Supplementary Material (ESI) for Chemical Communications

Supporting Information

Cobalt-mediated regio- and stereoselective assembly of dienamides by hydroaminative alkyne coupling of α,ω-diynes

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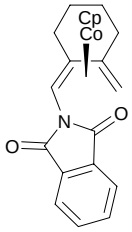
Experimental Section

General Methods. Reactions were carried out under argon using standard Schlenk techniques. THF was distilled over sodium-benzophenone ketyl and degassed by freeze-pump-thaw cycles. Thin layer chromatography (TLC) was performed on Merck 60 F_{254} silica gel. Merck Gerudan SI 60 Å silica gel (35–70 μm) was used for column chromatography. ^{1}H and ^{13}C spectra were recorded at room temperature at 400 MHz and 100 MHz, respectively, on a Bruker ARX400 spectrometer. Chemical shifts are given in ppm, referenced to the residual proton resonance of the solvents (δ = 7.26 ppm for $CDCl_3$, δ = 7.16 ppm for C_6D_6) or to the residual carbon resonance of the solvent (δ = 77.16 ppm for $CDCl_3$, δ = 128.06 ppm for C_6D_6). Coupling constants (J) are given in Hertz (Hz). The terms m, s, d, t and q refer to multiplet, singlet, doublet, triplet and quartet; br means that the signal is broad. Due to the boron quadrupole, ^{13}C NMR signals of carbon atoms attached to boron could not be observed due to line broadening. In the description of the ^{13}C NMR spectra, a number at the beginning of the information in parentheses refers to accidentally isochronous carbons. Elemental analyses were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie. Low resolution mass spectra (MS) and high resolution mass spectra (HRMS) were measured by the Service de Spectrométrie de Masse de l'ICSN-CNRS, Gif-sur-Yvette and the UCB Mass Spectrometry Laboratory. Melting points were obtained on a Büchi capillary apparatus and were uncorrected.

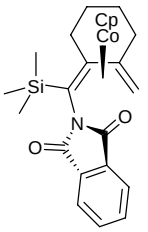
General procedure: To a solution (or slurry) of the NH-compound (2.5 mmol) in THF (20 mL) were simultaneously added by syringe pump over 24 h a solution of $CpCo(C_2H_4)_2$ (90 mg, 0.5 mmol) in THF (2 mL) and a solution of the diyne (0.5 mmol) in THF (2 mL). Solvent evaporation either gave the desired cobalt complex directly or the residue was purified via flash column chromatography using gradient mixtures of pentane and ether (deep red bands). Alternatively, the free ligands could be obtained by adding solid $FeNO_3 \cdot 9H_2O$ (0.5 mmol) at 0 °C to the crude product mixture. The cold bath was removed and the mixture stirred for 5 min. The solvent was promptly evaporated and the residue submitted to flash chromatography over silica gel using gradient mixtures of hexanes and ethyl acetate.

(*Z*)-2-[(2-Methylenecyclohexylidene)methyl]isoindoline-1,3-dione η^5-cyclopentadienylcobalt (**1**)



Red solid, m.p. 190–195 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.89–7.55 (m, 4H), 4.89 (s, 5H, Cp), 3.87 (s, 1H, C*H*N), 2.87–2.77 (m, 1H), 2.59–2.52 (m, 1H), 2.39–2.32 (m, 1H), 2.28–2.10 (m, 3H), 2.00 (d, J = 2.0 Hz, 1H, C=CHH_{exo}), 1.73–1.61 (m, 2H), –0.17 (br s, 1H, C=CHH_{endo}). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 167.2, 133.5, 132.0, 122.6, 98.5, 89.8, 82.1 (Cp), 44.4, 32.8, 31.2, 30.5, 23.5, 23.3. HRMS (ES+): Calcd for $C_{21}H_{20}CoNO_2Na$: 400.0724; found: 400.0746. Anal calcd (%) for $C_{21}H_{20}CoNO_2$: C, 65.85; H, 5.34; N, 3.71; found: C, 65.85; H, 5.38; N, 3.32.

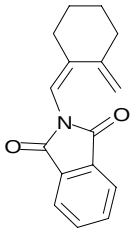
(*E*)-2-[(2-Methylenecyclohexylidene)(1-trimethylsilyl)methyl]isoindoline-1,3-dione η^5-cyclopentadienyl cobalt (**2**)



This complex shows hindered rotation of the phthalimido moiety, as evidenced by the NMR spectra.

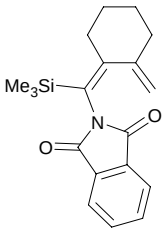
Red solid, m.p. 205–212 °C. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 7.55 (d, J = 7.2 Hz, 1H), 7.39 (d, J = 7.2 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.85 (t, J = 7.6 Hz, 1H), 4.87 (s, 5H, Cp), 3.13 (dt, J_1 = 16.0 Hz, J_2 = 5.2 Hz, 1H), 2.70 (ddd, J_1 = 14.8 Hz, J_2 = 8.4 Hz, J_3 = 5.6 Hz, 1H), 2.43–2.36 (m, 1H), 2.06 (br s, 1H, C=CHH_{exo}), 2.06–1.96 (m, 2H), 1.80–1.68 (m, 3H), 0.32 (s, 9H), 0.13 (br s, 1H, C=CHH_{endo}). ^{13}C NMR (100 MHz, C_6D_6, δ/ppm): 168.6, 167.9, 133.0 (2C), 132.0, 130.9, 122.2, 121.9, 105.9, 97.8, 96.8, 82.0 (Cp), 36.5, 32.6, 30.2, 24.0, 23.1, 1.25. HRMS (ES+): Calcd for $C_{24}H_{28}CoNSiO_2Na$: 472.1119; found: 472.1117.

(*Z*)-2-[(2-Methylenecyclohexylidene)methyl]isoindoline-1,3-dione (**3**)



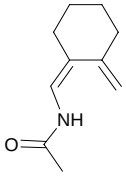
White solid, m.p. 127 °C. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 7.50–7.38 (m, 2H), 6.89–6.73 (m, 2H), 5.82 (s, 1H), 4.67 (s, 1H), 4.54 (s, 1H), 2.42–2.29 (m, 2H), 2.15–1.99 (m, 2H), 1.59–1.22 (m, 4H). ^{13}C NMR (100 MHz, C_6D_6, δ/ppm): 166.9, 147.0, 145.6, 133.6, 132.7, 123.1, 110.2, 108.9, 36.1, 34.8, 27.8, 27.7. HRMS (ES+): Calcd for $C_{16}H_{16}NO_2$: 254.1181; found: 254.1183 ([M+H]$^+$). Anal calcd (%) for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53; found: C, 75.85; H, 5.90; N, 5.60.

(*E*)-2-[(2-Methylenecyclohexylidene)(trimethylsilyl)methyl]isoindoline-1,3-dione (**4**)



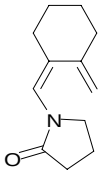
White solid, m.p. 162–169 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.85–7.75 (m, 2H), 7.75–7.62 (m, 2H), 4.59 (s, 1H), 4.50 (s, 1H), 2.51–2.48 (m, 2H), 2.28–2.25 (m, 2H), 1.88–1.78 (m, 2H), 1.78–1.65 (m, 2H), 0.20 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 168.3, 159.7, 147.9, 133.6, 132.3, 124.0, 123.1, 108.5, 36.9, 34.5, 27.9, 27.8, –0.4. HRMS (ES+): Calcd for $C_{19}H_{23}NO_2Si$: 325.1498; found: 325.1500. Anal calcd (%) for $C_{19}H_{23}NO_2Si$: C, 70.11; H, 7.12; N, 4.30; found: C, 69.88; H, 7.40; N, 4.55.

(*Z*)-*N*-[(2-Methylenecyclohexylidene)methyl]acetamide (**5**)



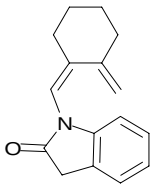
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.44–7.38 (m, 1H, N*H*), 6.69 (d, J = 11.0 Hz, 1H), 5.08 (br s, 1H), 4.82 (br s, 1H), 2.24–2.12 (m, 4H), 2.02 (s, 3H), 1.63–1.54 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 167.1, 147.2, 122.6, 115.3, 110.4, 36.6, 34.1, 27.7, 27.4, 23.6. HRMS (ES+): Calcd for $C_{10}H_{16}NO$: 166.1232; found: 166.1214 ($[M+H]^+$).

(*Z*)-1-[(2-Methylenecyclohexylidene)methyl]pyrrolidin-2-one (**6**)



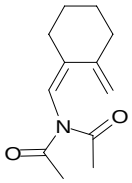
Yellow oil. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 6.94 (s, 1H), 4.92 (s, 1H), 4.63 (s, 1H), 3.07 (t, J = 7.2 Hz, 2H), 2.17 (t, J = 5.6 Hz, 2H), 2.11 (t, J = 5.6 Hz, 2H), 2.01 (t, J = 8.0 Hz, 2H), 1.63–1.50 (m, 4H), 1.26 (quint, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, C_6D_6, δ/ppm): 173.6, 151.4, 124.7, 118.1, 111.0, 47.2, 37.1, 35.9, 30.0, 28.3, 28.0, 18.5. HRMS (ES+): Calcd for $C_{12}H_{17}NO$: 191.1310; found: 191.1310.

(*Z*)-1-[(2-Methylenecyclohexylidene)methyl]indolin-2-one (**7**)



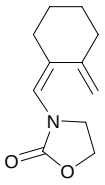
White solid, m.p. 86–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.42–7.23 (m, 2H), 7.07 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 6.22 (s, 1H), 5.09 (s, 1H), 4.81 (s, 1H), 3.61 (s, 2H), 2.39 (t, J = 5.8 Hz, 2H), 2.19 (t, J = 5.8 Hz, 2H), 1.75–1.58 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 174.4, 146.9, 145.0, 143.6, 128.0, 124.5, 122.8, 112.9, 110.4, 109.8, 35.9, 35.2, 29.9, 26.7, 25.9, one quaternary carbon coincides with one CH peak. HRMS (ES+): Calcd for $C_{16}H_{17}NONa$: 262.1208; found: 262.1215.

(*Z*)-*N*-Acetyl-*N*-[(2-methylenecyclohexylidene)methyl]acetamide (**8**)



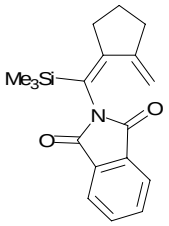
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 6.16 (s, 1H), 4.97 (s, 1H), 4.79 (s, 1H), 2.36 (s, 6H), 2.36–2.30 (m, 2H), 2.10–2.01 (m, 2H), 1.72–1.55 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 173.1, 146.8, 144.1, 118.4, 110.4, 35.0, 28.2, 26.7, 26.4, 25.5. HRMS (ES+): Calcd for $C_{12}H_{18}NO_2$: 208.1338; found: 208.1339 ($[M+H]^+$).

