

Supporting Information

Quantifying steric effects of α -diimine ligands. Oxidative addition of MeI to Rh(I) and migratory insertion in Rh(III) complexes.

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Kinetic data

Table S1. Observed pseudo first order rate constants, k_{obs} , for oxidative addition of MeI to **1a** in CH_2Cl_2 .

| [MeI]/M | $10^3 k_{\text{obs}}/\text{s}^{-1}$ | | | | |
|---------|-------------------------------------|------|------|------|------|
| | 15°C | 20°C | 25°C | 30°C | 35°C |
| 0.08 | | | 1.19 | | |
| 0.16 | 1.29 | 1.76 | 2.30 | 2.82 | 3.64 |
| 0.24 | | | 3.15 | | |
| 0.32 | | | 4.10 | | |

Table S2. Observed pseudo first order rate constants, k_{obs} , for oxidative addition of MeI to **1b** in CH_2Cl_2 .

| [MeI]/M | $10^3 k_{\text{obs}}/\text{s}^{-1}$ | | | | |
|---------|-------------------------------------|------|------|------|------|
| | 15°C | 20°C | 25°C | 30°C | 35°C |
| 0.8 | | | 0.81 | | |
| 1.6 | | | 1.62 | | |
| 2.4 | | | 2.24 | | |
| 3.2 | 1.90 | 2.56 | 3.45 | 4.46 | 5.66 |
| 4.8 | | | 4.72 | | |
| 6.4 | | | 5.21 | | |
| 8.0 | | | 6.66 | | |

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Table S3. Observed pseudo first order rate constants, k_{obs} , for oxidative addition of MeI to **1c** in CH_2Cl_2 .

| [MeI]/M | $10^3 k_{\text{obs}}/\text{s}^{-1}$ | | | | |
|---------|-------------------------------------|------|-------|------|------|
| | 15°C | 20°C | 25°C | 30°C | 35°C |
| 1.6 | | | 2.30 | | |
| 3.2 | 2.61 | 3.51 | 4.67 | 6.43 | 8.29 |
| 4.8 | | | 5.78 | | |
| 6.4 | | | 9.32 | | |
| 8.0 | | | 11.63 | | |

Table S4. Observed pseudo first order rate constants, k_{obs} , for oxidative addition of MeI to **1d** in CH_2Cl_2 .

| [MeI]/M | $10^3 k_{\text{obs}}/\text{s}^{-1}$ | | | | |
|---------|-------------------------------------|------|------|------|------|
| | 15°C | 20°C | 25°C | 30°C | 35°C |
| 0.024 | 1.97 | | | | |
| 0.048 | 4.50 | 5.61 | 7.20 | 8.17 | 9.51 |
| 0.072 | 6.91 | | | | |
| 0.096 | 9.21 | | | | |

Table S5. Observed pseudo first order rate constants, k_{obs} , for oxidative addition of MeI to **1e** in CH_2Cl_2 .

| [MeI]/M | $10^3 k_{\text{obs}}/\text{s}^{-1}$ | | | | |
|---------|-------------------------------------|------|------|------|------|
| | 15°C | 20°C | 25°C | 30°C | 35°C |
| 0.058 | | | 4.76 | | |
| 0.080 | 4.19 | 5.37 | 6.59 | 6.97 | 9.50 |
| 0.118 | | | 10.1 | | |
| 0.160 | | | 13.7 | | |

Table S6. Forward and reverse rate constants and equilibrium constants for oxidative addition of MeI to **1f** and migratory insertion in **2f** (measured in CH₂Cl₂).

| T/ °C | $10^3 \text{ } k_1/\text{M s}^{-1}$ | $10^4 \text{ } k_{-1}/\text{s}^{-1}$ | $10^4 \text{ } k_2/\text{s}^{-1}$ | $10^3 \text{ } k_{-2}/\text{s}^{-1}$ | K_1/M^{-1} | K_2 |
|-------|-------------------------------------|--------------------------------------|-----------------------------------|--------------------------------------|---------------------|-------|
| 15 | 5.31 | 1.63 | 1.55 | 3.67 | 32.57 | 4.38 |
| 20 | 7.37 | 3.18 | 3.02 | 6.65 | 23.51 | 4.58 |
| 25 | 8.34 | 5.23 | 5.82 | 11.3 | 15.97 | 5.16 |
| 30 | 11.1 | 8.22 | 8.22 | 17.8 | 13.49 | 4.81 |
| 35 | 10.9 | 10.6 | 15.2 | 26.2 | 10.36 | 5.80 |

