

General. All air sensitive materials were manipulated under nitrogen in a glovebox or by standard high-vacuum and Schlenk-techniques. Hexane, pentane, THF, THF-*d*₈, C₆H₆, C₆D₆ and diethyl ether were distilled from sodium and benzophenone. C₆D₅CD₃ was distilled from Na-K alloy. CH₂Cl₂ and CD₂Cl₂ were distilled from CaH₂. C₆D₅Br was distilled from P₂O₅. CHCl₃ and CDCl₃ were distilled from Na₂SO₄. C₆D₅Br and *o*-C₆D₄Cl₂ were distilled from P₂O₅. Methylcyclohexane-*d*₁₄ was distilled from Na-K alloy. ZnBr₂ was sublimed prior to use. Phenylacetylene, trimethylsilyl chloride, *n*-butyllithium (1.6 M solution in hexane), and BCl₃ (1.0 M solution in pentane) were purchased from Aldrich. Tolylacetylene was purchased from Lancaster, acetylene (1,2-¹³C₂, 99%) was purchased from Cambridge Isotope Laboratories. [Cp(CO)₂Re≡CTol]BCl₄,¹ [Cp(CO)₂Re≡CTol]BCl₄,² [Cp*(CO)₂Re≡CTol]BCl₄,³ phenylethynyllithium,⁴ 1,1,2-tribromo-2-phenylcyclopropane,⁵ 1-phenylacetylene (1-¹³C),⁶ *o*-allyl-phenylacetylene,⁷ were synthesized according to literature procedures.

¹H NMR spectra were obtained on a Bruker AC 250, AC 300, AM 500 or Varian Unity 500 spectrometer. ¹³C NMR spectra were obtained on a Bruker AM 500 spectrometer operating at 125 MHz. Infrared spectra were recorded on a Mattson Polaris FT IR spectrometer. Mass spectra were obtained on a Kratos MS-80 or Micromass AutoSpec spectrometer.

Cp(CO)₂Re=C(Tol)(C≡CPh) (1). A solution of LiC≡CTol (129 mg, 1.20 mmol) and ZnBr₂ (275 mg, 1.22 mmol, sublimed) in 2 mL THF was cooled to -35 °C was added to [Cp(CO)₂Re≡CTol][BCl₄] (625 mg, 1.19 mmol) in 1 mL THF at -35 °C. The entire cold reaction mixture was poured onto a silica gel column (30 x 2 cm) and eluted with 4:1 hexane : ether. Evaporation of a black fraction and recrystallization from CH₂Cl₂:hexane gave black crystals of **1** (409 mg, 0.779 mmol, 65%), mp 141 °C. ¹H NMR (CD₂Cl₂, 500 MHz) δ 2.15 (s, CH₃), 5.84 (s, C₅H₅), 7.16 (d, ³J = 8.6 Hz, aromatic CH), 7.38 (d, ³J = 7.8 Hz, aromatic CH), 7.50 (d, ³J = 7.5 Hz, aromatic CH),

7.64 (d, $^3J = 8.4$ Hz, aromatic CH), 8.09 (d, $^3J = 8.3$ Hz, aromatic CH). ^1H NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 500 MHz) δ 1.82 (s, CH_3), 5.16 (s, C_5H_5), 6.95 (d, $^3J = 8.1$ Hz, aromatic CH), 7.02 (t, $^3J = 7.6$ Hz, aromatic CH), 7.13 (tt, $^3J = 7.6$ Hz, $^4J = 1.3$ Hz, aromatic CH), 7.46 (dd, $^3J = 7.8$ Hz, $^4J = 1.3$ Hz, aromatic CH), 8.43 (d, $^3J = 8.3$ Hz, aromatic CH). ^{13}C NMR (CD_2Cl_2 , 125 MHz) δ 21.96 (q, $^1J_{\text{CH}} = 126.3$ Hz, CH_3), 95.10 (dp, $^1J_{\text{CH}} = 179.1$ Hz, $^{2,3}J_{\text{CH}} = 6.8$ Hz, C_5H_5), 110.45 (s, $\text{C}\equiv\text{CTol}$), 120.39 (t, $^3J_{\text{CH}} = 5.4$ Hz, $\text{C}\equiv\text{CTol}$), 125.51 (t, $^3J_{\text{CH}} = 8.5$ Hz, aromatic), 127.73 (dd, $^1J_{\text{CH}} = 158.9$ Hz, $^3J_{\text{CH}} = 6.2$ Hz, aromatic), 129.28 (dd, $^1J_{\text{CH}} = 162.6$ Hz, $^3J_{\text{CH}} = 7.8$ Hz, aromatic), 129.38 (dd, $^1J_{\text{CH}} = 161.5$ Hz, $^3J_{\text{CH}} = 8.6$ Hz, aromatic), 129.88 (dp, $^1J_{\text{CH}} = 158.6$ Hz, $^{2,3}J_{\text{CH}} = 5.3$ Hz, aromatic), 131.08 (dt, $^1J_{\text{CH}} = 161.9$ Hz, $^3J_{\text{CH}} = 6.9$ Hz, aromatic), 140.98 (sextet, $^3J_{\text{CH}} = 6.6$ Hz, aromatic), 156.40 (t, $^3J_{\text{CH}} = 7.2$ Hz, aromatic), 204.90 (CO), 251.90 (Re=C). ^{13}C $\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 125 MHz) δ 21.65 (CH_3), 94.62 (C_5H_5), 110.97 ($\text{C}\equiv\text{CTol}$), 119.79 (d, $\text{C}\equiv\text{CTol}$), 126.01, 128.18, 128.80, 129.19, 129.97, 131.09, 140.54, 156.60 (aromatic), 204.84 (CO), 251.79 (Re=C). ^{17}O NMR (CD_2Cl_2)⁸ δ 356.7. IR (CH_2Cl_2) 1963, 1889 cm^{-1} . HRMS(EI) m/z calcd for $\text{C}_{23}\text{H}_{17}\text{O}_2^{187}\text{Re}$ (M^+) 512.0786, found 512.0795.

$\text{Cp}(\text{CO})_2\text{Re}=\text{C}(\text{Tol})(\text{C}\equiv^{13}\text{CPh})$ ($1\text{-}^{13}\text{C}$) was synthesized from $[\text{Cp}(\text{CO})_2\text{Re}=\text{C-Tol}]\text{BCl}_4$ and $\text{Ph}^{13}\text{C}\equiv\text{CLi}^9$ in 65 % yield. ^1H NMR (CD_2Cl_2 , 300 MHz) δ 2.15 (s, CH_3), 5.84 (s, C_5H_5), 7.16 (d, $^3J = 8.5$ Hz, aromatic CH), 7.3-7.5 (m, aromatic CH), 7.64 (d, $^3J = 8.4$ Hz, aromatic CH), 8.09 (d, $^3J = 8.4$ Hz, aromatic CH). ^{13}C NMR (CD_2Cl_2 , 125 MHz) δ 21.96 (CH_3), 95.10 (C_5H_5), 110.45 ($\text{C}\equiv\text{C-Tol}$, $^1J_{\text{CC}} = 173.7$ Hz), 120.39 ($\text{C}\equiv^{13}\text{C-Tol}$, ^{13}C satellites were found with $^1J_{\text{CC}} = 90.9$ Hz and 173.5 Hz), 125.51 ($^1J_{\text{CC}} = 90.4$ Hz), 127.70, 129.26, 129.36 (d, $^2J_{\text{CC}} = 4.7$ Hz), 129.85, 131.06, 140.98, 156.40 (aromatic), 204.90 (CO), 251.90 (Re=C, $^2J_{\text{CC}} = 3.5$ Hz). IR (CH_2Cl_2) 1963, 1889 cm^{-1} .