(*Z*)-2-[(2-Methylenecyclohexylidene)methyl]isoxazolidin-3-one (**9**)



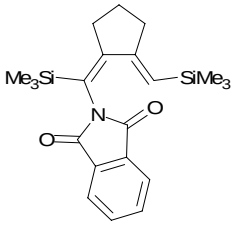
White solid, m.p. 80–85 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 6.32 (s, 1H), 5.06 (s, 1H), 4.71 (s, 1H), 4.34 (t, J = 7.6 Hz, 2H), 3.76 (t, J = 7.6 Hz, 2H), 2.25–2.12 (m, 4H), 1.69–1.58 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 157.8, 146.4, 127.0, 117.2, 111.9, 62.8, 44.6, 37.2, 35.7, 28.2, 28.0. HRMS (ES+): Calcd for $C_{11}H_{15}NO_2$: 193.1103; found: 193.1105.

(*E*)-2-[(2-Methylenecyclopentylidene)(trimethylsilyl)methyl]isoindoline-1,3-dione (**10a**)



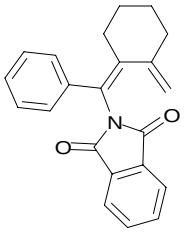
White solid, m.p. 174–176 °C. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 7.65–7.60 (m, 2H), 7.00–6.96 (m, 2H), 5.38 (s, 1H), 4.93 (s, 1H), 2.50 (t, J = 7.2 Hz, 2H), 2.21 (t, J = 7.2 Hz, 2H), 1.44 (quint, J = 7.2 Hz, 2H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, C_6D_6, δ/ppm): 167.4, 155.0, 147.7, 133.5, 132.5, 127.0, 122.9, 110.6, 35.4, 33.4, 23.5, –1.39. HRMS (ES+): Calcd for $C_{18}H_{21}NO_2SiNa$: 344.1239; found: 344.1241. Anal calcd (%) for $C_{18}H_{21}NO_2Si$: C, 69.41; H, 6.80; N, 4.50; found: C, 69.00; H, 6.95; N, 4.54.

2-[(*E*)-(Trimethylsilyl)(*E*)-2-(trimethylsilyl)methylene)cyclopentylidene)methyl]isoindoline-1,3-dione (**11a**)



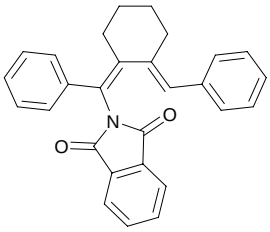
Pale yellow solid, m.p. 95–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.89–7.81 (m, 2H), 7.72–7.65 (m, 2H), 5.58 (br s, 1H), 2.64 (t, J = 7.2 Hz, 2H), 2.40 (td, J_1 = 7.6, J_2 = 2.4 Hz, 2H), 1.80 (quint, J = 7.6 Hz, 2H), 0.20 (s, 9H), –0.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 168.0, 156.6, 154.9, 133.8, 132.1 (2C), 125.8, 123.1, 33.8, 32.5, 23.6, –0.92, –1.23. HRMS (ES+): Calcd for $C_{21}H_{29}NO_2Si_2Na$: 406.1635; found: 406.1637. Anal calcd (%) for $C_{21}H_{29}NO_2Si_2$: C, 65.75; H, 7.62; N, 3.65; found: C, 66.02; H, 7.62; N, 4.01.

(*Z*)-2-[(2-Methylenecyclohexylidene)(phenyl)methyl]isoindoline-1,3-dione (**12a**)



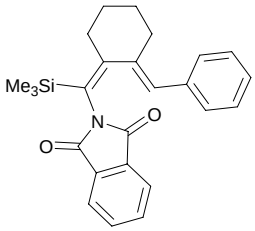
Brown oil. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 7.69 (d, J = 6.8 Hz, 2H), 7.63–7.52 (m, 2H), 7.20–7.13 (m, 2H), 7.12–7.04 (m, 1H), 6.90–6.86 (m, 2H), 5.13 (s, 1H), 4.68 (s, 1H), 2.51–2.40 (m, 4H), 1.56–1.47 (m, 4H). ^{13}C NMR (100 MHz, C_6D_6, δ/ppm): 167.4, 148.4, 145.0, 137.5, 133.4, 132.4, 129.4, 128.3, 123.1, 109.0, 36.4, 32.7, 27.8, 27.2, 2 C_{arom} unobserved. HRMS (ES+): Calcd for $C_{22}H_{20}NO_2$: 330.1494; found: 330.1498 ($[M+H]^+$).

(*Z*)-[(*E*)-(2-Benzylidenecyclohexylidene)(phenyl)methyl]isoindoline-1,3-dione (**13a**)



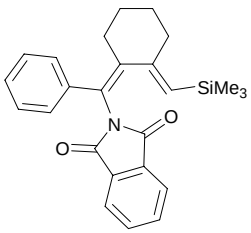
Yellow oil. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 7.70–6.70 (m, 14H), 6.21 (s, 1H), 2.89 (t, J = 6.0 Hz, 4H), 2.58 (d, J = 6.0 Hz, 4H). ^{13}C NMR (100 MHz, C_6D_6, δ/ppm): 167.8, 148.0, 140.9, 138.0–120.0 (C_{sp2} and solvent), 31.2, 29.5, 28.7, 28.4. HRMS (ES+): Calcd for $C_{28}H_{24}NO_2$: 406.1807; found: 406.1805 ($[M+H]^+$). Anal calcd (%) for $C_{28}H_{23}NO_2$: C, 82.94; H, 5.72; N, 3.45; found: C, 82.56; H, 5.75; N, 3.79.

(*E*)-2-[(*E*)-2-Benzylidenecyclohexylidene)(trimethylsilyl)methyl]isoindoline-1,3-dione (**14a**)



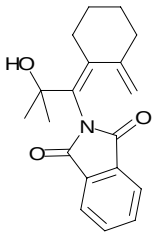
White solid, m.p. 185–198 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.82–7.78 (m, 2H), 7.65–7.62 (m, 2H), 7.18–7.05 (m, 3H), 6.89–6.85 (m, 2H), 6.13 (s, 1H), 2.60 (t, J = 6.0 Hz, 2H), 2.52 (t, J = 6.0 Hz, 2H), 1.92–1.82 (m, 2H), 1.70–1.61 (m, 2H), 0.25 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 168.4, 160.8, 141.4, 137.1, 133.6, 132.1, 128.9, 127.9, 126.2, 123.3, 123.1 (2C), 34.7, 30.2, 27.9, 27.4, –0.33. HRMS (ES+): Calcd for $C_{25}H_{28}NO_2Si$: 402.1889; found: 402.1885 ($[M+H]^+$). Anal calcd (%) for $C_{25}H_{27}NO_2Si$: C, 74.77; H, 6.78; N, 3.49; found: C, 74.79; H, 6.39; N, 3.80.

2-[(*Z*)-Phenyl(*E*)-2-(trimethylsilyl)methylene)cyclohexylidene)methyl]isoindoline-1,3-dione (**14b**).



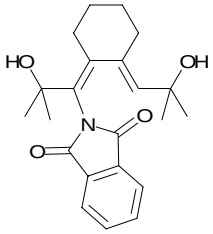
^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 5.24 (s, 1H), from the **15a**/**15b** mixture.

(*Z*)-2-[2-Hydroxy-2-methyl-1-(2-methylenecyclohexylidene)propyl]isoindoline-1,3-dione (**15a**)



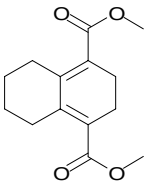
White solid, m.p. 130–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.88–7.80 (m, 2H), 7.76–7.68 (m, 2H), 4.50 (s, 2H), 2.79 (t, J = 6.0 Hz, 2H), 2.44 (s, 1H), 2.20 (t, J = 6.0 Hz, 2H), 1.83–1.77 (m, 2H), 1.68–1.49 (m, 2H), 1.49 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 168.7, 149.2, 148.0, 133.9, 132.6, 127.5, 123.5, 108.0, 73.0, 37.3, 32.3, 29.8, 28.2, 27.6. HRMS (ES+): Calcd for $C_{19}H_{22}NO_3$: 312.1600; found: 312.1599 ($[M+H]^+$). Anal calcd (%) for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50; found: C, 73.26; H, 6.80; N, 4.11.

2-[(*Z*)-2-Hydroxy-1-(*E*)-2-(2-hydroxy-2-methylpropylidene)cyclohexylidene]-2-methylpropyl)isoindoline-1,3-dione (**16a**)



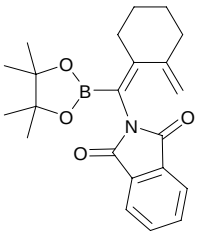
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.84–7.79 (m, 2H), 7.76–7.70 (m, 2H), 5.16 (s, 1H), 2.85–2.70 (m, 3H), 2.50–2.45 (m, 2H), 1.85–1.77 (m, 2H), 1.68–1.60 (m, 2H), 1.49 (s, 1H), 1.47 (s, 6H), 0.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 168.7, 149.6, 142.3, 134.2, 131.9, 130.3, 127.4, 123.5, 72.8, 70.5, 32.6, 31.0, 30.5, 29.8, 27.8, 27.5. HRMS (ES+): Calcd for $C_{22}H_{27}NO_4$: 369.1940; found: 369.1937.

Dimethyl 2,3,5,6,7,8-hexahydronaphthalene-1,4-dicarboxylate (**17c**)



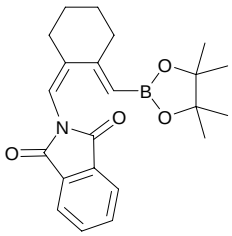
Colorless oil. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 3.45 (s, 6H), 3.00–2.90 (m, 4H), 2.38 (s, 4H), 1.40–1.30 (m, 4H). ^{13}C NMR (100 MHz, C_6D_6, δ/ppm): 167.7, 145.0, 126.5, 50.7, 28.0, 24.4, 22.4. HRMS (ES+): Calcd for $C_{14}H_{18}O_4$: 250.1205; found: 250.1205.

(*Z*)-2-[(2-Methylenecyclohexylidene)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]isoindoline-1,3-dione (**18a**)



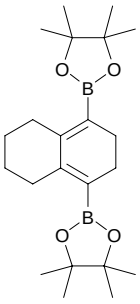
White solid, m.p. 170–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.49–7.45 (m, 2H), 6.77–6.71 (m, 2H), 4.80 (br s, 1H), 4.50 (br s, 1H), 3.00 (t, J = 6.0 Hz, 2H), 2.40 (t, J = 6.0 Hz, 2H), 1.74–1.67 (m, 2H), 1.43–1.36 (m, 2H), 1.02 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 167.7, 148.5 (2C), 133.3, 127.9, 122.7, 108.8, 83.7, 36.4, 33.8, 27.8 (2C), 24.3, C_{NB} unobserved. HRMS (ES+): Calcd for $C_{22}H_{26}BNO_4Na$: 402.1853; found: 402.1855. Anal calcd (%) for $C_{22}H_{26}BNO_4$: C, 69.67; H, 6.91; N, 3.69; found: C, 70.01; H, 6.64; N, 3.95.