Table S7. Observed pseudo first order rate constants, k_{obs} , for oxidative addition of MeI to **1g** in CH₂Cl₂.

| [MeI]/M | $10^3 \text{ } k_{\text{obs}}/\text{s}^{-1}$ | | | | |
|---------|--|------|------|------|------|
| | 15°C | 20°C | 25°C | 30°C | 35°C |
| 0.024 | 3.71 | | | | |
| 0.048 | 7.45 | 9.09 | 9.88 | 10.9 | 12.7 |
| 0.072 | 11.0 | | | | |
| 0.096 | 14.0 | | | | |

Table S8. Observed steady state absorbance ratios ($A_{1b}/A_{2b} = A(1993 \text{ cm}^{-1})/A(2074 \text{ cm}^{-1})$) and calculated first order rate constants, k_2 , for the migratory insertion reaction of **2b** in CH₂Cl₂.

| T (°C) | A_{1b}/A_{2b} | $10^2 \text{ } k_2 (\text{s}^{-1})$ |
|--------|-----------------|-------------------------------------|
| 15 | 24 | 2.28 |
| 20 | 26 | 3.33 |
| 25 | 27 | 4.66 |
| 30 | 29 | 6.47 |
| 35 | 34 | 9.62 |

k_2 is calculated from observed rate constant for disappearance of **1b** (from Table 2) using the relationship: $k_2 = k_{\text{obs}} \times (A_{1b}/A_{2b}) \times (\epsilon_{2b}/\epsilon_{1b})$ where the ratio of extinction coefficients ($\epsilon_{2b}/\epsilon_{1b}$) is estimated as 0.5 based on the value observed for complexes **1a** and **1b**.

