive complexes for C–H activation.

Experimental

General considerations

All manipulations of air sensitive materials were carried out in an MBraun glove box or using standard Schlenk techniques under an atmosphere of purified argon. Ethereal solvents, pentane, and toluene were purchased from Aldrich Chemical Co. or EMD and purified through alumina columns to remove water after sparging with argon to remove oxygen. NMR solvents were purchased from Cambridge Isotopes Laboratories, Inc. and degassed prior to use. NMR spectra were taken on Bruker instruments located in the Chemistry Department at The Scripps Research Institute, Florida. All chemical shifts are reported in units of ppm and referenced to the residual protonated solvent. The ^{13}C NMR assignments are based on decoupled ^{13}C, peak heights for overlapping signals, and DEPT experiments. All spectra were recorded at 23 °C. Combustion analyses were performed by facilities at Columbia Analytical Services, Tucson, Arizona. Multiple runs for the elemental analysis of complexes **2a**, **2c** and **3** did not afford reliable results, due to relatively labile solvent ligands. ESI-MS experiments were performed by facilities at the University of Illinois. Celite was dried at a temperature > 220 °C under dynamic vacuum for at least 24 h, then stored under argon. $RhCl_3\cdot(H_2O)_3$ was purchased from Pressure Chemical Co. and used without purification. All high-resolution mass spectra were obtained by UCLA Pasarow Mass Spectrometry Laboratory on either an ESI or a MALDI-TOF mass spectrometer.

Synthesis of $Rh(N^{py}N'O_2^{tBu})(Cl)(CH_3OH)$ (2a). A 50 mL Schlenk bomb was loaded with $RhCl_3\cdot(H_2O)_3$ (230 mg, 0.89 mmol) in water (5 mL). To this was added a solution of $H_2N^{py}N'O_2^{tBu}$ (485 mg, 0.89 mmol, 1 equiv.) in acetone (10 mL). The reaction mixture was heated at 80 °C for 5 min to afford a homogeneous orange solution. After 5 min, $NaHCO_3$ (150 mg, 1.78 mmol) was added to the reaction mixture and the mixture heated at 80 °C for 8 h. After 8 h, the reaction mixture was filtered through Celite, and the volatiles were removed *in vacuo*. The desired product was crystallized from a minimum amount of $CH_3OH–CH_2Cl_2$ (1 : 1) at −30 °C as light orange micro-crystals (414 mg, mmol, 72%). The NMR spectroscopic data are consistent with *trans*-isomer in $CDCl_3$: CH_3OH. ^1H NMR (400 MHz, $CD_3OD/CDCl_3$, 1 : 1): 9.41 (d, J_{HH} = 6 Hz, 1H, Py), 7.41 (t, J_{HH} = 7.5 Hz, 1H, Py), 7.00 (t, J_{HH} = 7 Hz, 1H, Py), 6.90 (d, J_{HH} = 3 Hz, 2H, Ar), 6.87 (d, J_{HH} = 3 Hz, 2H, Ar), 6.75 (d, J_{HH} = 8 Hz, 1H, Py), 4.90 (d, J_{HH} = 13 Hz, 2H, CHAr, CHAr′), 4.29 (s, 2H, CH_2Py), 3.53 (d, J_{HH} = 13 Hz, 2H, CHAr′, CHAr), 1.22 (s, 18H, t-Bu), 1.19 (s, 18H, t-Bu). $^{13}C\{^1H\}$ NMR ($CD_3OD/CDCl_3$): 157.1, 154.1, 148.7, 141.4, 138.1, 136.9, 125.8, 124.4, 123.95, 123.2, 122.3, 57.4, 56.3, 35.6, 34.7, 32.1, 30.10.

Synthesis of $Rh(N^{NMe2}N'O_2^{Me})(Cl)(CH_3OH)$ (2b). A 50 mL Schlenk bomb was loaded with $RhCl_3\cdot(H_2O)_3$ (306 mg, 1.19 mmol)

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in water (5 mL). To this was added a solution of $H_2N^{NMe2}N'O_2^{Me}$ (423 mg, 1.19 mmol, 1 equiv.) in acetone (10 mL). The reaction mixture was heated at 80 °C for 5 min to afford a homogeneous orange solution. After 5 min, $NaHCO_3$ (200 mg, 2.38 mmol) was added to the reaction mixture and the mixture heated at 80 °C for 6 h. After 6 h, the reaction mixture was filtered through Celite, and the volatiles were removed *in vacuo*. The desired product was crystallized from a minimum amount of CH_3OH–CH_2Cl_2 (1 : 1) at –30 °C as orange-red micro-crystals (420 mg, mmol, 69%). The NMR spectroscopic data are consistent with *trans*-isomer in $CDCl_3$: CH_3OH. ^1H NMR ($CD_3OD/CDCl_3$, 1 : 1): 6.78 (d, J_{HH} = 2 Hz, 2H, Ar), 6.65 (d, J_{HH} = 2 Hz, 2H, Ar), 5.39 (d, J_{HH} = 13 Hz, 2H, CHAr, CHAr′), 3.26 (d, J_{HH} = 13 Hz, 2H, CHAr, CHAr′), 2.84 (t, J_{HH} = 6 Hz, 2H,CH_2N), 2.17 (s, 6H, Me), 2.15 (s, 6H, Me), 2.13 (s, 6H, Me), 2.06 (t, J_{HH} = 6 Hz, 2H, CH_2N). $^{13}C\{^1H\}$ NMR ($CD_3OD/CDCl_3$): 161.1, 133.1, 129.8, 128.6, 124.1, 121.0, 67.3, 64.7, 57.5, 50.3, 20.4, 17.7. Anal. Calcd for $C_{22}H_{32}ClN_2O_3Rh(H_2O)$: C, 50.79; H, 6.86; Cl, 6.52; N, 5.15. Found: C, 50.86; H, 6.29; Cl, 6.53; N, 5.45. ESI-MS Calculated for $C_{23}H_{34}ClN_2O_3Rh$ $(M)^+$: 524.1313 Found 524.1308.

