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Carbon–nitrogen bond activation of amines by rhodium(III) porphyrin complexes

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ABSTRACT

Carbon–nitrogen bond activation of amines by rhodium porphyrin chloride has been achieved to give rhodium porphyrin alkyl complexes. Rhodium porphyrin hydride and rhodium porphyrin dimer were proposed as the intermediates in cleaving the C–N bond.

1. Introduction

Transition metal catalyzed cross-coupling reaction is one of the most powerful means leading to bond forming in organic synthesis. It is usually achieved through the selective cleavage of unreactive bonds, such as carbon–hydrogen bond [1], carbon–carbon bond [2] as well as carbon–oxygen bond [3]. However, cross-coupling reactions related to carbon–nitrogen bond activation (CNA) are relative fewer. Recently, it was discovered that cleavage of carbon–nitrogen bonds in aryltrimethylammonium salt [4] and aryltriazenes [5] can lead to the formation of carbon–carbon bonds to give a series of biaryls through Suzuki coupling. In addition, cleavage of unactivated aromatic carbon–nitrogen bonds in aniline derivatives [6] can also lead to the carbon–carbon bond formation to give ketones. This brings about our interest in carbon–nitrogen bond activation.

Furthermore, reported examples of CNA mainly made use of low valent transition metal complexes, examples include CNA of amines by palladium black [7]; CNA of arylamines [8], bridged lactams [9] and diaza [2.2.1] bicyclic alkenes [10] by platinum(II) complexes; chelation-assisted CNA with pincer-type ligand using monovalent rhodium complexes [11]; CNA of aziridines by early transition metal complexes [12] as well as CNA of cyanamides by a silyl–iron complex [13]. However, CNA by high valent transition metal complexes are rarely reported, examples include CNA of pyridine by thorium(IV) complexes [14] and CNA of amines by a rhodium(III) corrole complex [15] (corrole = tetradehydrocorrin). Previously we have reported a series of bond activation chemistry with Group 9 metalloporphyrin complexes, including the carbon–carbon bond activation (CCA) of nitroxides [16], nitriles [17], esters and amide [18], base-promoted carbon–hydrogen bond activation of toluenes [19] and alkanes [20]. In expanding the substrate scope in bond activation chemistry, we have examined the reactions of amines with rhodium porphyrin complexes and discovered the CNA of amines to give rhodium(III) porphyrin alkyls.

2. Results and discussion

Initially, Rh(ttp)Cl (ttp = 5,10,15,20-tetratolylporphyrin) reacted with tri-*n*-pentylamine (20 equiv.) in benzene at 120 °C for 16 days to give 28% yield of Rh(ttp)^{n}Pent. When THF was used as the solvent, the rate and yield were enhanced with 63% Rh(ttp)^{n}Pent obtained after 9 days. With the reaction performed in solvent free conditions, the rate of CNA was greatly enhanced and the reaction was completed in 1 day with 59% yield of Rh(ttp)^{n}Pent obtained (Table 1, Eq. (1), entry 9). The enhanced rate of reaction is probably due to the increased concentration of substrate. Therefore, CNA of amine was studied with neat amines.

$$\underset{\mathbf{1}}{\mathrm{Rh(ttp)Cl}} + \underset{\mathbf{2a\text{-}h}}{\mathrm{R_1R_2R_3N}} \xrightarrow[\mathrm{N_2,\ 1\ d}]{120\ ^{\circ}\mathrm{C}} \underset{\mathbf{3a\text{-}f}}{\mathrm{Rh(ttp)R_1}} \qquad (1)$$

The scope of amine substrates was then investigated (Table 1 and Eq. (1)). Both secondary and tertiary amines reacted with Rh(ttp)Cl to give the corresponding Rh(ttp)R.

The CNA yields for secondary amines were not satisfactory with only 6% yield of Rh(ttp)Et and trace amount of Rh(ttp)^{n}Bu obtained in 1 day and 3 days when diethylamine and dibutylamine were used, respectively (Table 1, entries 1 and 2). When tertiary amines were used, CNA yield was greatly enhanced (Table 1, entries 3–5 and 9). A 64% yield of Rh(ttp)^{n}Bu was obtained when Rh(ttp)Cl reacted with tri-*n*-butylamine for 1 day (Table 1, entry 5). Also, it was found that CNA yield gradually increased as the carbon chain length of the amine molecule increased (Table 1, entries 3–5),

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Table 1
CNA of amines.