2-[(*Z*)-(*E*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)cyclohexylidene)methyl]isoindoline-1,3-dione (**18b**)

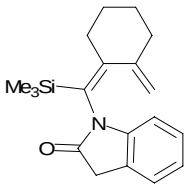


Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.48–7.41 (m, 2H), 6.74–6.71 (m, 2H), 6.56 (s, 1H), 5.47 (s, 1H), 2.33 (t, J = 6.0 Hz, 2H), 2.22 (t, J = 6.0 Hz, 2H), 1.73–1.67 (m, 2H), 1.50–1.44 (m, 2H), 1.07 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 163.1, 141.5, 141.3, 133.0, 132.5, 122.8, 112.7, 82.6, 40.0, 30.8, 27.2, 26.3, 24.5, C_{HB} unobserved.

5,8-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4,6,7-hexahydronaphthalene (**19c**)[1]



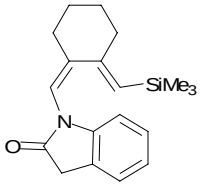
(*E*)-1-[(2-Methylenecyclohexylidene)(trimethylsilyl)methyl]indolin-2-one (**20a**)



[1] V. Gandon, D. Leboeuf, S. Amslinger, K. P. C. Vollhardt, M. Malacria and C. Aubert, *Angew. Chem. Int. Ed.*, 2005, **44**, 7114

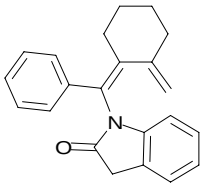
Orange oil. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 7.10–6.98 (m, 1H), 6.77–6.72 (m, 2H), 6.56 (d, J = 8.0 Hz, 1H), 4.91 (s, 1H), 4.53 (s, 1H), 3.12 (s, 2H), 2.42–2.36 (m, 1H), 2.29–2.15 (m, 2H), 2.02–1.96 (m, 1H), 1.65–1.60 (m, 1H), 1.47–1.22 (m, 3H), 0.17 (s, 9H). ^{13}C NMR (100 MHz, C_6D_6, δ/ppm): 173.7, 159.2, 146.9, 128.0, 127.3, 126.1, 124.6, 124.3, 121.2, 109.1, 108.4, 36.8, 35.0, 34.2, 27.8 (2C), –0.39. HRMS (ES+): Calcd for $C_{19}H_{25}NOSi$: 311.1705; found: 311.1701.

1-[(*Z*)-(*E*)-2-(Trimethylsilyl)methylene)cyclohexylidene)methyl]indolin-2-one (**20b**)



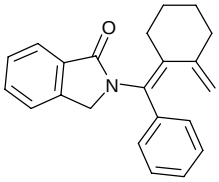
Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.28–7.22 (m, 2H), 7.05 (t, J = 6.8 Hz, 1H), 6.74 (d, J = 7.6 Hz, 1H), 6.03 (s, 1H), 5.66 (t, J = 4.0 Hz, 1H), 3.60 (s, 2H), 2.19–2.12 (m, 4H), 1.76 (s, 2H), 1.67–1.61 (m, 2H), 0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 174.8, 145.1, 140.2, 132.1, 128.4, 127.8, 124.6, 124.4, 122.4, 114.0, 109.6, 35.8, 26.7, 26.0, 22.5, 22.4, –0.88. HRMS (ES+): Calcd for $C_{19}H_{25}NOSi$: 311.1705; found: 311.1703.

(*Z*)-1-[(2-Methylenecyclohexylidene)(phenyl)methyl]indolin-2-one ((*Z*)-**21a**)



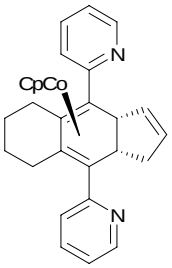
White solid, m.p. 85–89 °C. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 7.50–7.45 (m, 2H), 7.18–7.10 (m, 2H), 7.09–7.04 (m, 1H), 7.01–6.93 (m, 1H), 6.82–6.78 (m, 2H), 6.72–6.68 (m, 1H), 4.96 (s, 1H), 4.69 (s, 1H), 3.22 (s, 2H), 2.78–2.69 (m, 2H), 2.37–2.28 (m, 2H), 1.72–1.43 (m, 4H). ^{13}C NMR (100 MHz, C_6D_6, δ/ppm): 173.2, 148.3, 146.5, 143.7, 136.8, 129.4, 128.3, 124.8, 124.4, 124.3, 121.7, 109.5, 108.7, 36.0, 35.5, 32.7, 27.8, 27.2, 2 C_{arom} unobserved. HRMS (ES+): Calcd for $C_{22}H_{21}NONa$: 338.1521; found: 338.1522. Anal calcd (%) for $C_{22}H_{21}NO$: C, 83.78; H, 6.71; N, 4.44; found: C, 84.00; H, 6.72; N, 3.90.

(*E*)-1-((2-Methylenecyclohexylidene)(phenyl)methyl)indolin-2-one ((*E*)-**21a**)



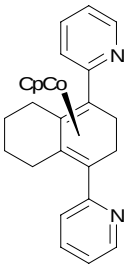
Pale yellow oil. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 7.45–7.42 (m, 2H), 7.16–6.69 (m, 7H), 4.88 (s, 1H), 4.87 (s, 1H), 3.22 (s, 2H), 2.42–2.20 (m, 4H), 1.76–1.25 (m, 4H).

2,2'-(3a,5,6,7,8,9a-Hexahydro-1*H*-cyclopenta[b]naphthalene-4,9-diyl)dipyridine η^5-cyclopentadienylcobalt (**23a**)



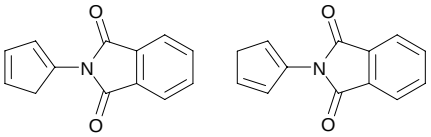
Red solid, m.p. 250 °C (dec). ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 8.58 (t, J = 5.6 Hz, 2H), 7.49–7.42 (m, 2H), 7.24–7.16 (m, 2H), 6.72–6.67 (m, 2H), 5.84–5.81 (m, 1H), 5.38–5.35 (m, 1H), 4.39 (s, 5H), 4.24–4.19 (m, 1H), 3.87 (ddd, J_1 = 16.8 Hz, J_2 = 8.4 Hz, J_3 = 4.8 Hz, 1H), 3.75–3.63 (m, 2H), 2.69–2.51 (m, 3H), 2.19–2.08 (m, 2H), 1.98–1.79 (m, 3H). ^{13}C NMR (100 MHz, C_6D_6, δ/ppm): 167.0, 166.8, 148.2, 148.0, 134.5, 134.4, 133.5, 128.0, 126.5, 122.8, 122.3, 118.2, 118.1, 93.5, 93.1, 84.1, 55.0, 45.4, 40.3 (2C), 29.9 (2C), 24.1, 23.9. HRMS (ES+): Calcd for $C_{28}H_{27}CoN_2Na$: 473.1404; found: 473.1408. Anal calcd (%) for $C_{28}H_{27}CoN_2$: C, 74.66; H, 6.04; N, 6.22; found: C, 75.01; H, 6.32; N, 5.93.

5,8-Di(pyridin-2-yl)-1,2,3,4,6,7-hexahydronaphthalene η^5-cyclopentadienylcobalt (**23b**)



Red oil. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 8.59 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.20 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 6.72 (dd, J_1 = 6.7 Hz, J_2 = 4.8 Hz, 2H), 4.55 (s, 5H), 3.72 (ddd, J_1 = 17.0 Hz, J_2 = 7.6 Hz, J_3 = 4.4 Hz, 2H), 2.45–2.36 (m, 2H), 2.36–2.28 (BB'm, 2H), 2.18–2.09 (m, 2H), 1.81–1.71 (m, 2H), 1.39–1.31 (AA'm, 2H). ^{13}C NMR (100 MHz, C_6D_6, δ/ppm): 167.3, 147.9, 134.6, 121.9, 118.5, 93.4, 83.8, 62.4, 29.4, 28.8, 24.1. HRMS (ES+): Calcd for $C_{25}H_{25}CoN_2Na$: 435.1247; found: 435.1250.

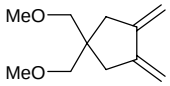
2-(Cyclopenta-1,3-dienyl)isoindoline-1,3-dione and 2-(cyclopenta-1,4-dienyl)isoindoline-1,3-dione (**25a** and **25b**)



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): Major isomer: 7.91–7.87 (m, 2H), 7.77–7.73 (m, 2H), 7.04–7.01 (m, 1H), 6.61–6.57 (m, 1H), 6.35–6.31 (m, 1H), 3.68 (br s, 2H); Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.95– 7.91 (m, 2H), 7.79–7.76 (m, 2H), 7.09–

7.06 (m, 1H), 6.76–6.72 (m, 1H), 6.35–6.31 (m, 1H), 3.19 (br s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): Mixture: 166.7, 136.4, 134.5, 134.0, 131.9, 131.5, 129.7, 128.5, 123.7, 123.6, 122.8, 121.5, 41.3, 40.0. HRMS (ES+): Calcd for $C_{19}H_9NO_2$: 211.0633; found: 211.0630.

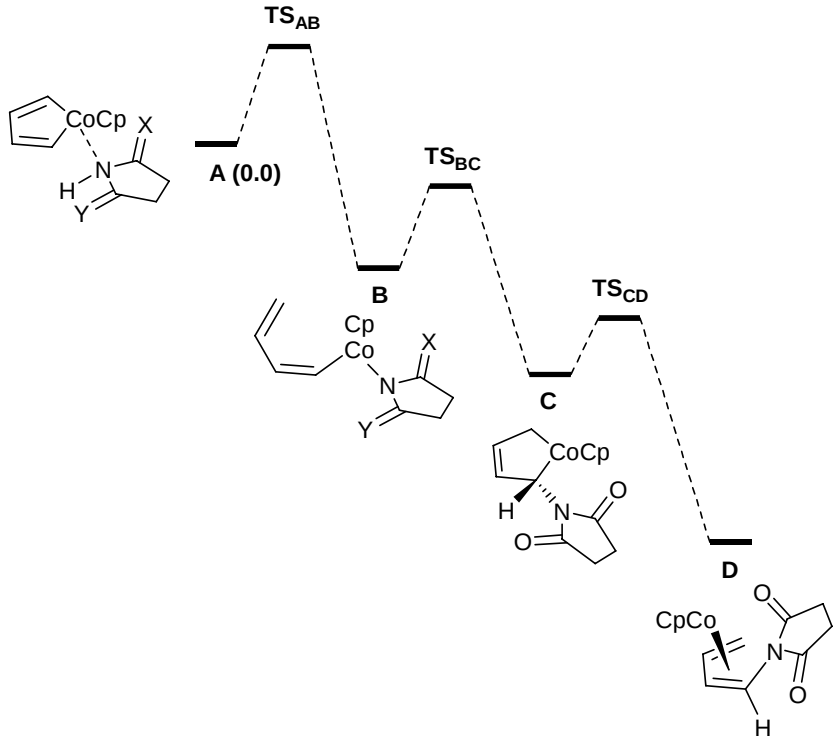
1,1-Bis(methoxymethyl)-3,4-dimethylenecyclopentane (**26**)



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 5.39 (br s, 2H), 4.90 (br s, 2H), 3.37 (s, 6H), 3.24 (s, 4H), 2.38 (s, 4H).