$\text{Ph}^{13}\text{C}\equiv^{13}\text{CH}$ (11). $n\text{-BuLi}$ (1.40 mL, 1.63 M in hexane, 2.28 mmol) was slowly added via syringe to a solution of 2.06 mmol $\text{H}^{13}\text{C}\equiv^{13}\text{CH}$ in 10 mL THF at -78

°C to form a solution of $\text{H}^{13}\text{C}\equiv^{13}\text{CLi}$. After warming up to room temperature, a small amount of $\text{Li}^{13}\text{C}\equiv^{13}\text{CLi}$ precipitated. ZnBr_2 (518 mg, 2.30 mmol) was added to the suspension at room temperature. A solution of $\text{Pd}(\text{PPh}_3)_4$ in 10 mL THF [prepared from $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (44 mg, 42 μmol) and PPh_3 (91.8 mg, 350 μmol)] and iodobenzene (0.190 mL, 346 mg, 1.70 mmol) were added to the Zn-acetylide solution. After 2 h, a 60:40 mixture of phenylacetylene and tolane was detected by GC as the major products. After addition of 30 mL water and extraction with 3x20 mL pentane, the combined organic phases were dried over MgSO_4 . To avoid a significant loss of the fairly volatile product, most of the solvent was removed by vacuum distillation (0.01 torr) at 0 °C while cooling the collection flask to -78 °C. The crude yellow oily distillate was finally purified by Kugelrohr-distillation (45 °C, 0.01 torr) to give $\text{Ph}^{13}\text{C}\equiv^{13}\text{CH}$ (**11**, 32.1 mg, 18.0%). ^1H NMR (acetone- d_6 , 300 MHz) δ =3.15 (dd, 1H, J =245.1, 56.0 Hz), 7.30-7.50 (m, 5H). ^{13}C NMR (acetone- d_6 , 75 MHz) label at δ 84.0 (ddtq, $^1J_{\text{CC}}$ = 175.7, $^2J_{\text{CH}}$ = 55.94 Hz, $^3J_{\text{CH}}$ = 6.0 Hz, $^{4,5}J_{\text{CH}}$ = 1.0 Hz, $\text{Ph}^{13}\text{C}\equiv^{13}\text{CH}$), 77.1 (dd, $^1J_{\text{CC}}$ = 175.7, $^2J_{\text{CH}}$ = 245.1 Hz, $\text{Ph}^{13}\text{C}\equiv^{13}\text{CH}$).

$\text{Ph}^{13}\text{C}\equiv^{13}\text{CLi}$ (12**).** *n*-BuLi (0.20 mL, 1.63 M in hexane, 0.326 mmol) was added via syringe to $\text{C}_6\text{H}_5^{13}\text{C}\equiv^{13}\text{CH}$ (**11**, 32.1 mg, 0.308 mmol) in 5 mL pentane. The fine white precipitate of **12** which formed was centrifuged. Supernatant solvent was removed with a syringe and the precipitate was washed with 3 x 5 mL pentane and centrifuged each time. The white solid was dried under vacuum for 12 h to give $\text{Ph}^{13}\text{C}\equiv^{13}\text{CH}$ (**12**, 29.0 mg, 86%).

$\text{Cp}(\text{CO})_2\text{Re}=\text{C}(\text{Tol})(^{13}\text{C}\equiv^{13}\text{CPh})$ (1- $^{13}\text{C}_2$**)** was synthesized from $[\text{Cp}(\text{CO})_2\text{Re}=\text{C-Tol}]\text{BCl}_4$ and $\text{Ph}^{13}\text{C}\equiv^{13}\text{CLi}$ in 75 % yield. ^1H NMR (CD_2Cl_2 , 300 MHz) δ 2.15 (s, CH_3), 5.84 (s, C_5H_5), 7.16 (d, 3J = 8.4 Hz, aromatic CH), 7.3-7.5 (m, aromatic CH), 7.64 (d, 3J = 8.4 Hz, aromatic CH), 8.09 (d, 3J = 8.4 Hz, aromatic CH). ^{13}C NMR ($\text{C}_6\text{D}_5\text{CD}_3$, 125 MHz) δ 21.66 (CH_3), 94.59 (C_5H_5), 110.93 (d, $^1J_{\text{CC}}$ = 173.5 Hz, $^{13}\text{C}\equiv^{13}\text{CTol}$), 119.76 (d, $^1J_{\text{CC}}$ = 173.5 Hz, $^{13}\text{C}\equiv^{13}\text{CTol}$), 126.01 (dd, $^1J_{\text{CC}}$ =

91.6 Hz, $^2J_{CC} = 12.7$ Hz, $^{13}C \equiv ^{13}CC$), 128.20, 129.13 (d, $^2J_{CC} = 5.1$ Hz), 129.94 ($^3J_{CC} = 5.0$ Hz), 131.08, 140.56, 156.56 (aromatic), 204.84 (CO), 251.79 (Re=C, $^1J_{CC} = 62.3$, $^2J_{CC} = 3.5$). IR (CH₂Cl₂) 1963, 1889 cm⁻¹. HRMS(EI) *m/z* calcd for C₂₁¹³C₂H₁₇O₂¹⁸⁷Re (M⁺) 514.0854, found 514.0852.

Cp(CO)₂Re=C(Ph)(C≡CTol) (2) was synthesized was synthesized from [CpRe(CO)₂≡CPh]BCl₄, tolylethynyllithium¹⁰, and ZnBr₂ in 65% yield. ¹H NMR (C₆D₆, 500 MHz) δ 1.90 (s, CH₃), 5.11 (s, C₅H₅), 6.83 (d, $^3J = 7.9$ Hz, aromatic CH), 7.20 (m, overlap with solvent peak, aromatic CH), 7.43 (d, $^3J = 8.2$ Hz, aromatic CH), 8.46 (d, 2H, $^3J = 8.0$ Hz, aromatic CH). ¹H NMR (CD₂Cl₂, 300 MHz) δ 2.28 (s, CH₃), 5.84 (s, C₅H₅), 7.20 (d, $^3J = 7.8$ Hz, aromatic CH), 7.34 (t, $^3J = 7.6$ Hz, aromatic CH), 7.51 (d, $^3J = 7.6$ Hz, aromatic CH), 7.54 (d, $^3J = 7.9$ Hz, aromatic CH), 8.07 (d, $^3J = 8.0$ Hz, aromatic CH). ¹³C NMR (C₆D₅CD₃, 125 MHz) δ 21.62 (CH₃), 94.54 (C₅H₅), 111.96 (C≡CTol), 121.32 (C≡CTol), 122.97, 127.17, 129.67, 130.01, 130.08, 131.29, 139.25, 159.46 (aromatic), 204.61 (CO), 253.90 (Re=C). ¹³C NMR (CD₂Cl₂, 125 MHz) δ 21.96 (CH₃), 95.10 (C₅H₅), 110.45 (C≡C-Tol), 120.23 (C≡C-Tol), 125.50, 127.70, 129.26, 129.36, 131.06, 140.98, 156.40 (aromatic), 204.91 (CO), 251.90 (Re=C). IR (CH₂Cl₂) 1965, 1889 cm⁻¹. HRMS(EI) *m/z* calcd for C₂₃H₁₇O₂¹⁸⁷Re (M⁺) 512.0786, found 512.0785.