Entry	Amine	Rh(ttp)R	Yield (%)
1	Et_2NH **2a**	Rh(ttp)Et **3a**	6
2[a]	$^nBu_2NH$ **2b**	Rh(ttp)^{n}Bu **3b**	Trace
3	Et_3N **2c**	Rh(ttp)Et **3a**	17
4	$^nPr_3N$ **2d**	Rh(ttp)^{n}Pr **3c**	47
5	$^nBu_3N$ **2e**	Rh(ttp)^{n}Bu **3b**	64
6[b]	$^nBu_3N$ **2e**	Rh(ttp)^{n}Bu **3b**	41
7[c]	$^nBu_3N$ **2e**	Rh(ttp)^{n}Bu **3b**	25
8[d]	$^nBu_3N$ **2e**	Rh(ttp)^{n}Bu **3b**	43
9	$^nPent_3N$ **2f**	Rh(ttp)^{n}Pent **3d**	59
10	$^iBu_3N$ **2g**	($^iBu_2NH$)Rh(ttp)Cl **3e**	57
11	*N*-methylpiperidine **2h**	Rh(ttp)Me **3f**	18

[a] Reaction was carried out for 3 days.
[b] Rh(ttp)I was used instead of Rh(ttp)Cl.
[c] 10 equiv. of KOH added.
[d] 10 equiv. of K_2CO_3 added.

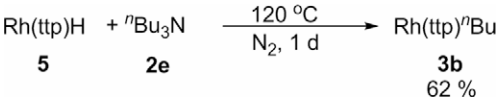
reaction yield increased from 17% for triethylamine to 64% for tri-*n*-butylamine. This gradual change in CNA yield is due to the enhanced solubility of Rh(ttp)Cl in the substrate. However, for branched chain trialkylamine of $^iBu_3N$ (Table 1, entry 10), the expected CNA product (Rh(ttp)^{i}Bu) was not observed. Instead ($^iBu_2NH$)Rh(ttp)Cl was obtained in high yield likely from the coordination of the organic coproduct after the CN bond cleavage and its formation will be discussed in the mechanism section. Reaction with a cyclic amine was also preformed (Table 1, entry 11) with 18% yield of Rh(ttp)Me obtained from *N*-methylpiperidine.

The base-promoted alkane CHA by Rh(ttp)Cl [20] and other base-promoted bond activation by transition metal complexes [19,21], have prompted us to examine the promoting effect of base on the CNA of amines. However, it was found that the addition of a base was not beneficial to product yield with only 25% and 43% yields of Rh(ttp)^{n}Bu obtained in the presence of KOH and K_2CO_3, respectively for the reactions between Rh(ttp)Cl and $^nBu_3N$ (Table 1, entries 7 and 8).

Counter anion effect was also investigated. Rh(ttp)I gave a lower yield of 41% of Rh(ttp)^{n}Bu in 1 day (Table 1, entry 6). Therefore, the use of weakly coordinating anion on rhodium porphyrin complex was not beneficial.

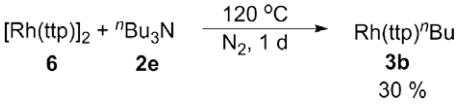
To gain an idea of the reactive intermediate and the reaction mechanism of CNA of amine, several reactive rhodium porphyrin species such as $[Rh(ttp)]^-$, $[Rh(ttp)]_2$ and Rh(ttp)H were treated to react with tri-*n*-butylamine under the same reaction conditions [20].

Scheme 1 illustrates the proposed mechanism of the CNA of amines. Initially, Rh(ttp)Cl reacts with the weakest C(α)–H bond of amine to give **4** [22,23]. Subsequent β-hydride elimination of **4** produces Rh(ttp)H and an enamine. Finally, Rh(ttp)H reacts with another amine molecule probably through sigma-bond metathesis to give Rh(ttp)R as the CNA product. The co-products, $Bu_2N(CH{=}CHCH_2CH_3)$ and $^nBu_2NH$, could not be detected in the crude reaction mixture probably due to their low concentration and overlapping of ^{1}H NMR signals with the substrate. The proposed step is supported by the fact that Rh(ttp)H reacted directly with $^nBu_3N$ to give Rh(ttp)^{n}Bu in 62% yield (Eq. (2)). In addition, Rh(ttp)Cl reacted with $^iBu_3N$ to give ($^iBu_2NH$)Rh(ttp)Cl (Table 1, entry 7). This suggests that $^iBu_2NH$ is generated in the reaction system. The carbon–nitrogen bond cleavage likely occurs through Rh(ttp)H directly without the generation of $Rh(ttp)^-$ and Bu_3NH^+ as the reaction between the acidic Rh(ttp)H and the weak base Bu_3N is endoergically unfavorable [24].