Crystallographic data

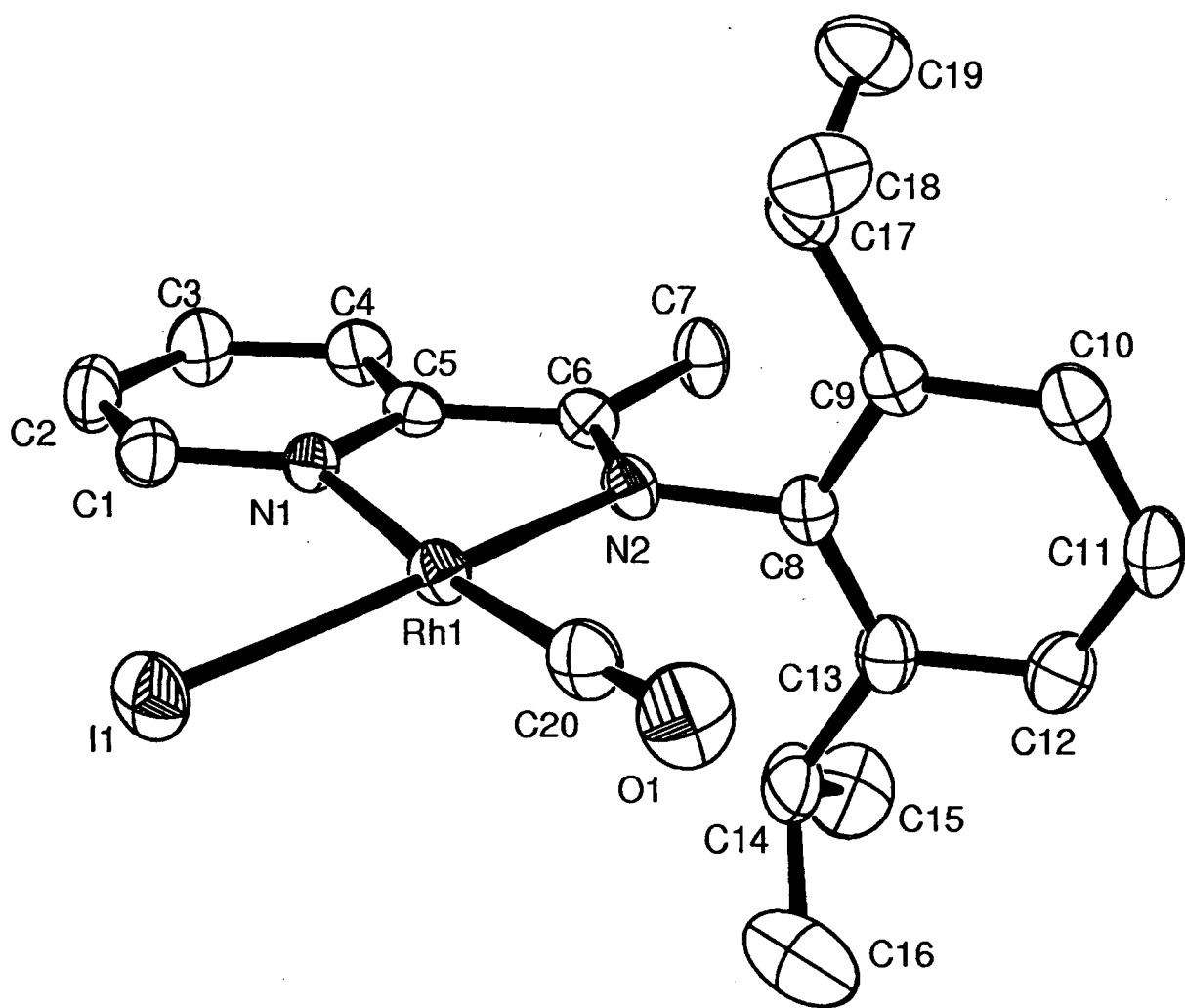


Figure S1. ORTEP plot of **1f**. Thermal ellipsoids are shown at the 50% probability level. Hydrogens and the solvent molecule are omitted for clarity. (CIF file provided: iah100).

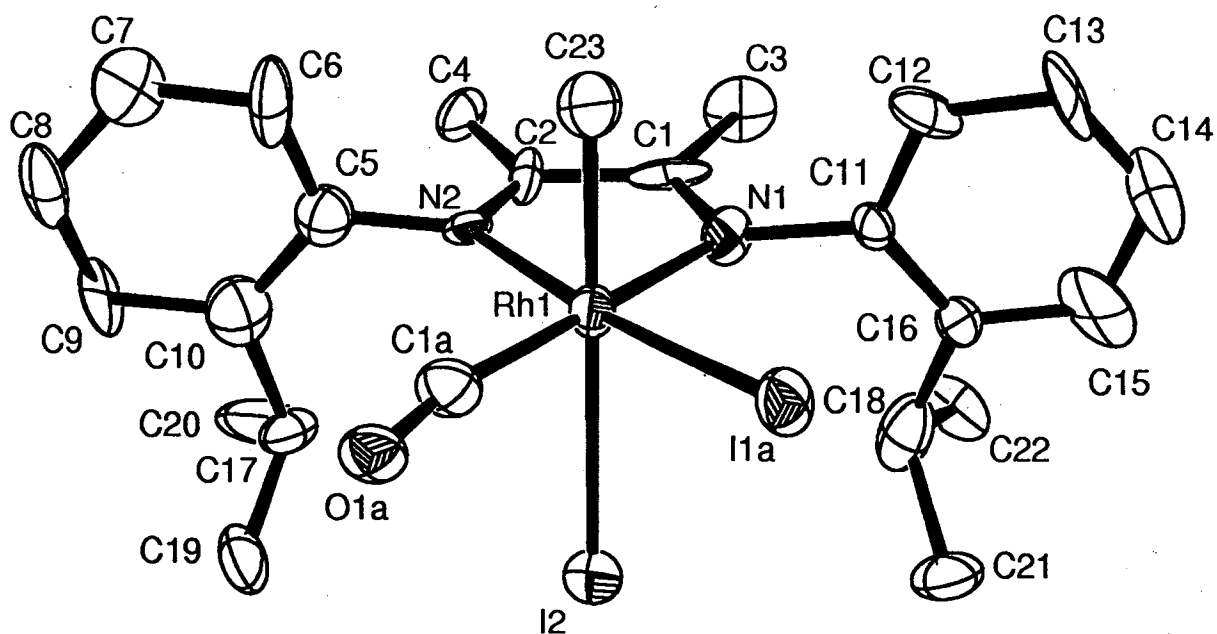


Figure S2. ORTEP plot for **2a**. Thermal ellipsoids are shown at the 50% probability level. Hydrogens and the solvent molecule are omitted for clarity. (CIF file provided: iah56a).