Cp(CO)₂Re=C(Tol)(C≡CTol) (3) was synthesized from [CpRe(CO)₂≡CTol]BCl₄, tolylethynyllithium¹⁰ and ZnBr₂ in 65% yield. Crystals suitable for an X-ray analysis were obtained by recrystallization from CH₂Cl₂:hexane. ¹H NMR (THF-*d*₈, 500 MHz) δ 2.15 (s, CH₃), 2.28 (s, CH₃), 5.83 (s, C₅H₅), 7.15 (d, $^3J = 8.6$ Hz, aromatic CH), 7.20 (d, $^3J = 8.5$ Hz, aromatic CH), 7.53 (d, $^3J = 8.4$ Hz, aromatic CH), 8.07 (d, $^3J = 8.3$ Hz, aromatic CH). ¹H NMR (C₆D₆, 500 MHz) δ 1.79 (s, CH₃), 1.91 (s, CH₃), 5.14 (s, C₅H₅), 6.85 (d, $^3J = 7.9$ Hz, aromatic CH), 6.99 (d, $^3J = 8.1$ Hz, aromatic CH), 7.45 (d, $^3J = 8.0$ Hz, aromatic CH), 8.53 (d, $^3J = 8.2$ Hz, aromatic CH). ¹³C NMR (THF-*d*₈, 125 MHz) δ=22.5 (CH₃), 22.8 (CH₃), 95.6 (C₅H₅),

111.1 (C≡C-Tol), 121.2 (C≡C-Tol), 123.4, 128.2, 130.0, 130.6, 131.6, 140.1, 140.7, 157.2 (aromatic), 205.4 (CO), 252.2 (Re=C). IR (CH₂Cl₂) 1961, 1888 cm⁻¹. HRMS(EI) *m/z* calcd for C₂₄H₁₉O₂¹⁸⁷Re (M⁺) 526.0943, found 526.0955.

[Cp(CO)₂Re]₂{[Tol(2 η -C≡C)](Ph)C=C(Ph)[(2 η -C≡C)Tol]} (4).
 Cp(CO)₂Re=C(Tol)(C≡CPh) (1) (26.6 mg, 52 μ mol) was heated in 30 μ L C₆D₅CD₃ at 120 °C for 4 h in a flame sealed melting point capillary under a N₂ atmosphere. Red crystals of 4 (15.1 mg, 58%) suitable for an X-ray analysis formed upon cooling to room temperature. Additional 4 (5.2 mg, 19%) was isolated from the remaining solution by preparative thin layer chromatography (silica gel, 4:1 hexane : ether, R_f=0.3). When the thermolysis of 1 was run at lower concentrations, the yields of 4 were significantly lower. ¹H NMR (CDCl₃, 500 MHz, 60 °C) δ 2.34(s, CH₃), 5.04 (s, Cp), 7.03 (d, ³J = 7.9 Hz, aromatic), 7.15 (m), 7.25 (d, ³J = 7.9 Hz, aromatic), 7.31 (d, ³J = 8.1 Hz, aromatic). ¹H NMR (C₆D₆, 500 MHz, 60 °C) δ 2.09(s, CH₃), 4.65 (s, Cp), 6.90 (t, ³J = 7.5 Hz, aromatic), 6.94 (d, 8.0 Hz, aromatic), 7.02 (d, ³J = 7.9 Hz, aromatic), 7.50 (d, ³J = 8.0 Hz, aromatic), 7.54 (d, ³J = 7.5 Hz, aromatic). ¹³C NMR (CDCl₃, 125 MHz, 60 °C) δ 21.24 (qt, ¹J_{C-H} = 126.0 Hz, ³J_{C-H} = 4.4 Hz, CH₃), 79.69 (s, =C≡C), 85.19 (s, broad, =CC≡C), 87.93 (dp, ¹J_{C-H} = 179.7 Hz, ^{3,4}J_{C-H} = 4.4 Hz, Cp), 127.54 (dt, ¹J_{C-H} = 159.8 Hz, ³J_{C-H} = 7.5 Hz, aromatic CH), 127.85 (dt, ¹J_{C-H} = 161.0 Hz, ³J_{C-H} = 7.4 Hz, aromatic CH), 128.8 (dt, ¹J_{C-H} = 157.2 Hz, ³J_{C-H} = 5.6 Hz, aromatic CH), 128.92 (t, ³J_{C-H} = 8.0 Hz, aromatic C), 129.15 (dt, ¹J_{C-H} = 160.8 Hz, ³J_{C-H} = 6.8 Hz, aromatic CH), 131.6 (dd, ¹J_{C-H} = 160.1 Hz, ³J_{C-H} = 6.4 Hz, aromatic CH), 134.98 (t, ³J_{C-H} = 3.5 Hz, C=C), 137.43 (t, ³J_{C-H} = 6.9 Hz, aromatic C), 141.30 (s, aromatic C), 204.35 (s, CO). IR (CH₂Cl₂) 1968, 1883 cm⁻¹. MS (FAB): *m/z* calcd for C₄₆H₃₄O₄¹⁸⁵Re₂ (M⁺) 1020.1517, found 1020.1562.

[Cp(CO)₂Re]₂{[Ph(2 η -C≡C)](Ph)¹³C=13C(Ph)[(2 η -C≡C)Tol]}
 (4-¹³C₂). A solution of Cp(CO)₂Re=C(Tol)(C≡¹³CPh) (1-¹³C) (10 mg) in 0.4 mL C₆D₆ in an NMR tube was degassed by 3 freeze-pump-thaw cycles. The tube was

flame-sealed under vacuum and heated at 90 °C for 36 h. ^1H NMR spectroscopy showed 30% conversion of $1\text{-}^{13}\text{C}$ to $4\text{-}^{13}\text{C}_2$. The product was not isolated from the mixture. ^1H NMR (C_6D_6 , 500 MHz) δ 2.06 (s, CH_3), 4.58 (s, C_5H_5), aromatic region was broad and overlapped with starting material. ^{13}C NMR (C_6D_6 , 125 MHz) δ 135.5 (label, broad signal).