Computational Details

All geometries of molecules and transition states were optimized fully without symmetry constraints using the Gaussian 03 program.[2] The DFT computations were carried out using the B3LYP functional as implemented in Gaussian. The computations employed the LACVP(d,p) basis set: The cobalt atom was described by a double-ζ basis set with the effective core potential of Hay and Wadt (LANL2DZ),[3] and the 6-31G(d,p) basis set[4] was used for the other elements. Frequency calculations were performed to confirm the nature of the stationary points and to obtain zero-point energies (ZPE). The connectivity between stationary points was established by intrinsic reaction coordinate calculations (IRC). The Chemcraft program was used to draw the calculated structures.[5]



[2] Gaussian 03, Revision B.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, Jr., J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[3] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.

[4] a) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724; b) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257; c) P. C. Hariharan, J. A. Pople, *Theo. Chim. Acta* **1973**, *28*, 213; d) P. C. Hariharan, J. A. Pople, *Mol. Phys.* **1974**, *27*, 209; e) M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163.

[5] http://www.chemcraftprog.com.

Table 1. Relative enthalpies and free energies.

	A → B		**B → C**		**C → D**	
	$\Delta H^{\ddagger}_{298}$ (kcal/mol)	ΔH_{298} (kcal/mol)	$\Delta H^{\ddagger}_{298}$ (kcal/mol)	ΔH_{298} (kcal/mol)	$\Delta H^{\ddagger}_{298}$ (kcal/mol)	ΔH_{298} (kcal/mol)
X = CH_2, Y = CH_2	25.3	–6.4	—	—	—	—
X = CH_2, Y = O	8.6	–5.4	—	—	—	—
X = O, Y = CH_2	9.7	–22.3	—	—	—	—
X = O, Y = O	3.2	–23.1	13.0	–6.3	3.1	–30.9
	$\Delta G^{\ddagger}_{298}$ (kcal/mol)	ΔG_{298} (kcal/mol)	$\Delta G^{\ddagger}_{298}$ (kcal/mol)	ΔG_{298} (kcal/mol)	$\Delta G^{\ddagger}_{298}$ (kcal/mol)	ΔG_{298} (kcal/mol)
X = CH_2, Y = CH_2	26.3	–5.4	—	—	—	—
X = CH_2, Y = O	9.0	–6.8	—	—	—	—
X = O, Y = CH_2	11.6	–18.0	—	—	—	—
X = O, Y = O	3.8	–22.9	14.8	–7.9	3.7	–30.5

This set of results shows that the mechanism previously described for pyridones[6] applies to the NH-compounds used: cyclopentylamine (X = Y = CH_2), 2-pyrrolidinone (X = CH_2, Y = O, or X = O, Y = CH_2) and succinimide (X = Y = O). However, the NH-activation step is much slower with alkylamines when compared to amides [$\Delta H^{\ddagger}_{298}$ (**A→B**) = 25.3, 8.6 (or 9.7 for another isomer) and 3.2 kcal/mol for cyclopentylamine (p*K*a = 44), 2-pyrrolidinone (p*K*a = 24), and succinimide (pK_a = 15) respectively].

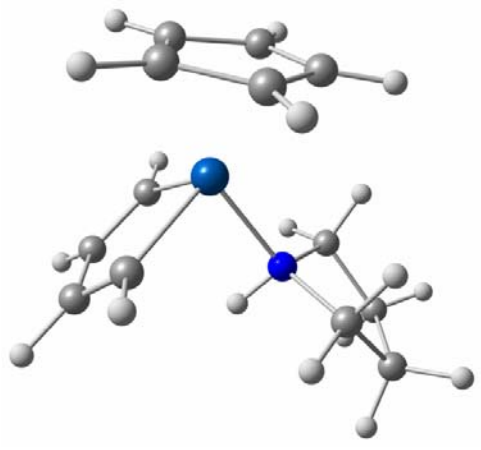
[6] C. Aubert, V. Gandon, A. Geny, T. J. Heckrodt, M. Malacria, E. Paredes and K. P. C. Vollhardt, *Chem. Eur.*, *J.* 2007, **13**, 7466.

Table 2. Enthalpies, free energies and imaginary frequencies.

	H_{298} (a.u.)[a]	G_{298} (a.u.)[a]	Imaginary frequency (cm^{-1})
A (X = CH_2, Y = CH_2)	–705.685210	–705.745207	—
A (X = CH_2, Y = O)	–779.722808	–779.782152	—
A (X = O, Y = CH_2)	–779.720740	–779.782194	—
A (X = O, Y = O)	–853.757769	–853.820253	—
TS_{AB} (X = CH_2, Y = CH_2)	–705.644880	–705.703269	736
TS_{AB} (X = CH_2, Y = O)	–779.709050	–779.767829	1222
TS_{AB} (X = O, Y = CH_2)	–779.705276	–779.763631	1304
TS_{AB} (X = O, Y = O)	–853.752721	–853.814139	997
B (X = CH_2, Y = CH_2)	–705.675008	–705.736652	—
B (X = CH_2, Y = O)	–779.731483	–779.793035	—
B (X = O, Y = CH_2)	–779.756240	–779.810956	—
B (X = O, Y = O)	–853.794644	–853.856720	—
TS_{BC}	–853.773874	–853.833068	258
C	–976.739036	–976.795993	—
TS_{CD}	–853.783254	–853.844078	309
D	–976.785151	–976.846704	—

[*a*] Includes thermal correction at 298 K.

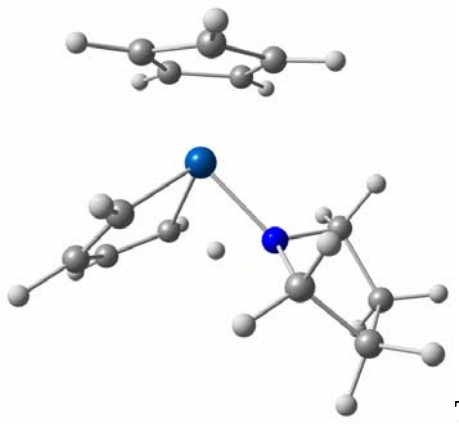
Table 3. Coordinates of the calculated species [atomic symbol, x, y, z (Å)].



A (X = CH_2, Y = CH_2)

6	-0.615040000	2.684442000	0.736041000
6	2.036760000	-0.415712000	-1.173732000
6	-0.614936000	2.684608000	-0.735307000
6	3.529600000	-0.379119000	-0.779210000
6	-0.681639000	1.460204000	1.295994000
6	-0.681574000	1.460509000	-1.295573000
6	3.529722000	-0.381813000	0.778916000
6	-2.539634000	-0.715819000	-0.711530000
6	2.036744000	-0.416216000	1.173789000
6	-2.539433000	-0.716359000	0.711714000
7	1.301689000	0.127165000	0.000125000
6	-1.559155000	-1.657302000	-1.155515000
1	1.786340000	0.171843000	-2.057884000
6	-1.558805000	-1.658098000	1.154729000
6	-0.969411000	-2.233612000	-0.000701000
27	-0.671728000	0.027151000	0.000049000
1	-0.584129000	3.617544000	1.303184000
1	4.006770000	0.527812000	-1.162669000
1	-0.583851000	3.617840000	-1.302231000
1	1.409844000	1.143233000	0.000238000
1	4.071062000	-1.235956000	1.194706000
1	-0.718817000	1.305835000	-2.376523000
1	1.787368000	0.171949000	2.057833000
1	-3.164737000	-0.100078000	-1.341962000
1	-3.164347000	-0.101018000	1.342726000
1	-1.319373000	-1.891321000	-2.183757000

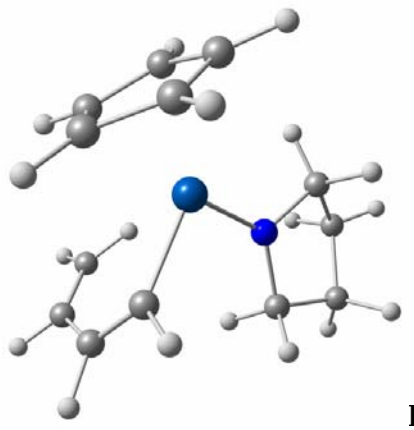
1	-1.318755000	-1.892898000	2.182732000
1	-0.171504000	-2.966512000	-0.001059000
1	4.073262000	-1.230179000	-1.198276000
1	4.009654000	0.522275000	1.165572000
1	-0.719227000	1.305171000	2.376877000
1	1.693690000	-1.441546000	-1.335315000
1	1.692398000	-1.441520000	1.335915000



TS_{AB} (X = CH_2, Y = CH_2)

6	-0.829292000	2.593560000	0.940086000
6	2.138900000	0.268851000	-1.129724000
6	-0.847626000	2.690348000	-0.505125000
6	3.605393000	0.118456000	-0.636405000
6	-0.398806000	1.416420000	1.489616000
6	-0.707963000	1.507743000	-1.151755000
6	3.489016000	-0.621253000	0.725383000
6	-2.581651000	-0.625877000	-0.679391000
6	2.005439000	-1.040783000	0.793115000
6	-2.513370000	-0.847054000	0.717110000
7	1.316051000	0.008921000	0.049355000
6	-1.591617000	-1.457971000	-1.306466000
1	1.929502000	1.259865000	-1.537196000
6	-1.496274000	-1.823127000	0.968124000
6	-0.956275000	-2.210456000	-0.283160000
27	-0.624963000	-0.021525000	-0.014305000
1	-1.177677000	3.431635000	1.549163000
1	4.080639000	1.095661000	-0.510744000
1	-0.959765000	3.654768000	-1.001420000
1	0.627813000	0.962330000	0.941548000

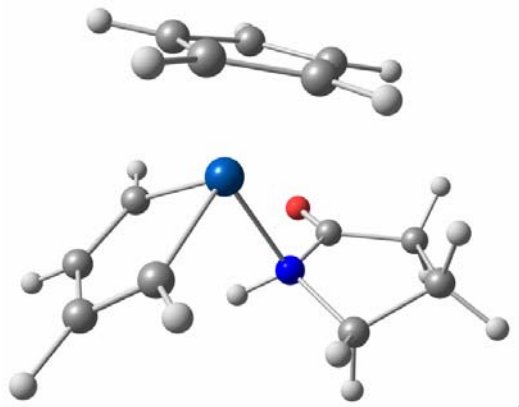
1	4.165271000	-1.478771000	0.802404000
1	-0.690185000	1.453795000	-2.242085000
1	1.622563000	-1.110022000	1.817893000
1	-3.245334000	0.063665000	-1.181236000
1	-3.103419000	-0.337669000	1.466313000
1	-1.393793000	-1.525135000	-2.367118000
1	-1.200417000	-2.200460000	1.937100000
1	-0.139752000	-2.903708000	-0.431828000
1	4.207221000	-0.443610000	-1.357391000
1	3.721048000	0.058458000	1.551081000
1	-0.496460000	1.229490000	2.557641000
1	1.938002000	-0.467452000	-1.930432000
1	1.881144000	-2.037258000	0.328607000



B (X = CH_2, Y = CH_2)