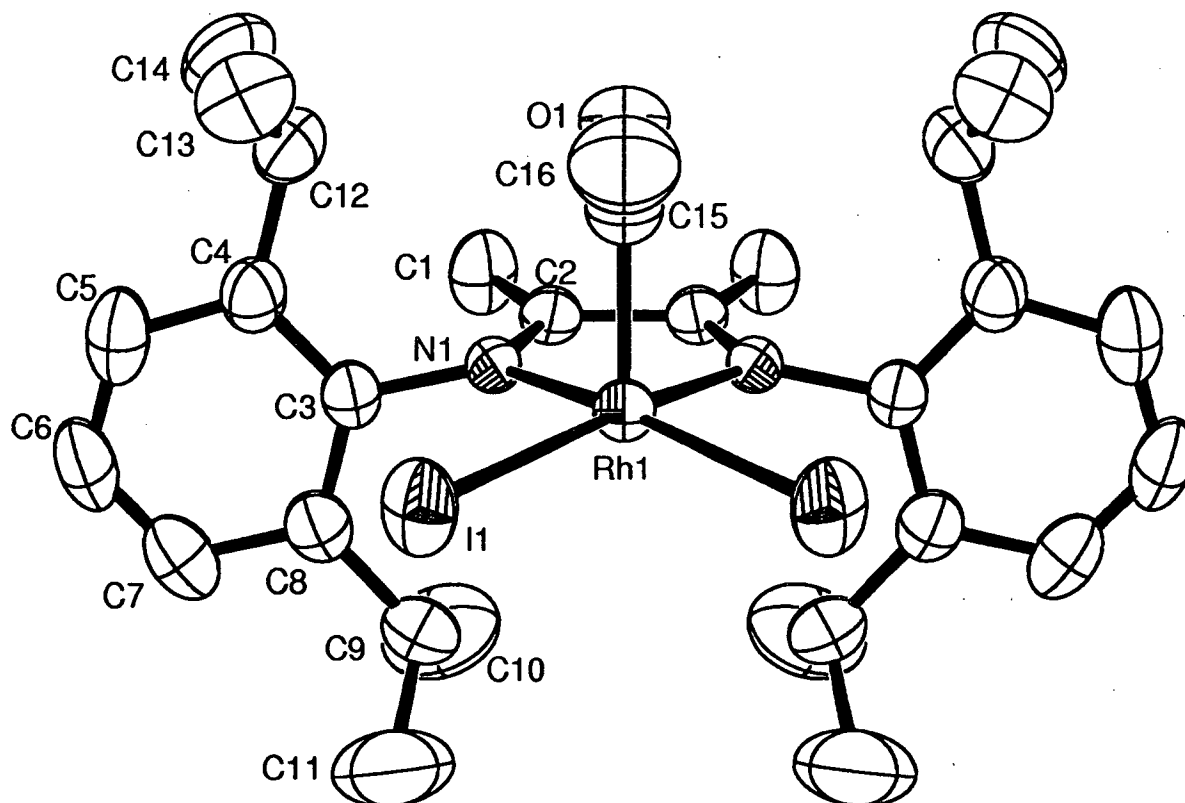


Figure S3. ORTEP plot for **3c**. Thermal ellipsoids are shown at the 50% probability level. Hydrogens and the solvent molecule are omitted for clarity. (CIF file provided: iah4m).