[Cp(CO) $_2$ Re] $_2$ {[Ph($^{2\eta}\text{-C}\equiv^{13}\text{C}$)](Tol) $^{13}\text{C}=\text{}^{13}\text{C}$ (Ph)[($^{2\eta}\text{-}^{13}\text{C}\equiv\text{C}$)Tol]} (4- $^{13}\text{C}_4$). A solution of Cp(CO) $_2$ Re=C(Tol)($^{13}\text{C}\equiv^{13}\text{C}$ Ph) ($1\text{-}^{13}\text{C}_2$) (10 mg) in 0.4 mL C_6D_6 in an NMR tube was degassed by 3 freeze-pump-thaw cycles. The tube was flame-sealed under vacuum and heated at 90 °C for 36 h. ^1H NMR spectroscopy showed 30% conversion of $1\text{-}^{13}\text{C}$ to $4\text{-}^{13}\text{C}_2$. The product was not isolated from the mixture. ^1H NMR (C_6D_6 , 500 MHz) δ 2.03 (s, CH_3), 4.58 (s, C_5H_5), aromatic region was broad and overlapped with starting material. ^{13}C NMR (C_6D_6 , 125 MHz) δ 80.7 (AA' part of an AA'XX' pattern, $^3J_{\text{C}_2\text{-C}_2'} = 8.6$ Hz, $^1J_{\text{C}_3\text{-C}_3'} = 78.3$ Hz, $^1J_{\text{C}_2\text{-C}_3} = 76.3$ Hz, $^2J_{\text{C}_2\text{-C}_3} = 1.6$ Hz), 135.5 (XX' part of AA'XX' pattern, broad). All carbon-carbon coupling constants were obtained by simulation with DNMR (Figure 1).

The [1,3] rearrangement product Cp(CO) $_2$ Re= ^{13}C (Ph)($^{13}\text{C}\equiv\text{C-Tol}$), $2\text{-}^{13}\text{C}_2$ was identified as a side product (2-3 % yield) of the thermolysis by its ^{13}C label enhanced signals [δ 111.95 (d, $^1J_{\text{CC}} = 64.4$ Hz), 253.90 (d, $^1J_{\text{CC}} = 64.4$ Hz)].

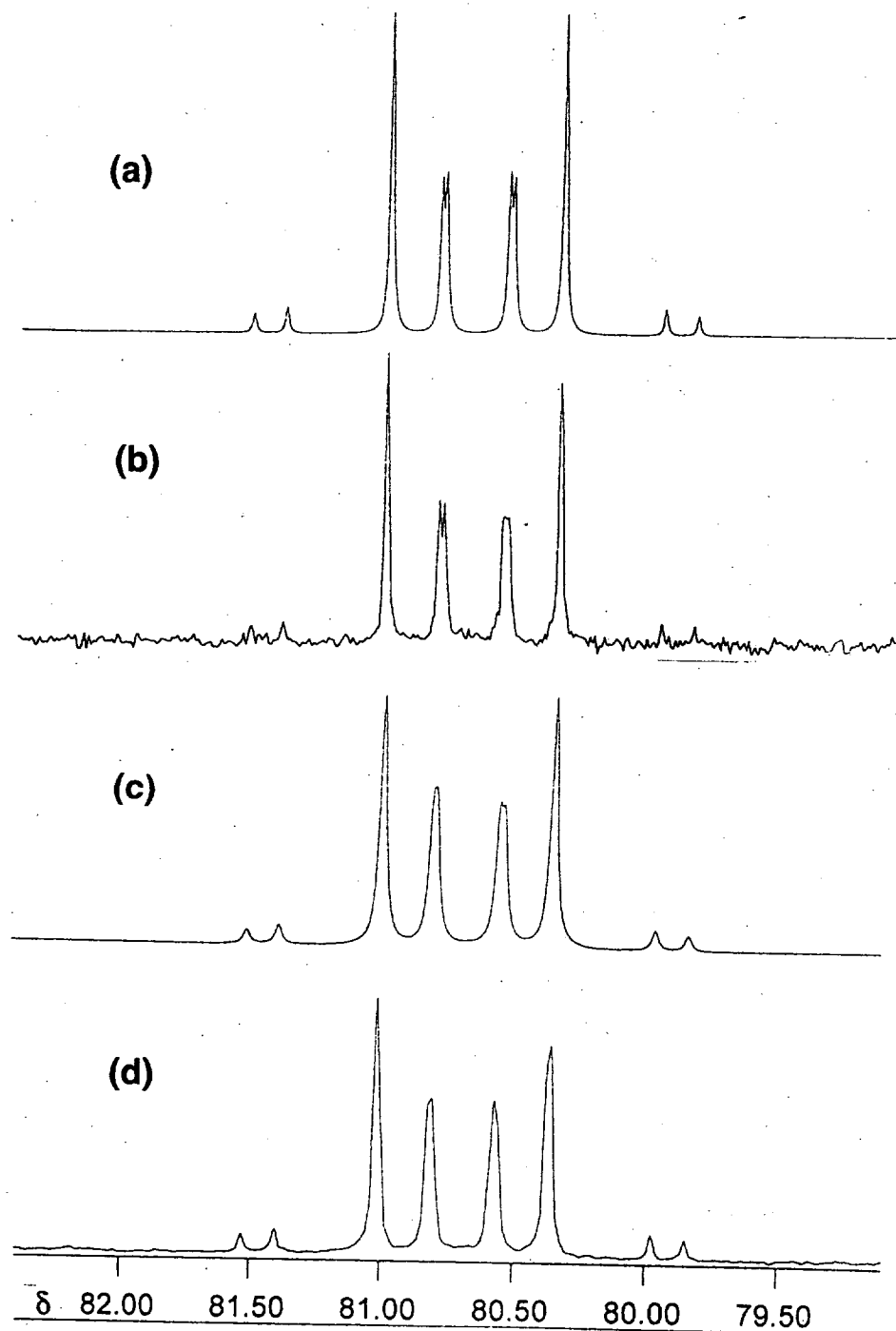


Figure 1. AA' part of the AA'XX' pattern at δ 80.7 in the ^{13}C NMR spectrum of $4\text{-}^{13}\text{C}_2$. (a) Simulated spectrum with 1.9 Hz line width. (b) Experimental spectrum after 64 scans without line broadening. (c) Simulated spectrum with 3.5 Hz line width. (d) Experimental spectrum after 13K scans with 3 Hz Lorentzian line broadening.

Kinetic Measurements of the Conversion of 1 to 4. (a) A carefully degassed $\text{C}_6\text{D}_5\text{CD}_3$ solution of **1** (13.6 mg, 0.0266 mmol, 0.402 mL total volume and 0.0662 M at 120 °C) containing 1,4-bis-trimethylsilylbenzene (1.1 mg, internal NMR standard) was heated at 120 ± 0.3 °C in a resealable 5 mm NMR tube. ^1H NMR spectra were acquired at room temperature after 0, 14, 40, 69, 87, 122, 147, 185, and 241 min at 120 °C. The decrease of the Cp resonance of **1** at δ 5.10 ppm was followed. The 2nd order rate constant was determined over the 1st half-life; $k_2 = 1.45 \pm 0.03 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$.

(b) A $\text{C}_6\text{D}_5\text{CD}_3$ solution of **1** (22.3 mg, 0.0436 mmol, 0.318 mL total volume and 0.137 M at 120 °C) containing 1,4-bis-trimethylsilylbenzene (1.7 mg, internal NMR standard) was heated at 120 ± 0.3 °C. ^1H NMR spectra were acquired at room temperature after 0, 30, 40, 52, 63, and 82 min at 120 °C. $k_2 = 1.41 \pm 0.06 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$

(c) A solution of **1** in 75 μL $\text{C}_6\text{D}_5\text{CD}_3$ (17.7 mg, 0.0346 mmol, 0.111 mL total volume and 0.31 M at 120 °C) was heated at 120 ± 0.3 °C. Before ^1H NMR spectra were acquired, solvent was completely removed under high vacuum and the solid residue was dissolved in 0.4 mL CDCl_3 containing cyclohexane (8.0 μL , internal NMR standard). After a spectrum was obtained, solvent and internal standard were pumped off thoroughly on a vacuum line for 2 h. The solid was then redissolved in 75 μL $\text{C}_6\text{D}_5\text{CD}_3$ and thermolysis was resumed.¹¹ This procedure was necessary since **1** was not completely soluble in $\text{C}_6\text{D}_5\text{CD}_3$ at room temperature at the high initial concentration. ^1H NMR spectra were acquired at room temperature after 0, 3, 18, 24, 41, 67, and 84 min at 120 °C. $k_2 = 1.46 \pm 0.09 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$.