6	-0.566911000	3.152114000	0.520691000
6	2.218868000	0.580032000	-0.715655000
6	-0.617208000	2.591851000	-0.837000000
6	3.609185000	-0.023349000	-0.436421000
6	-0.174859000	2.554584000	1.657980000
6	-0.569671000	1.306110000	-1.235759000
6	3.340714000	-0.973176000	0.739663000
6	-2.656585000	-0.395376000	-0.363794000
6	1.956113000	-1.525557000	0.378551000
6	-2.256774000	-0.359370000	1.000381000
7	1.222137000	-0.393717000	-0.223930000
6	-2.132694000	-1.582621000	-0.943546000
1	2.080132000	1.526082000	-0.179123000
6	-1.548756000	-1.574907000	1.280949000
6	-1.468157000	-2.323437000	0.092086000

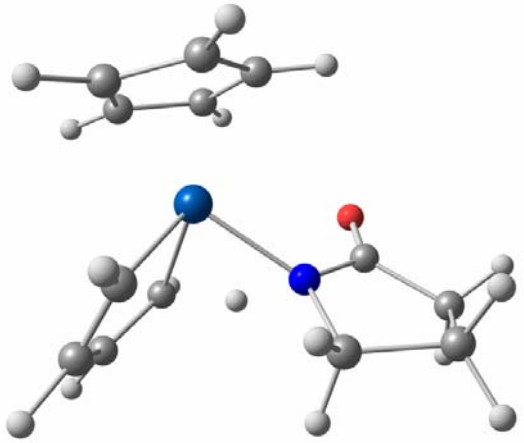
27	-0.539416000	-0.332589000	-0.264486000
1	-0.863223000	4.200550000	0.584392000
1	4.358698000	0.742149000	-0.216516000
1	-0.705493000	3.355205000	-1.616128000
1	0.162948000	1.523004000	1.675930000
1	4.094546000	-1.758104000	0.852361000
1	-0.589072000	1.133484000	-2.317968000
1	1.406876000	-1.936222000	1.229289000
1	-3.194568000	0.382522000	-0.884391000
1	-2.455608000	0.439989000	1.699434000
1	-2.231505000	-1.885023000	-1.977071000
1	-1.095634000	-1.832197000	2.229371000
1	-0.952777000	-3.265527000	-0.038134000
1	3.962599000	-0.594293000	-1.303414000
1	3.288528000	-0.413367000	1.681018000
1	-0.173904000	3.094242000	2.600712000
1	2.053488000	0.795261000	-1.776223000
1	2.063646000	-2.333220000	-0.363679000



A (X = CH_2, Y = O)

6	-1.796196000	2.302366000	0.717837000
6	1.852660000	1.021847000	-1.335881000
6	-1.831209000	2.293968000	-0.752183000
6	2.799318000	-0.190876000	-1.310504000
6	-1.282657000	1.186899000	1.272774000
6	-1.334547000	1.176885000	-1.316407000
6	3.184456000	-0.307672000	0.171540000
6	-0.615510000	-2.053176000	-1.110720000
6	2.046986000	0.367963000	0.933688000
6	-1.935334000	-1.597021000	-0.828212000

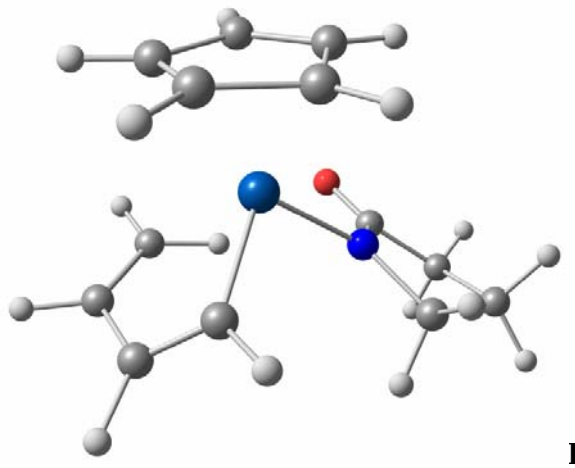
7	1.134544000	0.925413000	-0.037704000
6	0.034088000	-2.272692000	0.138860000
1	2.421069000	1.960038000	-1.371403000
6	-2.083952000	-1.513805000	0.588668000
6	-0.857239000	-1.946465000	1.186711000
27	-0.653042000	-0.097948000	-0.033266000
1	-2.172561000	3.152284000	1.290963000
1	3.657749000	-0.050558000	-1.971073000
1	-2.238787000	3.135908000	-1.315734000
1	-1.191064000	1.035990000	2.348749000
1	0.701902000	1.786951000	0.303461000
1	3.335260000	-1.327603000	0.532956000
8	1.920171000	0.477338000	2.126952000
1	-0.197437000	-2.228644000	-2.092598000
1	-2.690238000	-1.333571000	-1.554885000
1	1.055408000	-2.609212000	0.267264000
1	-2.972022000	-1.192176000	1.112788000
1	-0.643457000	-1.988552000	2.245500000
1	2.261790000	-1.084440000	-1.639046000
1	4.098188000	0.251966000	0.406220000
1	-1.320293000	1.017015000	-2.397403000
1	1.138264000	1.013291000	-2.156305000



TS_{AB} (X = CH_2, Y = O)

6	-1.006138000	2.445132000	1.240881000
6	2.058372000	1.097106000	-0.853293000
6	-1.108297000	2.738592000	-0.178634000
6	3.378901000	0.327470000	-1.072475000
6	-0.639706000	1.176328000	1.576978000
6	-0.984963000	1.660664000	-0.986351000

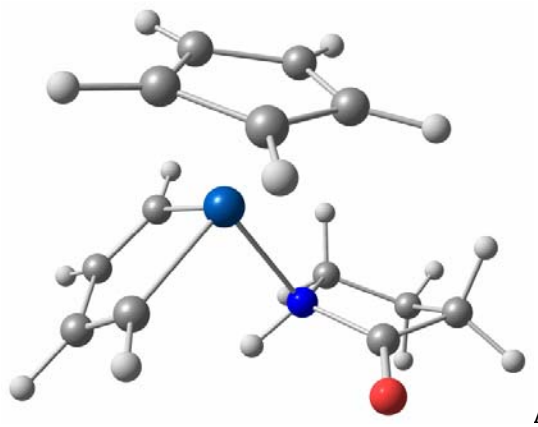
6	3.507345000	-0.521160000	0.197182000
6	-1.428616000	-1.470087000	-1.509628000
6	2.058089000	-0.732251000	0.647499000
6	-2.516390000	-0.727452000	-0.948406000
7	1.254801000	0.218277000	0.018163000
6	-0.821903000	-2.200973000	-0.448364000
1	2.238229000	2.061732000	-0.360254000
6	-2.548995000	-0.984869000	0.452388000
6	-1.495885000	-1.903718000	0.758167000
27	-0.733394000	-0.005848000	-0.071508000
1	-1.239190000	3.210864000	1.984498000
1	4.225758000	0.996758000	-1.245641000
1	-1.258082000	3.758963000	-0.533257000
1	-0.647357000	0.823032000	2.606425000
1	0.514024000	0.813652000	0.921028000
1	4.007841000	-1.482588000	0.064079000
8	1.671926000	-1.568253000	1.447954000
1	-1.137471000	-1.487360000	-2.550622000
1	-3.187673000	-0.072275000	-1.485113000
1	0.068751000	-2.808926000	-0.525145000
1	-3.241070000	-0.546974000	1.157562000
1	-1.216276000	-2.259268000	1.738742000
1	3.284431000	-0.323388000	-1.948647000
1	4.032183000	0.014900000	0.998534000
1	-1.038505000	1.748434000	-2.073470000
1	1.526151000	1.299730000	-1.784434000



B (X = CH_2, Y = O)

6	-1.758715000	2.454471000	0.612634000

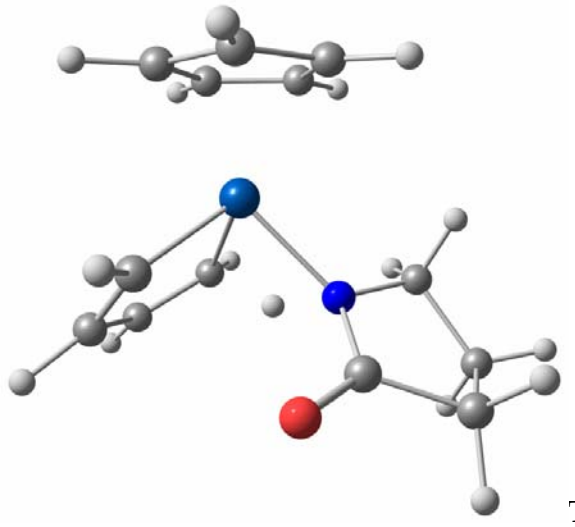
6	2.114187000	0.335224000	-1.380232000
6	-1.401464000	2.442617000	-0.800791000
6	3.544834000	-0.040992000	-0.926699000
6	-1.110123000	1.714804000	1.541746000
6	-0.841796000	1.331238000	-1.320793000
6	3.483050000	0.142070000	0.595984000
6	-1.023737000	-1.814251000	-1.172807000
6	1.994235000	-0.054918000	0.921542000
6	-2.278343000	-1.144825000	-0.954358000
7	1.276857000	0.032138000	-0.224852000
6	-0.563573000	-2.301526000	0.106744000
1	2.048477000	1.402719000	-1.644225000
6	-2.492571000	-1.092800000	0.435623000
6	-1.437008000	-1.832682000	1.088761000
27	-0.599837000	-0.111535000	-0.130963000
1	-2.628271000	3.039540000	0.917139000
1	4.312466000	0.563175000	-1.418688000
1	-1.623217000	3.323749000	-1.405870000
1	-1.483433000	1.616168000	2.556254000
1	-0.108918000	1.296802000	1.388513000
1	4.097979000	-0.557389000	1.167532000
8	1.526653000	-0.224569000	2.054652000
1	-0.574402000	-2.026807000	-2.132895000
1	-2.891968000	-0.681883000	-1.713645000
1	0.370483000	-2.815501000	0.282066000
1	-3.310917000	-0.591087000	0.932431000
1	-1.301734000	-1.933270000	2.156414000
1	3.742526000	-1.091353000	-1.168431000
1	3.768928000	1.156095000	0.903670000
1	-0.543070000	1.283548000	-2.368698000
1	1.795584000	-0.232066000	-2.262936000



A (X = O, Y = CH_2)

6	1.442037000	2.589130000	-0.466448000
6	-2.063052000	-0.184403000	0.915642000
6	1.453752000	2.409660000	0.992788000
6	-3.201935000	-0.708461000	0.050685000
6	1.131112000	1.479264000	-1.162450000
6	1.163029000	1.159687000	1.406554000
6	-3.360312000	0.386976000	-1.013249000
6	1.311772000	-1.939356000	0.938505000
6	-1.914431000	0.885251000	-1.221800000
6	2.398179000	-1.259237000	0.297126000
7	-1.217338000	0.636084000	0.074967000
6	0.382286000	-2.295638000	-0.062451000
8	-1.879512000	-0.357126000	2.093529000
6	2.131541000	-1.234509000	-1.105166000
6	0.871993000	-1.856449000	-1.330137000
27	0.715388000	-0.042460000	-0.044309000
1	1.678404000	3.552877000	-0.922664000
1	-4.083150000	-0.900178000	0.664448000
1	1.699020000	3.234524000	1.665269000
1	1.101446000	1.455176000	-2.254290000
1	-0.910934000	1.474596000	0.577508000
1	-3.809440000	0.031413000	-1.943486000
1	-1.844772000	1.941874000	-1.480365000
1	1.203827000	-2.110937000	2.000189000
1	3.274302000	-0.853607000	0.781664000
1	-0.562787000	-2.795210000	0.111632000
1	2.765192000	-0.784443000	-1.855964000
1	0.393187000	-2.000954000	-2.289202000