Synthesis of $Rh(N^{py}N'O_2^{Me})(Cl)(H_2O)$ (2c). A 50 mL Schlenk bomb was loaded with $RhCl_3\cdot(H_2O)_3$ (250 mg, 0.97 mmol) in water (5 mL). To this was added a solution of $H_2N^{py}N'O_2^{Me}$ (365 mg, 0.97 mmol, 1 equiv.) in acetone (10 mL). The reaction mixture was heated at 80 °C for 5 min to afford a homogeneous orange solution. After 5 min, $NaHCO_3$ (163 mg, 1.94 mmol) was added to the reaction mixture and the mixture heated at 80 °C for 5 h. After 5 h, the reaction mixture was filtered through Celite, and the volatiles were removed *in vacuo*. The desired product was crystallized from a minimum amount of CH_3OH–CH_2Cl_2 (1 : 1) at –30 °C as bright orange micro-crystals (360 mg, mmol, 70%). The NMR spectroscopic data are consistent with *cis*-isomer in $CDCl_3$: CH_3OH. ^1H NMR (400 MHz, $CD_3OD/CDCl_3$, 1 : 1): 8.50 (d, J_{HH} = 5.5 Hz, 1H, Py), 7.59 (t, J_{HH} = 6 Hz, 1H, Py), 7.13 (m, 2H, Py), 6.79 (s, 1H, Ar), 6.70 (s, 1H, Ar), 6.41 (s, 1H, Ar), 6.35 (s, 1H, Ar), 5.53 (d, J_{HH} = 13 Hz, 1H, CHAr), 4.98 (d, J_{HH} = 15 Hz, 1H, CHAr), 4.19 (d, J_{HH} = 15 Hz, 1H, CHPy), 3.77 (d, J_{HH} = 13 Hz, 1H, CHPy), 3.53 (d, J_{HH} = 13 Hz, 1H, CHAr), 2.75 (d, J_{HH} = 13 Hz, 1H, CHAr), 2.33 (s, 3H, Me), 2.15 (s, 3H, Me), 2.00 (s, 3H, Me), 1.85 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ($CD_3OD/CDCl_3$): 163.0, 149.6, 149.5, 139.5, 132.7, 132.6, 130.1, 129.4, 128.8, 128.3, 127.0, 126.5, 124.1, 123.9, 122.1, 121.8, 69.7, 66.8, 61.8, 20.50, 20.46, 18.1, 17.2. ESI-MS Calculated for $C_{24}H_{27}ClN_2O_2Rh$ $(M - OH)^+$: 513.0843 Found 513.0809.

Synthesis of $Rh(N^{py}N'O_2^{Me})(Ph)(CH_3OH)$ (3). A 50 mL Schlenk bomb was loaded with **2c** (100 mg, 0.184 mmol) in CH_2Cl_2–CH_3OH (2 : 1) (30 mL). To this was added Ph_2Hg (72 mg, 0.202 mmol) (*Caution!* Ph_2Hg is extremely toxic) as a solid. The reaction mixture was stirred vigorously for 30 min. After 30 min, the reaction mixture was filtered through Celite, and the volatiles were removed *in vacuo*. The desired product was crystallized from a minimum amount of CH_3OH–CH_2Cl_2 (1 : 1) at –30 °C as orange micro-crystals (65 mg, mmol, 60%). The NMR spectroscopic data are consistent with *cis*-isomer in $CDCl_3$: CH_3OH. ^1H NMR ($CDCl_3/CD_3OD$, 1 : 1): 8.34 (br, d, J_{HH} = 6, 1H, Py), 7.51 (t, J_{HH} = 7.5, 1H, Py), 7.06 (t, J_{HH} = 6.5, 2H, Py), 6.84 (s, 1H, Ar), 6.81 (s, 5H, Ph), 6.55 (br, s, 1H, Ar), 6.24 (br, s, 2H, Ar), 4.59 (d, J_{HH} = 13, 1H, CHN), 4.17 (d, J_{HH} = 12.5, 1H, CHN), 3.97 (d, J_{HH} = 15, 1H, CHN), 3.79 (d, J_{HH} = 15, 1H, CHN), 3.18 (d, J_{HH} = 13, 1H, CHN), 2.55 (d, J_{HH} = 12, 1H, CHN), 2.35 (s, 3H, MeAr), 2.14 (s, 3H, MeAr), 1.96 (s, 6H, MeAr). $^{13}C\{^1H\}$NMR ($CD_3OD/CDCl_3$): 148.5, 137.5, 137.2, 133.0, 132.0, 129.0, 128.7, 127.7, 123.9, 123.7, 122.1, 121.7, 120.9, 69.9, 67.0, 61.6, 20.50, 20.42, 18.0, 17.1. ESI-MS Calculated for $C_{30}H_{32}N_2O_2Rh$ $(M - OCH_3)^+$: 555.1519 Found 555.1514.

Acknowledgements

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