Solvent Dependence of the Rate of Conversion of 1 to 4. (a) A methylcyclohexane- d_{14} solution of **1** (3.5 mg, 6.9 μmol , 0.647 mL total volume and 0.011 M at 120 °C) containing 1,4-bis-trimethylsilylbenzene (0.4 mg, internal NMR

standard) was heated at 120 ± 0.3 °C. ^1H NMR spectra were acquired at 60 °C after 0, 22, 35, 76, 333, 399, and 592 min at 120 °C. $k_2 = 3.9 \pm 0.1 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$.

(b) A $\text{C}_6\text{D}_5\text{Br}$ solution of **1** (18.1 mg, 35.3 μmol , 0.471 mL total volume and 0.0749 M at 120 °C) containing 1,4-bis-trimethylsilylbenzene (1.7 mg, internal NMR standard) was heated at 120 ± 0.3 °C. ^1H NMR spectra were acquired at room temperature after 0, 14, 28, 42, 55, 69, 83, 97, 110, and 124 min at 120 °C. $k_2 = 1.46 \pm 0.04 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$.

(c) A $o\text{-C}_6\text{D}_4\text{Cl}_2$ solution of **1** (14.1 mg, 27.6 μmol , 0.573 mL total volume and 0.0481 M at 120 °C) containing 1,4-bis-trimethylsilylbenzene (1.5 mg, internal NMR standard) was heated at 120 ± 0.3 °C. ^1H NMR spectra were acquired at room temperature after 0, 10, 70, 167, 249, and 513 min at 120 °C. $k_2 = 1.05 \pm 0.03 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$.

Cp(CO)₂Re-C(Tol)=¹³C=¹³C(Ph)(PPh₂CH₃) (5). Addition of Ph_2PCH_3 (10.0 mg, 50 μmol) to $\text{Cp(CO)}_2\text{Re=C(Tol)(}^{13}\text{C}\equiv^{13}\text{CPh)}$ (**1-¹³C₂**) (4.6 mg, 23 μmol) in 0.4 mL CD_2Cl_2 at -15 °C produced a bright orange solution. The clean formation of **5** was established by ^1H , ^{13}C , and ^{31}P NMR spectroscopy without isolating the product. ^1H NMR (CD_2Cl_2 , 500 MHz) δ 2.20 (s, tolyl- CH_3), 2.28 (d, $^2J_{\text{PH}} = 12.8$ Hz, PCH_3), 5.01 (s, C_5H_5), 6.90-7.02 (m, aromatic CH), 7.09 (t, $^3J = 7.4$ Hz, aromatic CH), 7.25-7.38 (m, aromatic CH), 7.51 (t, $^3J = 7.2$ Hz, aromatic CH), 7.62 (d, $^3J = 8.3$ Hz, aromatic CH), 7.75-7.90 (m, aromatic CH). ^{13}C NMR (CD_2Cl_2 , 125 MHz) δ 59.23 (dd, $^1J_{\text{CC}} = 93.7$ Hz, $^1J_{\text{CP}} = 104.7$ Hz, $^{13}\text{C}=\text{}^{13}\text{CP}$), 185.4 (dd, $^1J_{\text{CC}} = 93.8$ Hz, $^2J_{\text{CP}} = 7.0$ Hz, $^{13}\text{C}=\text{}^{13}\text{CP}$). ^{31}P NMR (CD_2Cl_2 , 202 MHz) δ 19.5 (dd, $^1J_{\text{CP}} = 105.3$ Hz, $^2J_{\text{CP}} = 6.1$ Hz).

1-(Trimethylsilyl)-2-phenylcyclopropene (13).¹² *n*-Butyllithium (0.5 mL, 1.6 M solution in hexane, 0.80 mmol, 2.1 equiv) was added via syringe over 15 min to a solution of 1,1,2-tribromo-2-phenylcyclopropane (133.0 mg, 0.385 mmol) in 3 mL THF at -100 °C (ethanol slush). The resulting yellow orange solution of

2-phenylcyclopropenyllithium was slowly warmed up to -78 °C over 1 h. The reaction mixture darkened significantly and LiBr precipitated. ZnBr₂ (88 mg, 0.391 mmol) in 1 mL THF was added at -78 °C to form 2-phenylcyclopropenylzinc bromide. Trimethylsilyl chloride (100 µL, 0.788 mmol) was added and the solution turned yellow orange instantly. After warming to room temperature, solvent was evaporated under vacuum and the residual amber oil was dissolved and purified by a preparative TLC (silica gel, hexane) to give 1-Phenyl-2-(trimethylsilyl)cyclopropene (**13**, 50.0 mg, 0.265 mmol, 69%, R_f = 0.8) as a bright yellow solid. ¹H NMR (CDCl₃, 500 MHz) δ 0.30 (s, Si(CH₃)₃), 1.12 (s, CH₂), 7.32 (t, ³J = 7.7 Hz, aromatic CH), 7.42 (t, ³J = 7.7 Hz, aromatic CH), 7.60 (d, ³J = 7.7 Hz, aromatic CH). ¹³C NMR (CD₂Cl₂, 125 MHz) δ 1.26 [quartet of septets, ¹J_{CH} = 118.7 Hz, ³J_{CH} = 1.9 Hz, Si(CH₃)₃], 5.72 (t, ¹J_{CH} = 167.0 Hz, CH₂), 110.01 (10 lines, ³J_{CH} = 2.5 Hz, C=CTMS), 128.52 (dd, ¹J_{CH} = 159.5 Hz, ³J_{CH} = 7.8 Hz, aromatic), 128.57 (dd, ¹J_{CH} = 161.1 Hz, ³J_{CH} = 6.0 Hz, aromatic), 129.36 (dtd, ¹J_{CH} = 158.2 Hz, ³J_{CH} = 6.8 Hz, ²J_{CH} = 2.5 Hz, aromatic), 130.91 (t, ³J_{CH} = 7.6 Hz, aromatic), 131.40 (t, ²J_{CH} = 1.4 Hz, aromatic).