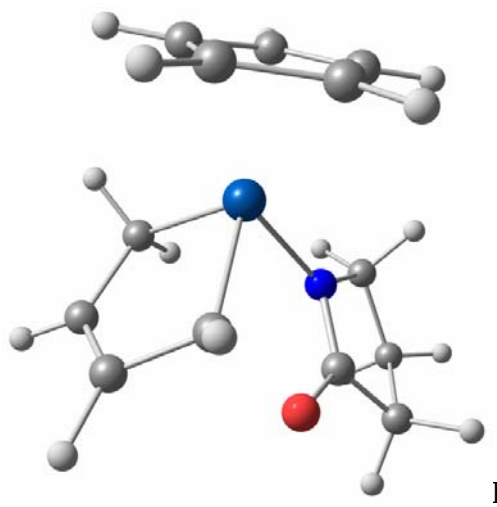
1	-2.887596000	-1.658662000	-0.399611000
1	-3.990833000	1.194304000	-0.624604000
1	1.146559000	0.864760000	2.456400000
1	-1.406274000	0.313809000	-2.001168000



TS_{AB} (X = O, Y = CH_2)

6	-1.006138000	2.445132000	1.240881000
6	2.058372000	1.097106000	-0.853293000
6	-1.108297000	2.738592000	-0.178634000
6	3.378901000	0.327470000	-1.072475000
6	-0.639706000	1.176328000	1.576978000
6	-0.984963000	1.660664000	-0.986351000
6	3.507345000	-0.521160000	0.197182000
6	-1.428616000	-1.470087000	-1.509628000
6	2.058089000	-0.732251000	0.647499000
6	-2.516390000	-0.727452000	-0.948406000
7	1.254801000	0.218277000	0.018163000
6	-0.821903000	-2.200973000	-0.448364000
1	2.238229000	2.061732000	-0.360254000
6	-2.548995000	-0.984869000	0.452388000
6	-1.495885000	-1.903718000	0.758167000
27	-0.733394000	-0.005848000	-0.071508000
1	-1.239190000	3.210864000	1.984498000
1	4.225758000	0.996758000	-1.245641000
1	-1.258082000	3.758963000	-0.533257000
1	-0.647357000	0.823032000	2.606425000
1	0.514024000	0.813652000	0.921028000

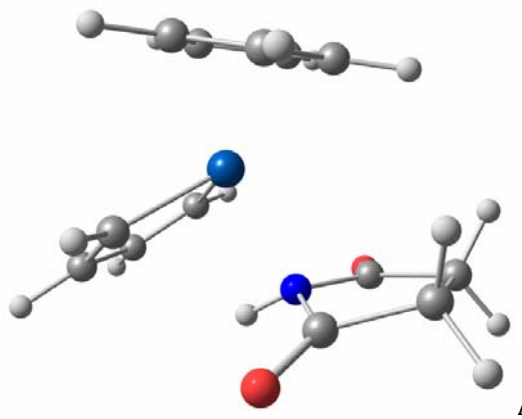
1	4.007841000	-1.482588000	0.064079000
8	1.671926000	-1.568253000	1.447954000
1	-1.137471000	-1.487360000	-2.550622000
1	-3.187673000	-0.072275000	-1.485113000
1	0.068751000	-2.808926000	-0.525145000
1	-3.241070000	-0.546974000	1.157562000
1	-1.216276000	-2.259268000	1.738742000
1	3.284431000	-0.323388000	-1.948647000
1	4.032183000	0.014900000	0.998534000
1	-1.038505000	1.748434000	-2.073470000
1	1.526151000	1.299730000	-1.784434000



B (X = O, Y = CH_2)

6	-1.758715000	2.454471000	0.612634000
6	2.114187000	0.335224000	-1.380232000
6	-1.401464000	2.442617000	-0.800791000
6	3.544834000	-0.040992000	-0.926699000
6	-1.110123000	1.714804000	1.541746000
6	-0.841796000	1.331238000	-1.320793000
6	3.483050000	0.142070000	0.595984000
6	-1.023737000	-1.814251000	-1.172807000
6	1.994235000	-0.054918000	0.921542000
6	-2.278343000	-1.144825000	-0.954358000
7	1.276857000	0.032138000	-0.224852000
6	-0.563573000	-2.301526000	0.106744000
1	2.048477000	1.402719000	-1.644225000
6	-2.492571000	-1.092800000	0.435623000
6	-1.437008000	-1.832682000	1.088761000
27	-0.599837000	-0.111535000	-0.130963000

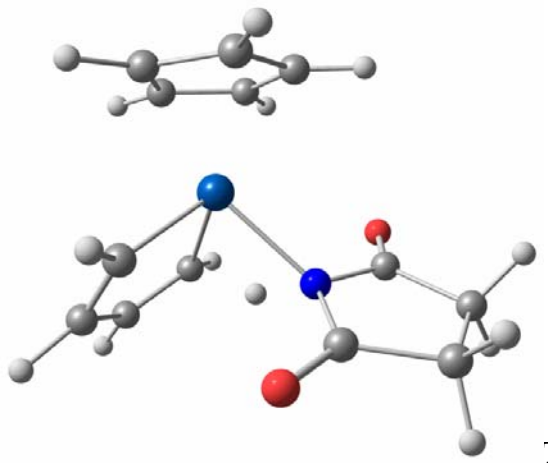
1	-2.628271000	3.039540000	0.917139000
1	4.312466000	0.563175000	-1.418688000
1	-1.623217000	3.323749000	-1.405870000
1	-1.483433000	1.616168000	2.556254000
1	-0.108918000	1.296802000	1.388513000
1	4.097979000	-0.557389000	1.167532000
8	1.526653000	-0.224569000	2.054652000
1	-0.574402000	-2.026807000	-2.132895000
1	-2.891968000	-0.681883000	-1.713645000
1	0.370483000	-2.815501000	0.282066000
1	-3.310917000	-0.591087000	0.932431000
1	-1.301734000	-1.933270000	2.156414000
1	3.742526000	-1.091353000	-1.168431000
1	3.768928000	1.156095000	0.903670000
1	-0.543070000	1.283548000	-2.368698000
1	1.795584000	-0.232066000	-2.262936000



A (X = O, Y = O)

6	-1.761248000	2.257439000	0.960582000
6	1.911106000	0.674742000	-1.076687000
6	-1.730094000	2.415296000	-0.501148000
6	2.873714000	-0.495359000	-0.900692000
6	-1.322843000	1.064879000	1.404643000
6	-1.267278000	1.344352000	-1.170172000
6	2.973233000	-0.708352000	0.618372000
6	-2.016839000	-1.408059000	-1.088322000
6	1.908286000	0.194442000	1.235391000
6	-2.310687000	-1.418229000	0.311093000
7	1.180108000	0.812586000	0.157610000
6	-0.718649000	-1.953693000	-1.273889000

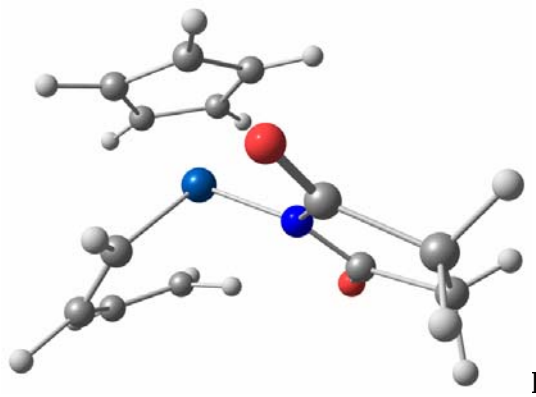
8	1.781801000	1.387821000	-2.035345000
6	-1.201325000	-2.025622000	0.988359000
6	-0.231246000	-2.340143000	0.013779000
27	-0.724548000	-0.110949000	-0.017845000
1	-2.110856000	3.059685000	1.613279000
1	3.822223000	-0.249255000	-1.382265000
1	-2.046127000	3.342629000	-0.982385000
1	-1.277351000	0.790230000	2.458341000
1	0.729573000	1.709395000	0.355768000
1	2.810481000	-1.739893000	0.939337000
1	-1.167034000	1.304588000	-2.254788000
8	1.715379000	0.407656000	2.402983000
1	-2.660581000	-1.012735000	-1.860546000
1	-3.221667000	-1.061673000	0.768729000
1	-0.210991000	-2.082015000	-2.220136000
1	-1.112761000	-2.178166000	2.054853000
1	0.734813000	-2.787226000	0.212892000
1	2.458084000	-1.363821000	-1.420296000
1	3.940015000	-0.398210000	1.026808000



TS_{AB} (X = O, Y = O)

6	-1.143875000	2.194940000	1.581874000
6	2.089293000	0.879652000	-0.682062000
6	-1.217533000	2.695171000	0.220478000
6	3.439895000	0.162779000	-0.762592000
6	-0.815201000	0.881594000	1.715463000
6	-1.038955000	1.752142000	-0.729748000
6	3.355590000	-0.988138000	0.243253000
6	-2.473436000	-0.609610000	-1.212317000

6	1.939115000	-0.917766000	0.809584000
6	-2.675975000	-0.951509000	0.161390000
7	1.248430000	0.165149000	0.212939000
6	-1.367475000	-1.363612000	-1.697675000
8	1.796139000	1.883062000	-1.285323000
6	-1.722515000	-1.963487000	0.507415000
6	-0.924602000	-2.203929000	-0.629701000
27	-0.806903000	-0.031555000	-0.058140000
1	-1.342935000	2.849547000	2.433591000
1	4.230214000	0.885973000	-0.543797000
1	-1.348693000	3.756390000	0.009385000
1	-0.814126000	0.362897000	2.672619000
1	0.493670000	0.689933000	1.005308000
1	3.508515000	-1.976871000	-0.198945000
1	-1.032285000	1.981062000	-1.794400000
8	1.469308000	-1.655572000	1.647523000
1	-3.043631000	0.120454000	-1.768510000
1	-3.428834000	-0.531176000	0.812442000
1	-0.955519000	-1.322962000	-2.696369000
1	-1.589692000	-2.411060000	1.481712000
1	-0.071443000	-2.868706000	-0.662551000
1	3.589472000	-0.169755000	-1.794208000
1	4.063113000	-0.899081000	1.073148000



B (X = O, Y = O)