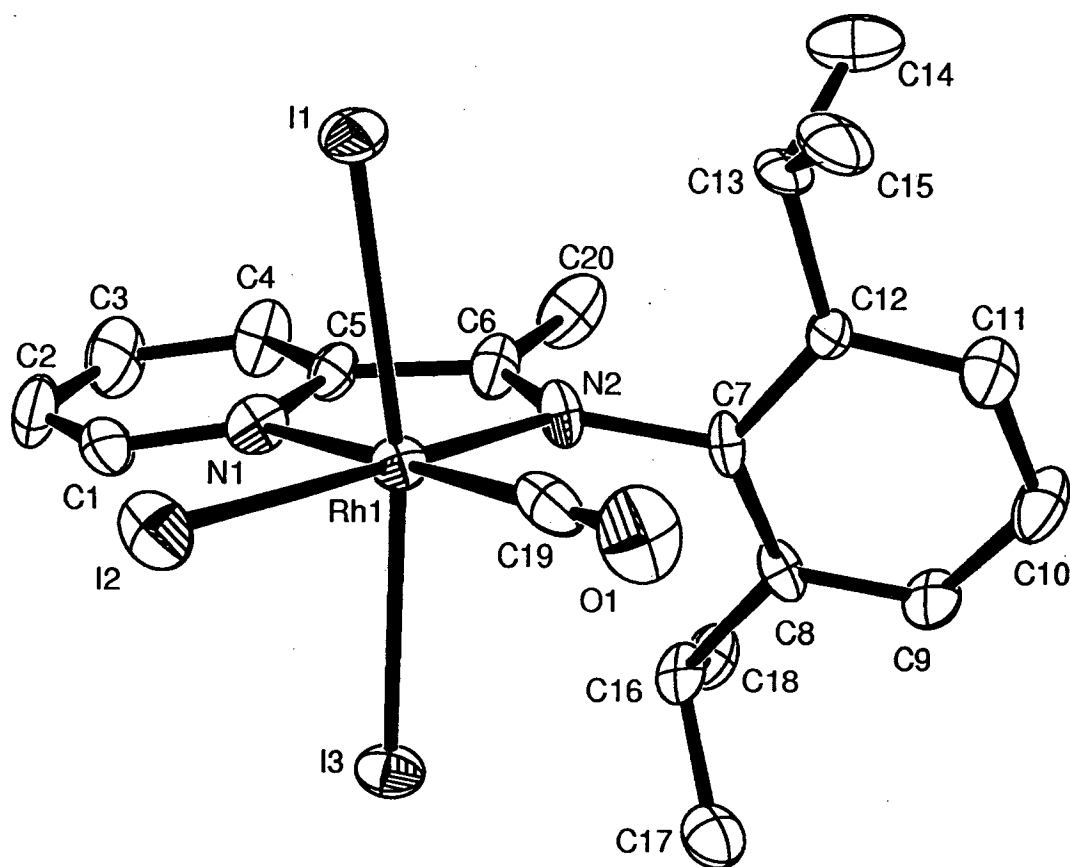


Figure S4. ORTEP plot for **4f**. Thermal ellipsoids are shown at the 50% probability level. Hydrogens are omitted for clarity. (CIF file provided: iah82)

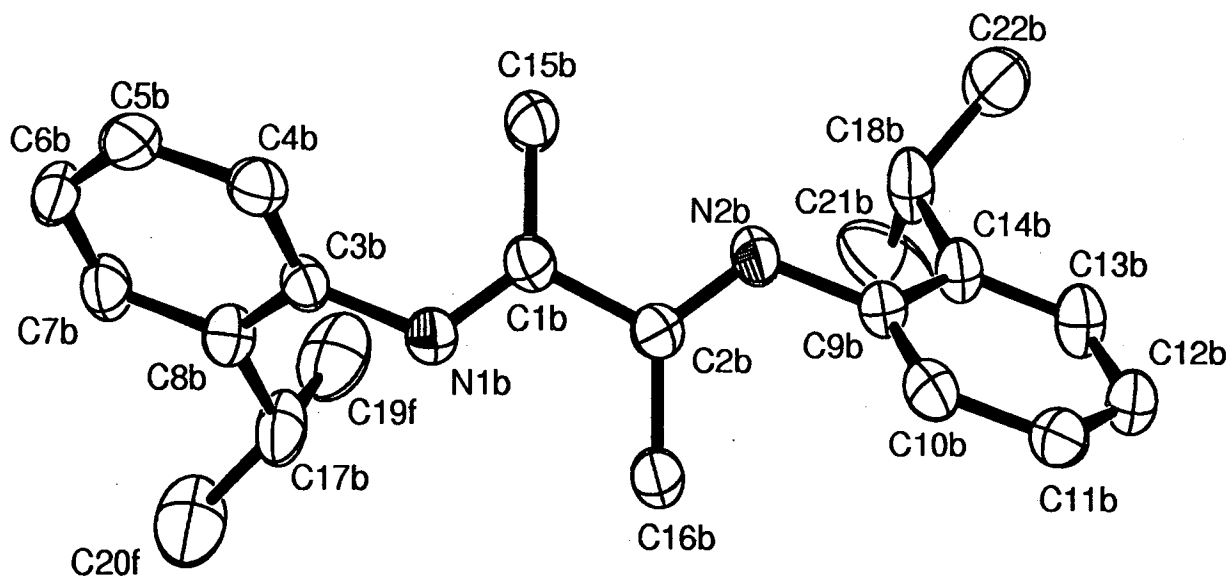


Figure S5. ORTEP plot for $\text{ArN}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{NAr}$ ($\text{Ar} = 2\text{-}^i\text{PrC}_6\text{H}_4$) (one of two independent molecules of similar geometry present in the unit cell). Thermal ellipsoids are shown at the 50% probability level. Hydrogens are omitted for clarity. (CIF file provided: iah55m)