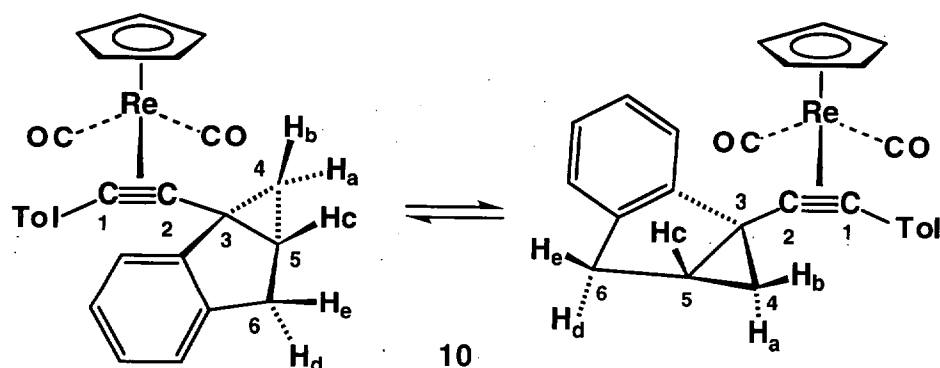
[Cp(CO)₂Re][Tol(²η-C≡C)](Ph)C=CH₂] (**8**). *n*-Butyllithium (0.11 mL, 1.6 M in hexane, 180 µmol) was added to a resealable NMR tube under N₂ and the solvent was evaporated under high vacuum to yield a colorless oil. THF-*d*₈ (0.25 mL) was transferred into the tube by vacuum distillation at -78 °C. 1,1,2-tribromo-2-phenylcyclopropane (27.6 mg, 80 µmol), ZnBr₂ (18 mg, 80 µmol, in 0.1 mL THF-*d*₈), and 1,4 bis(trimethylsilyl)benzene (2.0 mg, internal NMR standard) were sequentially added under a stream of N₂ to the cold solution. The resulting yellow solution of 2-phenylcyclopropenylzinc bromide was frozen (liquid N₂) and [Cp(CO)₂Re≡CTol]BCl₄ (42 mg, 80 µmol) was added as a solid. Upon thawing at -110 °C (ethanol slush) the color of the solution turned dark immediately. A ¹H NMR spectrum taken at -85 °C showed that **8** had formed in 90% yield. No signals that could be assigned to **7** were detectable. Preparative thin layer chromatography (silica gel, 10:1 hexane : diethyl

ether) gave **8** (30.3 mg, 72 %, yellow band, $R_f=0.3$). ^1H NMR (CD_2Cl_2 , 500 MHz) δ 2.33 (s, CH_3), 5.55 (s, C_5H_5), 5.81 (d, $^2J = 1.6$ Hz, $=\text{CHH}$), 5.95 (d, $^2J = 1.6$ Hz, $=\text{CHH}$), 7.06 (d, $^3J = 8.1$ Hz, aromatic CH), 7.16 (d, $^3J = 8.1$ Hz, aromatic CH), 7.30-7.40 (m, aromatic CH). ^{13}C NMR (CD_2Cl_2 , 125 MHz) δ 21.35 (q, $^1J_{\text{CH}} = 126.5$ Hz, CH_3), 80.20 (dd, $^3J_{\text{CH}(\text{trans})} = 15.8$ Hz, $^3J_{\text{CH}(\text{cis})} = 9.0$ Hz, $\text{C}\equiv\text{CTol}$), 83.8 (t, $^3J_{\text{CH}} = 4.6$ Hz $\text{C}\equiv\text{CTol}$), 88.60 (dp, $^1J_{\text{CH}} = 180.7$ Hz, $^3,^4J_{\text{CH}} = 7.8$ Hz, $\text{Hz}, \text{C}_5\text{H}_5$), 123.4 (dd, $^1J_{\text{CH}} = 159.2$ Hz, $^1J_{\text{CH}} = 160.3$ Hz, $=\text{CH}_2$), 127.7 (d, $^1J_{\text{CH}} = 158.1$ Hz, aromatic), 128.2 (dt, $^1J_{\text{CH}} = 158.1$ Hz, $^3J_{\text{CH}} = 6.8$ Hz, aromatic), 128.4 (s, aromatic), 128.5 (d, $^1J_{\text{CH}} = 158.1$ Hz, aromatic), 129.1 (dp, $^1J_{\text{CH}} = 159.2$ Hz, $^2,^3J_{\text{CH}} = 4.5$ Hz, aromatic), 132.8 (dd, $^1J_{\text{CH}} = 160.3$ Hz, $^3J_{\text{CH}} = 6.7$ Hz, aromatic), 138.2 (sextet, $^3J_{\text{CH}} = 6.7$ Hz, aromatic), 141.3 (s, aromatic), 141.6 (s, aromatic), 205.3 (s, CO). IR (CH_2Cl_2) 1968, 1883 cm^{-1} . HRMS(EI) m/z calcd for $\text{C}_{24}\text{H}_{19}\text{O}_2^{187}\text{Re}$ (M^+) 526.0943, found 526.0936.

$\text{Cp}(\text{CO})_2\text{Re}=\text{C}(\text{Tol})(\text{C}\equiv\text{CC}_6\text{H}_4\text{-o-allyl})$ (9**)** was synthesized from $[\text{Cp}(\text{CO})_2\text{Re}\equiv\text{CTol}]\text{BCl}_4$, *o*-allyl-phenylethynyllithium,¹³ and ZnBr_2 in 59% yield. ^1H NMR (CD_2Cl_2 , 500 MHz) δ 2.16 (s, CH_3), 3.54 (dt, $^3J = 6.3$ Hz, $^4J = 1.5$ Hz, ArCH_2), 5.01 (dq, $^3J = 17.1$ Hz, $^2,^4J = 1.6$ Hz, $=\text{CHH}$), 5.08 (dq, $^3J = 10.1$ Hz, $^4J = 1.5$ Hz, $=\text{CHH}$), 5.83 (s, C_5H_5), 6.02 (ddt, $^3J = 17.0$ Hz, $^3J = 10.1$ Hz, $^3J = 6.3$ Hz, $\text{CH}=\text{CH}_2$), 7.15 (d, $^3J = 8.3$ Hz, aromatic CH), 7.25 (overlapping doublet and triplet, $^3J = 8.1$ Hz, aromatic CH), 7.44 (dt, $^3J = 7.6$ Hz, $^4J = 1.5$ Hz aromatic CH), 8.04 (d, $^3J = 8.3$ Hz, aromatic CH). ^{13}C NMR (CD_2Cl_2 , 125 MHz) δ 21.89 (qt, $^1J_{\text{CH}} = 126.5$ Hz, $^3J_{\text{CH}} = 4.5$ Hz, CH_3), 39.39 (tdd, $^1J_{\text{CH}} = 127.4$ Hz, $^3J_{\text{CH}(\text{trans})} = 11.2$ Hz, $^3J_{\text{CH}(\text{cis})} = 7.0$, ArCH_2), 94.87 (dp, $^1J_{\text{CH}} = 154.7$ Hz, $^2,^3J_{\text{CH}} = 5.6$ Hz, C_5H_5), 114.65 (s, $\text{C}\equiv\text{CAr}$), 116.35 (ddt, $^1J_{\text{CH}} = 154.7$ Hz, $^1J_{\text{CH}} = 158.1$ Hz, $^4J_{\text{CH}} = 5.6$, $\text{C}=\text{CH}_2$), 118.58 (d, $^3J_{\text{CH}} = 5.8$ Hz, $\text{C}\equiv\text{CAr}$), 127.13 (dd, $^1J_{\text{CH}} = 160.3$ Hz, $^3J_{\text{CH}} = 9.0$ Hz), 127.48 (dd, $^1J_{\text{CH}} = 160.3$ Hz, $^3J_{\text{CH}} = 9.0$ Hz), 129.56 (ddd, $^1J_{\text{CH}} = 160.3$ Hz, $^3J_{\text{CH}} = 7.3$ Hz, $^2J_{\text{CH}} = 2.3$ Hz), 129.77 (ddt, $^1J_{\text{CH}} = 160.3$ Hz, $^3J_{\text{CH}} = 9.0$ Hz, $^2J_{\text{CH}} = 4.6$ Hz), 129.99 (d, $^1J_{\text{CH}} = 158.9$ Hz), 132.34 (dd, $^1J_{\text{CH}} = 161.5$ Hz, $^3J_{\text{CH}} = 7.9$ Hz), 136.89 (ddt, $^1J_{\text{CH}} = 153.9$ Hz, $^3J_{\text{CH}} = 7.9$