6	1.945036000	2.396387000	0.549047000
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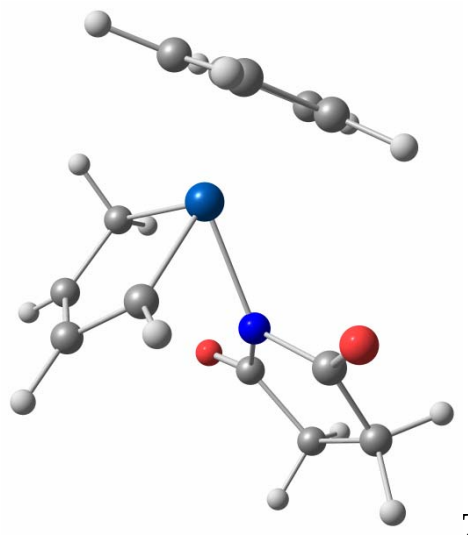
6	1.372545000	1.859584000	1.770754000
6	-3.525287000	-0.312809000	0.530604000
6	1.423300000	2.103419000	-0.671003000
6	0.725541000	0.678831000	1.677929000

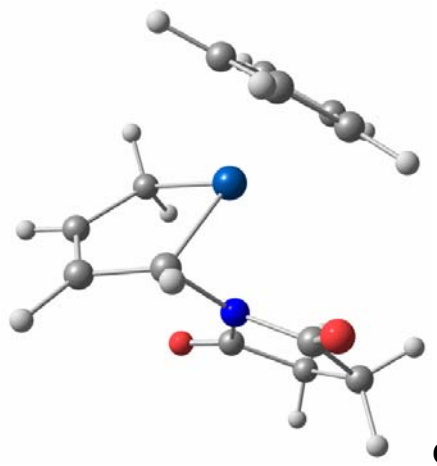
6	-3.448918000	0.607581000	-0.691204000
6	2.165114000	-1.510126000	0.546628000
6	-1.947659000	0.761409000	-0.951570000
6	2.643142000	-0.853168000	-0.607910000
7	-1.232624000	0.019350000	-0.035138000
6	0.918251000	-2.129244000	0.207966000
8	-1.700090000	-1.386320000	1.753781000
6	1.758899000	-1.169843000	-1.707509000
6	0.723928000	-1.967185000	-1.213645000
27	0.686825000	-0.093563000	-0.042301000
1	2.864027000	2.982189000	0.611659000
1	-3.978737000	0.158942000	1.407697000
1	1.503807000	2.394576000	2.712423000
1	1.946817000	2.355715000	-1.588124000
1	0.367682000	1.831469000	-0.819562000
1	-3.923771000	0.193943000	-1.586190000
1	0.240749000	0.183093000	2.516316000
8	-1.455982000	1.446554000	-1.841301000
1	2.606609000	-1.470959000	1.531924000
1	3.534574000	-0.245749000	-0.670863000
1	0.260201000	-2.652996000	0.885315000
1	1.852803000	-0.798296000	-2.718900000
1	-0.139771000	-2.306053000	-1.768605000
1	-4.069969000	-1.244725000	0.352955000
1	-3.882177000	1.599052000	-0.529922000



TS_{BC}

6	-0.463171000	2.015950000	1.588918000

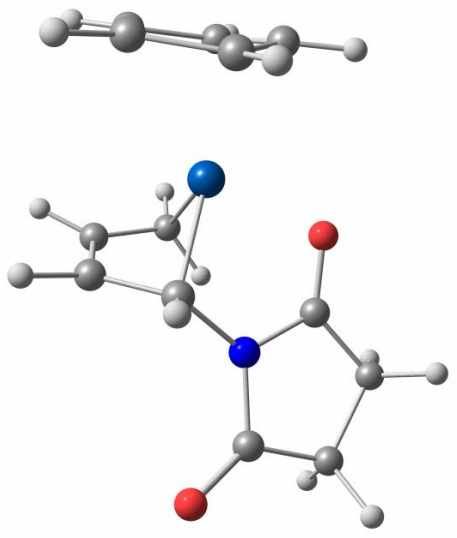
6	0.006642000	2.764968000	0.562659000
6	-0.119811000	0.625788000	1.454628000
6	0.883782000	2.071048000	-0.413062000
27	0.893287000	0.128924000	-0.006345000
6	-2.049323000	0.550963000	-0.725877000
6	1.844471000	-1.202943000	-1.477915000
7	-1.103193000	-0.166589000	0.038916000
6	2.338340000	-1.349327000	0.772353000
6	-1.653938000	-1.395094000	0.468971000
6	2.681791000	-0.116142000	-1.157471000
6	-3.051085000	-1.569782000	-0.124106000
6	2.952302000	-0.165044000	0.253266000
6	1.629997000	-1.963770000	-0.276247000
6	-3.372906000	-0.217014000	-0.757328000
1	-3.008996000	-2.382621000	-0.857223000
1	-1.089382000	2.398501000	2.392910000
1	-0.255003000	3.818410000	0.446724000
1	0.588785000	2.284055000	-1.445597000
1	1.916919000	2.420620000	-0.273942000
1	1.430038000	-1.422383000	-2.452585000
8	-1.856179000	1.618340000	-1.267711000
1	2.339650000	-1.664153000	1.806712000
1	3.010705000	0.656616000	-1.838176000
1	3.572309000	0.527771000	0.805230000
1	0.996252000	-2.833125000	-0.179630000
1	-3.736444000	-0.266412000	-1.786343000
8	-1.106120000	-2.185464000	1.210545000
1	-0.376408000	-0.081694000	2.243129000
1	-4.109887000	0.353881000	-0.181888000
1	-3.739100000	-1.884897000	0.664171000



C

6	-0.331756000	2.185241000	1.426979000
6	0.253142000	2.842573000	0.420977000
6	-0.284432000	0.704726000	1.316639000
6	0.824323000	2.009255000	-0.683516000
27	0.830348000	0.115270000	-0.121234000
6	-2.121197000	0.585647000	-0.587330000
6	1.833565000	-1.446971000	-1.344479000
7	-1.251295000	0.032581000	0.414506000
6	2.231657000	-1.183853000	0.913902000
6	-1.626548000	-1.319957000	0.701376000
6	2.630073000	-0.295937000	-1.190508000
6	-2.638138000	-1.783331000	-0.334163000
6	2.845665000	-0.091563000	0.220330000
6	1.577829000	-1.990901000	-0.039224000
6	-2.869507000	-0.573528000	-1.241625000
1	-2.242230000	-2.662114000	-0.850491000
1	-0.813238000	2.668613000	2.275666000
1	0.265983000	3.932949000	0.373492000
1	0.190727000	2.080626000	-1.582628000
1	1.829143000	2.339748000	-0.971161000
1	1.463649000	-1.842722000	-2.281396000
8	-2.249815000	1.751187000	-0.863405000
1	2.200840000	-1.317186000	1.986316000
1	2.975773000	0.351767000	-1.983769000
1	3.429702000	0.701422000	0.665778000
1	0.971371000	-2.858310000	0.182276000
1	-2.465558000	-0.714151000	-2.249196000

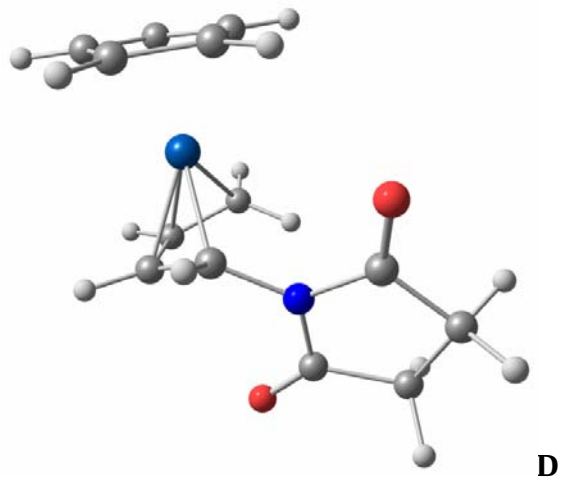
8	-1.211650000	-1.951778000	1.644002000
1	-0.263051000	0.130519000	2.242007000
1	-3.918814000	-0.290903000	-1.350210000
1	-3.540961000	-2.104290000	0.194166000



TS_{CD}

6	-0.048849000	2.034177000	-0.060388000
6	-0.541802000	1.887547000	1.227370000
6	0.560630000	0.903482000	-0.742581000
6	-0.315844000	0.649861000	1.926085000
27	-0.925895000	-0.056322000	0.133995000
6	-2.496987000	-1.613223000	-0.493469000
6	-2.995435000	0.551530000	-1.163757000
6	-2.999810000	-0.896062000	0.615358000
6	-3.395486000	0.424936000	0.155548000
6	-2.344278000	-0.687620000	-1.551807000
1	-0.359547000	2.887563000	-0.659023000
1	-1.251918000	2.625654000	1.597590000
1	0.619372000	1.012151000	-1.825246000
1	0.707322000	0.310194000	2.070372000
1	-0.943333000	0.458198000	2.793781000
1	-2.122878000	-2.628224000	-0.476682000
1	-3.090693000	1.431523000	-1.787671000
1	-3.214194000	-1.307996000	1.593802000
1	-3.865828000	1.185911000	0.765735000
1	-1.967597000	-0.911642000	-2.542517000
6	1.574203000	-1.119956000	0.132621000
6	2.921290000	-1.769584000	0.362470000

6	3.935322000	-0.654814000	0.033701000
6	3.093994000	0.537534000	-0.428646000
7	1.739802000	0.175508000	-0.269864000
8	0.455005000	-1.625355000	0.284389000
1	3.012933000	-2.645187000	-0.287285000
1	4.532144000	-0.350476000	0.898407000
8	3.478364000	1.598917000	-0.856591000
1	4.636251000	-0.921797000	-0.761342000
1	2.979859000	-2.129083000	1.393855000



D

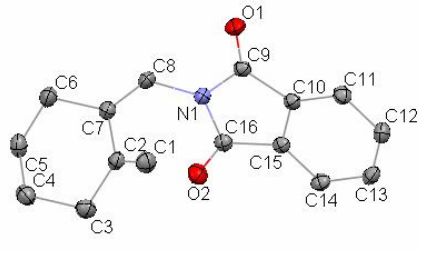
6	0.125723000	-1.573395000	-0.954850000
6	0.462698000	-2.096176000	0.321060000
6	-0.437937000	-0.253874000	-1.026364000
6	0.240548000	-1.292466000	1.471327000
27	1.279434000	-0.281019000	0.029532000
6	2.312230000	1.185222000	1.103496000
6	2.618176000	0.862048000	-1.157434000
6	3.194218000	0.063889000	0.913361000
6	3.415849000	-0.098810000	-0.477945000
6	1.960258000	1.682022000	-0.176592000
1	0.481539000	-2.073178000	-1.850799000
1	1.084418000	-2.986539000	0.368908000
1	-0.339354000	0.262183000	-1.979239000
1	-0.684461000	-0.751759000	1.629156000
1	0.757176000	-1.577474000	2.383809000
1	1.965463000	1.565644000	2.053714000
1	2.536617000	0.976655000	-2.230143000