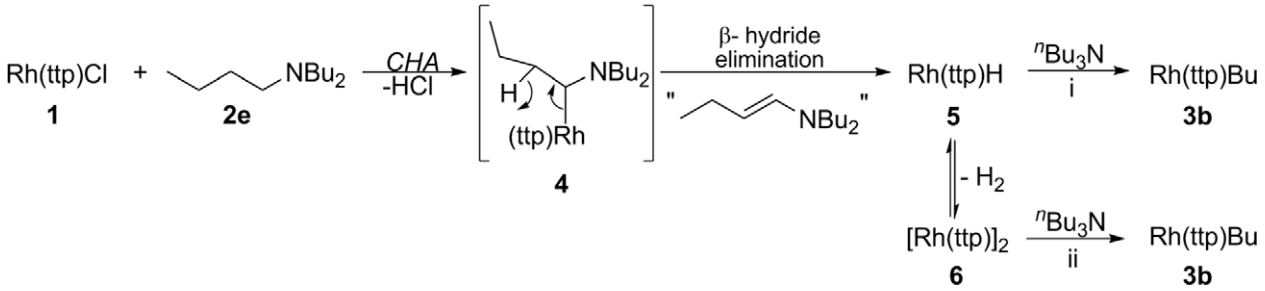
(2)

Under thermal conditions, it was reported that Rh(ttp)H would be converted to $[Rh(ttp)]_2$ and dihydrogen which was removed during the workup process [25]. The possible intermediacy of $[Rh(ttp)]_2$ to give CNA product was also examined. From the independent experiment between $[Rh(ttp)]_2$ and $^nBu_3N$, we found that $[Rh(ttp)]_2$ cleaved the C–N bond of $^nBu_3N$, probably through carbon–hydrogen bond activation to give Rh(ttp)H and **4** which then likely gives also Rh(ttp)H a β-hydride elimination for subsequently C–N bond activation. Indeed $[Rh(ttp)]_2$ reacted with $^nBu_3N$ to give Rh(ttp)^{n}Bu with 59% yield (Eq. (3)). However, no $Rh(ttp)NBu_2$ was not detected since late transition metal–amido complex with nitrogen center bearing group is relatively unstable [26]. Even if it had formed, it would have decomposed quickly. More probably, this direct radical substitution does not occur since it is an energetically very uphill reaction to yield a unstable Bu_2N nitrogen-centered radical intermediate or transition state. Eq. (3) supports the possible occurrence of pathway ii (Scheme 1). This also explains the lower yield for CNA reactions of secondary amines. Since secondary amines, such as Et_2NH, are less hindered ligand, they coordinate better and induce disproportionation of $[Rh^{II}(ttp)]_2$ species to give $[(ttp)RhL_2]^+$ and $[Rh(ttp)^-]$ [27] to result in a lower CNA yield. Alternatively, $[Rh^{II}(ttp)]_2$ can be rationalized to undergo rapid CHA to give **4** and Rh(ttp)H for the CNA.



(3)

As shown previously, addition of an inorganic base lowered the CNA yield (Table 1, entries 7 and 8). In the presence of base, Rh(ttp)H will likely be converted to the inactive $[Rh(ttp)]^-$ [28]. Indeed, no Rh(ttp)^{n}Bu was obtained in the independent experiment between $[Rh(ttp)]^-$ and $^nBu_3N$.



Scheme 1. Proposed mechanism for CNA of amine.

3. Conclusion

In summary, we have discovered the carbon–nitrogen bond activation of amines by rhodium(III) porphyrin complexes. The CNA yield increased as the substrate changed from a secondary to a *tertiary* amine. Rh(ttp)H and $[Rh(ttp)]_2$ are shown to be the probable intermediates for the C–N bond cleavage.