Hz, $^2J_{\text{CH}} = 2.9$ Hz), 140.57 (s, broad), 140.76 ($^3J_{\text{CH}} = 6.8$ Hz), 157.05 (t, $^3J_{\text{CH}} = 6.5$ Hz) all aromatic, 205.05 (s, CO), 252.5 (s, Re=C). IR (CH₂Cl₂) 1963, 1889 cm⁻¹. HRMS(EI) m/z calcd for C₂₆H₂₁O₂¹⁸⁷Re (M⁺) 552.1099, found 552.1089.

Thermolysis of Cp(CO)₂Re=C(Tol)(C≡CC₆H₄-o-allyl) (9) to Rhenium Cyclopropyl Alkyne Complex 10. A toluene solution of **9** (22.0 mg, 39.8 μmol) was heated at 120 °C for 4 h in a sealed tube under N₂. Solvent was evaporated under vacuum and the resulting solid was recrystallized from hexane three times to give **10** (9.2 mg, 42%) of fine light yellow crystals. Due to hindered rotation about the alkyne-Re(CO)₂Cp bond, a 4:1 ratio of two isomers was observed by ¹H NMR and ¹³C NMR spectroscopy at -80 °C.



Major Isomer of 10: ¹H NMR (CD₂Cl₂, 500 MHz, -80 °C) δ 0.85 (t, $^2,^3J = 4.6$ Hz, H_a), 1.74 (dd, $^3J = 8.4$ Hz, t, $^2J = 4.2$ Hz, H_b), 2.29 (s, CH₃), 2.43 (ddd, $^3J = 8.1$ Hz, $^3J = 6.8$ Hz, $^3J = 5.2$ Hz, H_c), 3.00 (d, $^2J = 17.1$ Hz, H_d), 3.32 (dd, $^2J = 17.3$ Hz, $^3J = 6.8$ Hz, H_e), 5.55 (s, C₅H₅), 7.0-7.3 (m, aromatic CH). ¹³C NMR (CD₂Cl₂, 125 MHz, -80 °C) δ 20.69 (q, $^1J_{\text{CH}} = 126.9$ Hz, CH₃), 26.62 (d, $^1J_{\text{CH}} = 173.8$ Hz, C₅), 28.36 (t, $^1J_{\text{CH}} = 162.6$ Hz, C₄), 34.05 (t, $^1J_{\text{CH}} = 131.3$ Hz, C₆), 35.52 (s, C₃), 70.81 (t, $^3J_{\text{CH}} = 5.0$ Hz, C₁), 84.17 (s, C₂), 88.38 (dp, $^1J_{\text{CH}} = 180.7$ Hz, $^3,^4J_{\text{CH}} = 6.8$ Hz, C₅H₅) 123.78 (dd, $^1J_{\text{CH}} = 159.2$ Hz, $^3J_{\text{CH}} = 6.8$ Hz, aromatic), 124.89 (dd, $^1J_{\text{CH}} = 158.2$ Hz, $^3J_{\text{CH}} = 6.5$ Hz, aromatic), 125.26 (dd, $^1J_{\text{CH}} = 159.2$ Hz, $^3J_{\text{CH}} = 7.8$ Hz, aromatic),

125.61 (dd, $^1J_{\text{CH}} = 159.2$ Hz, $^3J_{\text{CH}} = 5.9$ Hz, aromatic), 126.92 (t, $^3J_{\text{CH}} = 8.3$ Hz, aromatic), 128.40 (dt, $^1J_{\text{CH}} = 158.2$ Hz, $^3J_{\text{CH}} = 4.8$ Hz, aromatic), 132.19 (dd, $^1J_{\text{CH}} = 161.1$ Hz, $^3J_{\text{CH}} = 5.9$ Hz, aromatic), 136.38 (q, $^3J_{\text{CH}} = 6.8$ Hz, aromatic), 141.08 (s, aromatic), 145.71 (s, aromatic), 204.81 (s, CO), 207.28 (s, CO).

Minor Isomer of 10: ^1H NMR (CD_2Cl_2 , 500 MHz, -80°C) δ 0.97 (t, $^2,^3J = 4.4$ Hz, H_a), 1.88 (dd, $^3J = 8.3$ Hz, $^2J = 4.2$ Hz, H_b), 2.06 (ddd, $^3J = 8.1$ Hz, $^3J = 6.8$ Hz, $^3J = 5.2$ Hz, H_c), 2.30 (s, CH_3), 2.98 (d, $^2J = 16.6$ Hz, H_d), 3.29 (partly overlaps with H_e signal of major isomer, H_e), 5.43 (s, C_5H_5), 7.0-7.3 (m, aromatic CH), 7.41 (d, $^3J = 8.3$ Hz, aromatic CH). ^{13}C NMR (CD_2Cl_2 , 125 MHz, -80°C) δ 20.73 (q, $^1J_{\text{CH}} = 127.0$ Hz, CH_3), 28.00 (d, $^1J_{\text{CH}} = 171.8$ Hz, C_5), 28.01 (t, $^1J_{\text{CH}} = 162.8$ Hz, C_4), 33.34 (s, C_3), 33.97 (t, $^1J_{\text{CH}} = 131.3$ Hz, C_6), 71.00 (t, $^3J_{\text{CH}} = 5.1$ Hz, C_1), 83.03 (s, C_2), 88.04 (dp, $^1J_{\text{CH}} = 180.7$ Hz, $^3,^4J_{\text{CH}} = 6.6$ Hz, C_5H_5) 123.69 (aromatic, coupling could not be resolved because of overlap with peaks of the major isomer), 125.03 (dd, $^1J_{\text{CH}} = 158.2$ Hz, $^3J_{\text{CH}} = 6.5$ Hz, aromatic), 125.44 (dd, $^1J_{\text{CH}} = 160.8$ Hz, $^3J_{\text{CH}} = 6.9$ Hz, aromatic), 125.62 (aromatic, coupling could not be resolved because of overlap with peaks of the major isomer), 127.39 (t, $^3J_{\text{CH}} = 8.1$ Hz, aromatic), 128.47 (aromatic, coupling could not be resolved because of overlap with peaks of the major isomer), 131.60 (dd, $^1J_{\text{CH}} = 161.1$ Hz, $^3J_{\text{CH}} = 5.9$ Hz, aromatic), 136.55 (aromatic, coupling could not be resolved because of overlap with peaks of the major isomer), 141.29 (s, aromatic), 145.88 (s, aromatic), 205.27 (s, CO), 206.48 (s, CO).