1	3.620867000	-0.543308000	1.700405000
1	4.014651000	-0.871916000	-0.940533000
1	1.253216000	2.472724000	-0.379748000
6	-2.001650000	1.428961000	-0.095889000
6	-3.413392000	1.466911000	0.480433000
6	-3.885573000	0.007953000	0.480508000
6	-2.750327000	-0.784563000	-0.163560000
7	-1.678678000	0.099718000	-0.385716000
8	-1.274862000	2.381475000	-0.295656000
1	-4.027657000	2.121439000	-0.144891000
1	-4.061370000	-0.390777000	1.484319000
8	-2.758131000	-1.963794000	-0.439137000
1	-4.799505000	-0.161876000	-0.094593000
1	-3.376562000	1.919899000	1.475320000

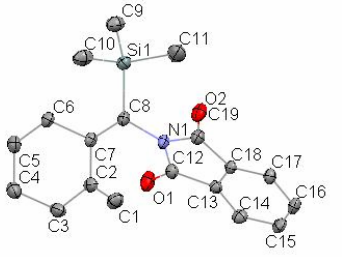
X-ray Analyses

Crystal structure determinations: X-ray intensity data were measured on Bruker-Nonius SMART 1000 or APEX diffractometers (running under SMART control, v. 5.054 and 5.631, respectively) with monochromated Mo-Kα radiation (λ = 0.71073 Å). An arbitrary hemisphere of data was collected for all samples, with extra redundancy for triclinic crystals. Data were reduced using Bruker-Nonius programs SAINT (v. 7.07), SADABS (v. 2004/1), and XPREP (v. 2005/3). The space group for each compound was assigned based on systematic absences observed within the data. Structures were solved by direct methods[7] and expanded using Fourier methods and refined routinely. All refinements were performed using teXsan (v. 1.10, Jan. 1999, Molecular Structure Corp. and Rigaku Corp). Refinements were based on F, with the "observed" cutoff being I>3σ<I. Hydrogen atoms were included in geometrically calculated positions with thermal parameters tied to the atom to which they are bonded. A summary of the crystal and structure refinement data can be found in Table 4. CCDC 664315–664320 contain the supplementary data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

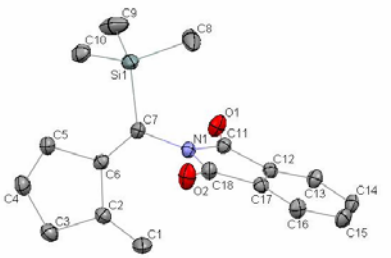
[7] SIR-92, Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Cryst*. **1993**, *26*, 343.



3



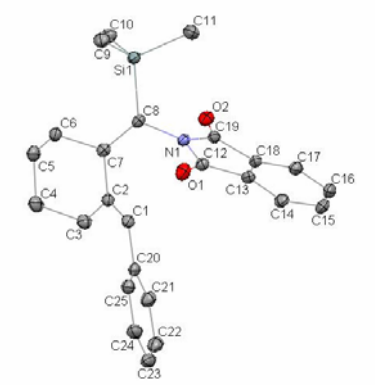
4



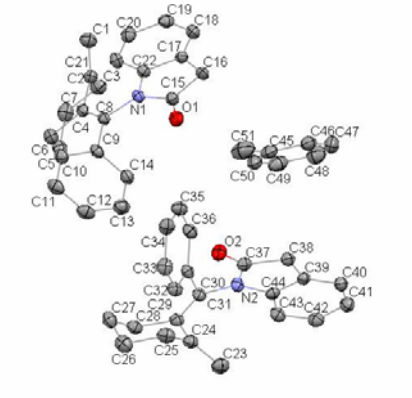
10a

Table 4. Crystal data and structure refinement for compounds **3**, **4** and **10a** (plot at 30% probability ellipsoids)

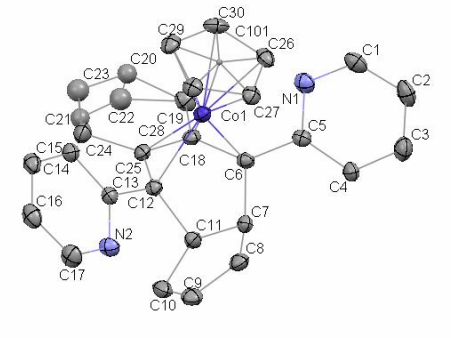
	3	**4**	**10a**
Formula	$C_{16}H_{15}NO_2$	$C_{19}H_{23}NO_2Si$	$C_{18}H_{21}NO_2Si$
CCDC	664316	664315	664317
M ($g.mol^{-1}$)	253.30	325.48	311.45
Crystal class	triclinic	monoclinic	orthorhombic
Space group	P -1	P 2_1/c	P 2_1 2_1 2_1
a (Å)	7.848(1)	14.133(3)	7.839(1)
b (Å)	8.298(1)	7.884(2)	8.782(1)
c (Å)	10.572(2)	17.470(4)	24.758(4)
α (°)	79.270(2)	90	90
β (°)	81.141(2)	113.466(3)	90
γ (°)	82.075(2)	90	90
Volume ($Å^3$)	664.1(2)	1785.5(7)	1704.3(4)
Z	2	4	4
T (K)	177.2	158.2	150.2
θ min, max	2.5, 23.5	3.5, 22.5	3.5, 26
Reflection used	1727	1960	1683
R, R_w, GOF	0.0364, 0.0472, 1.651	0.0463, 0.0536, 1.633	0.0357, 0.0492, 1.669



14a



21a

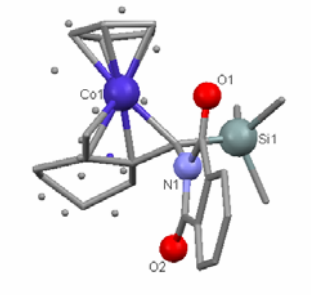


23a

Table 4. Crystal data and structure refinement for compounds **13a**, **14a** and **23a** (plot at 30% probability ellipsoids)

	14a	**21a**	**23a**
Formula	$C_{25}H_{27}NO_2Si$	$C_{25.50}H_{25}NO$	$C_{28}H_{27}CoN_2$
CCDC	664319	664318	664320
M ($g.mol^{-1}$)	401.58	361.48	450.47
Crystal class	monoclinic	triclinic	triclinic
Space group	P $2_1/c$	P -1	P -1
a (Å)	13.559(2)	9.437(2)	8.5711(9)
b (Å)	10.626(1)	9.472(2)	11.404(1)
c (Å)	15.443(2)	25.437(6)	11.822(1)
α (°)	90	81.578(3)	71.659(2)
β (°)	101.663(2)	84.642(3)	76.963(2)
γ (°)	90	62.402(3)	84.780(2)
Volume ($Å^3$)	2179.2(5)	1992.6(7)	1068.4(2)
Z	4	4	2
T (K)	160.2	154.2	156.2
θ min, max	3.5, 25.5	3.5, 23.5	3.5, 24.5
Reflection used	2825	3647	2731
R, R_w, GOF	0.0383, 0.0509, 1.540	0.0422, 0.0402, 1.507	0.0375, 0.0394, 1.575

Comments on the refinement of compound **2**:



The initial structure solution refined to a reasonable model, with the cobalt atom coordinated to the two double bonds emanating from the cyclohexane ring and to the cyclopentadienyl ligand. The two cyclohexane carbon atoms distal from the double bonds were disordered by a backbone twist, as is common in such cases.

A large peak in a difference Fourier map was interpreted as the cobalt atom of an enantiomorphous molecule of the compound located on the same site as the observed molecule and sharing a common position of the $SiMe_3$ and C_8H_4NO moieties. Its occupancy refined to near 20% when it was included. Subsequent difference Fourier maps and applied restraints allowed the refinement of the complete disordered molecule. The disordered carbon atoms were refined with isotropic thermal parameters, one common one for the dialkylidenecyclohexane ligand atoms and a second common one for the cyclopentadienyl atoms. The minority cobalt was refined anisotropically. All C–C distances and C–C–C angles in the minority component were constrained to be equal to those in the majority component, and the Cp ligand was restrained to be flat.

The occupancy of the majority component refined to 0.833(3). The presence of this disorder means that the geometrical parameters of the structure are relatively unreliable, and that there may be some unrealistic distances, angles, and torsion angles in the CIF.

In addition to the disorder, there was clear evidence of inversion twinning, and the twin parameter, reported as the Flack parameter, refined to 0.20(2). Note that this phenomenon is distinct from the disorder described above, which describes the inclusion of some 17% of "left-handed molecules" in a "right-handed" crystal. The twinning pertains to the presence of 20% of "left-handed" crystals in the sample, each of which contain an average of 17% "right-handed" molecules.

Calculations for this crystal structure were performed first with teXsan, then with SHELXL.

Comments on compound **23a**:

The compound crystallizes in the triclinic space group P-1. There are some relatively close contacts of 3.35 Å between carbon atoms. More significantly, there are two H–H contacts less than 2.3 Å: H2 ... H30 (y–1) = 2.27, and H26 ... H29 (x–1) = 2.21 Å. Both of these involve a disorder in the cyclopentene ring, discussed below, The molecule contains a cobalt bonded to a Cp ring and to a planar four carbon fragment fused to a cyclohexane. As is often observed in such molecules, the cyclohexane moiety is disordered by conformational isomerism. The reported ratio of 70:30 was estimated by isotropic refinement of the disordered atoms and adjustment until the thermal parameters were approximately equal. Peaks in a difference Fourier map were located in positions appropriate for the major component, but not the minor one. When hydrogen atoms were calculated, the equatorial nuceli overlapped. Thus, H18 and H19 were given full occupancy, while the axial hydrogens, H17, H20, H31, and H32 were given partial occupancy. The nitrogen atoms in the pyridine moieties were identified initially on the basis of thermal parameter refinement and confirmed by lack of nearby peaks in the final difference Fourier map. They are attached to the terminal carbons of the bonded butadiene. In addition, there is a planar five-membered ring fused to the same two atoms. Looking at the distances around the ring, especially those to C9 [C9–C9 = 1.367(4), C9–C10 = 1.428(4)] strongly suggested that it was a cyclopentene. Initial assignment of the allylic and aliphatic carbon atoms was apparently confirmed by a difference Fourier map showing two peaks near C10 and one near C8. However, inspection of what was intended to be the final

difference Fourier map showed a single peak near C10 and two peaks near C8, all in good geometry to be hydrogen atoms. Assignment of these as half-occupancy hydrogen atoms and adjustment of the occupancies of the other hydrogens on C8 and C10 produced a significant reduction in all residuals (R 3.86% to 3.71%, wR 3.99%, to 3.83%, GOF 1.60 to 1.53). (Note that these residuals are *prior* to the inclusion of the minority hydrogens on the cyclohexane). It is these disordered hydrogen atoms that are involved in the closest H...H contacts noted above. These contacts were examined in detail and it appears that both can be lengthened to unremarkable values by small movements of the carbon atoms to which they are attached to become unremarkable. These motions are parallel to the largest rms amplitude of the thermal motions of both carbons involved. Given this finding and the significant nature of the reduction in the residuals, the disorder of the cyclopentene appears real. It is probably not 50:50, but a refinement of the occupancies of hydrogen atoms was judged to be beyond the quality of the data set.