4. Experimental

4.1. General

All materials were purchased from commercial suppliers and used without further purification unless otherwise specified. Rhodium trichloride ($RhCl_3{\cdot}xH_2O$) was obtained from Johnson Matthey. *n*-Hexane for chromatography was distilled from calcium hydride. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl under N_2. Benzene was distilled from sodium under N_2. Rh(ttp)Cl [29], Rh(ttp)I [30], Rh(ttp)H [31], $[Rh(ttp)]_2$ [31] and Rh(ttp)Na [32] were prepared according to the literature methods. All CNA reactions were conducted under N_2 and shielded from light with aluminium foil wrapping. Thin-layer chromatography was performed on precoated silica gel 60 F_{254} plates. Column chromatography was performed on silica gel (70–230 and 230–400 mesh).

^{1}H NMR spectra were recorded on either a Bruker DPX-300 (300 MHz) or Bruker AV 400 (400 MHz) spectrometer. Chemical shifts were referenced with the residual solvent protons in $CDCl_3$ (δ 7.26 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in scale downfield from TMS (δ 0.00 ppm). ^{13}C NMR spectra were recorded on Bruker AV 400 (100 MHz) spectrometer. Chemical shifts were referenced to the solvent peak of $CDCl_3$ (δ 77.0 ppm). Coupling constants (J) were reported in Hertz (Hz).

High resolution mass spectra (HRMS) were performed on a ThermoFinnigan MAT 95 XL mass spectrometer in fast atom bombardment (FAB) mode using 3-nitrobenzyl alcohol (NBA) matrix.

4.2. Reaction between Rh(ttp)Cl and tripentylamine in benzene

Rh(ttp)Cl (10.1 mg, 0.012 mmol) and tripentylamine (0.07 mL, 20 equiv.) were added to benzene (2.0 mL) and the mixture was degassed for three freeze–pump–thaw cycles and filled with N_2. The mixture was then heated at 120 °C for 16 days. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)^{n}Pent [20] (0.3 mg, 0.004 mmol, 28%), with R_f = 0.78 (hexane/CH_2Cl_2 = 1:1) was collected. ^{1}H NMR ($CDCl_3$, 300 MHz) δ −4.96 (dt, 2H, $^2J_{Rh-H}$ = 2.8 Hz, J = 8.1 Hz), −4.49 (quin, 2H, J = 7.8 Hz), −1.62 (quin, 2H, J = 7.4 Hz), −0.52 (sext, 2H, J = 7.3 Hz), −0.27 (t, 3H, J = 7.4 Hz), 2.69 (s, 12H), 7.52 (t, 8H, J = 5.9 Hz), 7.98 (dd, 4H, J = 2.1 Hz, 8.6 Hz), 8.08 (dd, 4H, J = 2.7 Hz, 8.6 Hz), 8.70 (s, 8H).

4.3. Reaction between Rh(ttp)Cl and tripentylamine in tetrahydrofuran (THF)

Rh(ttp)Cl (10.1 mg, 0.012 mmol) and tripentylamine (0.07 mL, 20 equiv.) were added to THF (2.0 mL) and the mixture was degassed for three freeze–pump–thaw cycles and filled with N_2. The mixture was then heated at 120 °C for 9 days. The solvent was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)^{n}Pent [20] (6.6 mg, 0.008 mmol, 63%) was collected.

4.4. Reaction between Rh(ttp)Cl and diethylamine

Rh(ttp)Cl (11.5 mg, 0.014 mmol) and diethylamine (2.0 mL) were degassed for three freeze–pump–thaw cycles. The mixture was then heated at 120 °C under N_2 for 1 day. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)Et [16] (0.6 mg, 0.001 mmol, 6%), with R_f = 0.72 (hexane/CH_2Cl_2 = 1:1) was collected. ^{1}H NMR ($CDCl_3$, 300 MHz), δ −4.87 (dq, 2H, $^2J_{Rh-H}$ = 3.0 Hz, J = 7.5 Hz), −4.47 (dt, 3H, $^3J_{Rh-H}$ = 1.5 Hz, J = 7.5 Hz), 2.69 (s, 12H), 7.53 (t, 8H, J = 6.3 Hz), 8.00 (d, 4H, J = 7.5 Hz), 8.08 (d, 4H, J = 7.2 Hz), 8.71 (s, 8H).

4.5. Reaction between Rh(ttp)Cl and dibutylamine

Rh(ttp)Cl (11.5 mg, 0.014 mmol) and dibutylamine (2.0 mL) were degassed for three freeze–pump–thaw cycles. The mixture was then heated at 120 °C under N_2 for 1 day. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)Bu, with R_f = 0.72 (hexane/CH_2Cl_2 = 1:1) was collected. ^{1}H NMR ($CDCl_3$, 300 MHz) δ −4.95 (dt, 2H, $^2J_{Rh-H}$ = 3.0 Hz, J = 8.1 Hz), −4.50 (quin, 2H, J = 7.9 Hz), −1.57 (sext, 2H, J = 7.4 Hz), −0.83 (t, 3H, J = 7.2 Hz), 2.70 (s, 12H), 7.53 (t, 8H, J = 6 Hz), 7.99 (dd, 4H, J = 2.1 Hz, J = 7.8 Hz), 8.08 (dd, 4H, J = 2.1 Hz, 7.8 Hz), 8.71 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz) 12.2, 15.1(d, $^1J_{Rh-C}$ = 27 Hz), 19.3, 21.5, 29.5, 122.4, 127.3, 127.4, 131.3, 133.6, 134.0, 137.1, 139.3, 143.2; HRMS (FABMS): calcd for $(C_{52}H_{46}N_4Rh)^+$ m/z 829.2772, found m/z 829.27688.

4.6. Reaction between Rh(ttp)Cl and triethylamine

Rh(ttp)Cl (11.5 mg, 0.014 mmol) and triethylamine (2.0 mL) were degassed for three freeze–pump–thaw cycles and filled with N_2. The mixture was then heated at 120 °C for 1 day. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)Et [16] (2.0 mg, 0.002 mmol, 17%) was collected.

4.7. Reaction between Rh(ttp)Cl and tripropylamine

Rh(ttp)Cl (10.1 mg, 0.012 mmol) and tripropylamine (2.0 mL) were degassed for three freeze–pump–thaw cycles and filled with N_2. The mixture was then heated at 120 °C for 1 day. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)^{n}Pr [16] (5.3 mg, 0.007 mmol, 47%), with R_f = 0.72 (hexane/CH_2Cl_2 = 1:1) was collected. ^{1}H NMR ($CDCl_3$, 300 MHz) δ −4.98 (dt, 2H, $^2J_{Rh-H}$ = 3.3 Hz, J = 8.3 Hz), −4.46 (sext, 2H, J = 8.7 Hz), −1.75 (t, 3H, J = 7.2 Hz), 2.69 (s, 12H), 7.53 (t, 8H, J = 5.7 Hz), 8.00 (dd, 4H, J = 2.1 Hz, 7.7 Hz), 8.07 (dd, 4H, J = 2.1 Hz, 8.0 Hz), 8.71 (s, 8H).

4.8. Reaction between Rh(ttp)Cl and tributylamine

Rh(ttp)Cl (11.3 mg, 0.014 mmol) and tributylamine (2.0 mL) were degassed for three freeze–pump–thaw cycles and filled with N_2. The mixture was then heated at 120 °C for 1 day. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a

solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)^{n}Bu (7.4 mg, 0.009 mmol, 64%) was collected.

4.9. Reaction between Rh(ttp)I and tributylamine

Rh(ttp)I (11.3 mg, 0.012 mmol) and tributylamine (2.0 mL) were degassed for three freeze–pump–thaw cycles and filled with N_2. The mixture was then heated at 120 °C for 1 day. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)^{n}Bu (4.3 mg, 0.005 mmol, 41%) was collected.

4.10. Reaction between Rh(ttp)Cl and tributylamine in the presence of KOH

Rh(ttp)Cl (11.3 mg, 0.014 mmol), tributylamine (2.0 mL) and KOH (7.8 mg, 0.14 mmol) were degassed for three freeze–pump–thaw cycles. The mixture was then heated at 120 °C under N_2 for 1 day. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)^{n}Bu (3.0 mg, 0.003 mmol, 25%) was collected.

4.11. Reaction between Rh(ttp)Cl and tributylamine in the presence of K_2CO_3

Rh(ttp)Cl (11.3 mg, 0.014 mmol), tributylamine (2.0 mL) and K_2CO_3 (19.3 mg, 0.14 mmol) were degassed for three freeze–pump–thaw cycles. The mixture was then heated at 120 °C under N_2 for 1 day. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)^{n}Bu (5.0 mg, 0.006 mmol, 43%) was collected.

4.12. Reaction between Rh(ttp)Cl and tripentylamine

Rh(ttp)Cl (10.1 mg, 0.013 mmol) and tripentylamine (2.0 mL) were degassed for three freeze–pump–thaw cycles and filled with N_2. The mixture was then heated at 120 °C for 1 day. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)^{n}Pent [20] (6.2 mg, 0.007 mmol, 59%) was collected.

4.13. Reaction between Rh(ttp)Cl and triisobutylamine

Rh(ttp)Cl (11.3 mg, 0.014 mmol) and triisobutylamine (2.0 mL) were degassed for three freeze–pump–thaw cycles and filled with N_2. The mixture was then heated at 120 °C for 1 day with the reaction. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1) followed by ethyl acetate: CH_2Cl_2 (1:2). A red product (^{i}Bu$_2$NH)Rh(ttp)Cl (7.5 mg, 0.008 mmol, 57%), with R_f = 0.91 (ethyl acetate/CH_2Cl_2 = 1:2) was collected. ^{1}H NMR ($CDCl_3$, 400 MHz) δ −5.58 (br, 1H), δ −4.69 (dt, 2H, $^2J_{Rh-H}$ = 3.0 Hz, J = 8.1 Hz), −2.76 (quin, 2H, J = 7.9 Hz), −1.88 (hept, 2H, J = 6.8 Hz), −1.26 (d, 6H, J = 6.8 Hz), −0.93 (d, 6H, J = 6.8 Hz), 2.70 (s, 12H), 7.54 (t, 8H, J = 9.3 Hz), 7.98 (d, 4H, J = 7.6 Hz), 8.21 (d, 4H, J = 8.4 Hz), 8.88 (s, 8H). ^{13}C NMR ($CDCl_3$, 100 MHz) 17.5, 18.7, 21.5, 22.1, 55.8, 121.1, 127.1, 127.6, 132.7, 134.1, 134.6, 137.2, 139.1, 142.6; HRMS (FABMS): calcd for $(C_{56}H_{55}N_5RhCl)^+$ m/z 935.3196, found m/z 935.32.

4.14. Reaction between Rh(ttp)Cl and N-methylpiperidine

Rh(ttp)Cl (10.3 mg, 0.013 mmol) and *N*-methylpiperidine (2.0 mL) were degassed for three freeze–pump–thaw cycles. The mixture was then heated at 120 °C under N_2 for 1 day. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)Me [16] (1.8 mg, 0.002 mmol, 18%), with R_f = 0.72 (hexane/CH_2Cl_2 = 1:1) was collected. ^{1}H NMR ($CDCl_3$, 300 MHz) δ −5.82 (d, 3H, $^2J_{Rh-H}$ = 3 Hz), 2.69 (s, 12H), 7.53 (d, 8H, J = 7.5 Hz), 8.01 (dd, 4H, J = 2.4, 8.4 Hz), 8.07 (dd, 4H, J = 2.4, 8.4 Hz), 8.73 (s, 8H).

4.15. Reaction between Rh(ttp)H and tributylamine

Rh(ttp)H (10.0 mg, 0.013 mmol) and tributylamine (2.0 mL) were degassed for three freeze–pump–thaw cycles. The mixture was then heated at 120 °C under N_2 for 1 day. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)^{n}Bu (6.5 mg, 0.008 mmol, 62%) was collected.

4.16. Reaction between [Rh(ttp)]$_2$ and tributylamine

[Rh(ttp)]$_2$ (10.0 mg, 0.0065 mmol) and tributylamine (2.0 mL) were degassed for three freeze–pump–thaw cycles. The mixture was then heated at 120 °C under N_2 for 1 day. Excess amine was then removed under vacuum and the red crude mixture was purified by silica gel column chromatography eluting with a solvent mixture of hexane: CH_2Cl_2 (1:1). A red product Rh(ttp)^{n}Bu (3.0 mg, 0.003 mmol, 59%) with R_f = 0.72 (hexane/CH_2Cl_2 = 1:1) was collected.

4.17. Reaction between Rh(ttp)Na and tributylamine

Rh(ttp)Na (0.012 mmol) and tributylamine (2.0 mL) were degassed for three freeze–pump–thaw cycles. The mixture was then heated at 120 °C under N_2 for 1 day. Excess amine was then removed under vacuum and a green crude mixture was obtained.

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