Rapidly Equilibrating Isomers of 10. At 50°C , the resonances for the major and the minor isomers were averaged. ^1H NMR (CD_2Cl_2 , 500 MHz, 50°C) δ 0.94 (t, $^2,^3J = 4.6$ Hz, H_a), 1.83 (dd, $^3J = 8.4$ Hz, $^2J = 4.2$ Hz, H_b), 2.32 (broad, H_c), 2.37 (s, CH_3), 3.04 (d, $^2J = 16.8$ Hz, H_d), 3.42 (dd, $^2J = 16.8$ Hz, $^3J = 6.7$ Hz, H_e), 5.48 (s, C_5H_5), 7.1-7.3 (m, aromatic CH), 7.4-7.5 (m, aromatic CH). ^1H NMR (C_6D_6 , 250 MHz, 90°C) δ 0.85 (dd, $^3J = 4.8$ Hz, $^2J = 4.2$ Hz, H_a), 1.75 (dd, $^3J = 8.4$ Hz, $^2J = 4.0$ Hz, H_b), 2.12 (s, CH_3), 2.20 (ddd, $^3J = 8.3$ Hz, $^3J = 6.5$ Hz, $^3J = 5.0$ Hz, H_c), 2.81

(d, $^2J = 16.9$ Hz, H_d), 3.24 (dd, $^2J = 16.9$ Hz, $^3J = 6.6$ Hz, H_e), 4.92 (s, C₅H₅), 7.00 (d, $^3J = 8.1$ Hz, aromatic CH), 7.05 (m, aromatic CH), 7.26 (m, aromatic CH), 7.56 (d, $^3J = 8.2$ Hz, aromatic CH). ^{13}C NMR (CD₂Cl₂, 125 MHz, 50°C) δ 21.40 (q, $^1J_{\text{CH}} = 126.3$ Hz, CH₃), 28.81 (broad d, $^1J_{\text{CH}} = 173.7$ Hz, C₅), 29.15 (t, $^1J_{\text{CH}} = 161.2$ Hz, C₄), 35.39 (t, $^1J_{\text{CH}} = 131.0$ Hz, C₆), 72.62 (t, $^3J_{\text{CH}} = 5.1$ Hz, C₁), 84.20 (s, C₂), 88.88 (dp, $^1J_{\text{CH}} = 179.7$ Hz, $^{3,4}J_{\text{CH}} = 6.6$ Hz, C₅H₅), 124.64 (dd, $^1J_{\text{CH}} = 159.2$ Hz, $^3J_{\text{CH}} = 7.8$ Hz, aromatic), 125.96 (dd, $^1J_{\text{CH}} = 160.2$ Hz, $^3J_{\text{CH}} = 6.9$ Hz, aromatic), 126.41 (dd, $^1J_{\text{CH}} = 160.1$ Hz, $^3J_{\text{CH}} = 6.8$ Hz, aromatic), 126.69 (dd, $^1J_{\text{CH}} = 160.2$ Hz, $^3J_{\text{CH}} = 6.8$ Hz, aromatic), 129.11 (s, aromatic), 129.43 (d, $^1J_{\text{CH}} = 158.2$ Hz, $^{2,3}J_{\text{CH}} = 5.0$ Hz, aromatic), 132.51 (dt, $^1J_{\text{CH}} = 160.1$ Hz, $^3J_{\text{CH}} = 5.9$ Hz, aromatic), 137.47 (q, $^3J_{\text{CH}} = 6.3$ Hz, aromatic), 142.16 (s, aromatic), 147.25 (s, aromatic), 205.04 (s, CO), 206.30 (s, CO). ^{13}C NMR (C₆D₆, 125 MHz, 90 °C) δ 21.05 (q, $^1J_{\text{CH}} = 126.0$ Hz, CH₃), 28.71 (d, $^1J_{\text{CH}} = 170.9$ Hz, C₅), 28.84 (t, $^1J_{\text{CH}} = 161.1$ Hz, C₄), 35.20 (t, $^1J_{\text{CH}} = 130.9$ Hz, C₆), 35.23 (s, C₃), 72.99 (t, $^3J_{\text{CH}} = 5.1$ Hz, C₁), 83.93 (s, C₂), 88.08 (dp, $^1J_{\text{CH}} = 179.7$ Hz, $^{3,4}J_{\text{CH}} = 6.6$ Hz, C₅H₅), 124.67 (dd, $^1J_{\text{CH}} = 158.4$ Hz, $^3J_{\text{CH}} = 6.8$ Hz, aromatic), 125.82 (dd, $^1J_{\text{CH}} = 159.8$ Hz, $^3J_{\text{CH}} = 5.6$ Hz, aromatic), 126.31 (dd, $^1J_{\text{CH}} = 158.2$ Hz, $^3J_{\text{CH}} = 6.8$ Hz, aromatic), 126.58 (dd, $^1J_{\text{CH}} = 159.2$ Hz, $^3J_{\text{CH}} = 6.8$ Hz, aromatic), 129.32 (ddq, $^1J_{\text{CH}} = 158.2$ Hz, $^{2,4}J_{\text{CH}} = 6.3$ and 4.9 Hz, aromatic), 129.61 (t, $^3J_{\text{CH}} = 8.0$ Hz, aromatic), 132.29 (dd, $^1J_{\text{CH}} = 159.2$ Hz, $^3J_{\text{CH}} = 5.9$ Hz, aromatic), 136.93 (q, $^3J_{\text{CH}} = 6.0$ Hz, aromatic), 141.87 (s, aromatic), 147.21 (s, aromatic), 204.17 (s, CO), 205.33 (s, CO). IR (CH₂Cl₂) 1964, 1877 cm⁻¹. HRMS(EI) m/z calcd for C₂₆H₂₁O₂¹⁸⁷Re (M⁺) 552.1099, found 552.1103.

X-ray Crystal Structure Determination of Cp(CO)₂Re=C(Tol)(C≡CTol) (3). A black opaque prism-shaped crystal of dimensions 0.45 x 0.42 x 0.22 mm was selected for structural analysis. Intensity data for this compound were collected using a Bruker SMART ccd area detector¹⁴ mounted on a Bruker P4 goniometer using graphite-monochromated Mo K α radiation (λ =

0.71073 Å). The sample was cooled to 133(2) K. The intensity data, which nominally covered one and a half hemispheres of reciprocal space, were measured as a series of ϕ oscillation frames each of 0.3° for 5 sec / frame. The detector was operated in 512 x 512 mode and was positioned 5.00 cm from the sample. Coverage of unique data parameters were determined from a non-linear least squares fit of 8021 peaks in the range $3.0 < \theta < 25.0^\circ$. The first 50 frames were repeated at the end of data collection and yielded 270 peaks showing a variation of -7.19 % during the data collection. A total of 7369 data were measured in the range $1.88 < \theta < 27.79^\circ$. The data were corrected for absorption by the empirical method¹⁵ giving minimum and maximum transmission factors of 0.1094 and 0.3554. The data were merged to form a set of 3713 independent data with $R(\text{int}) = 0.0227$.

The monoclinic space group $P2(1)/n$ was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods¹⁶ on F^2 . Hydrogen atom positions were initially determined by geometry and were refined using a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. A total of 244 parameters were refined against 3713 data to give $wR(F^2) = 0.1041$ and $S = 1.155$ for weights of $w = 1/[\sigma^2(F^2) + (0.0628 P)^2 + 3.0166 P]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final $R(F)$ was 0.0389 for the 3533 observed, $[F > 4\sigma(F)]$, data. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 2.202 and -3.042 e/Å³, respectively.

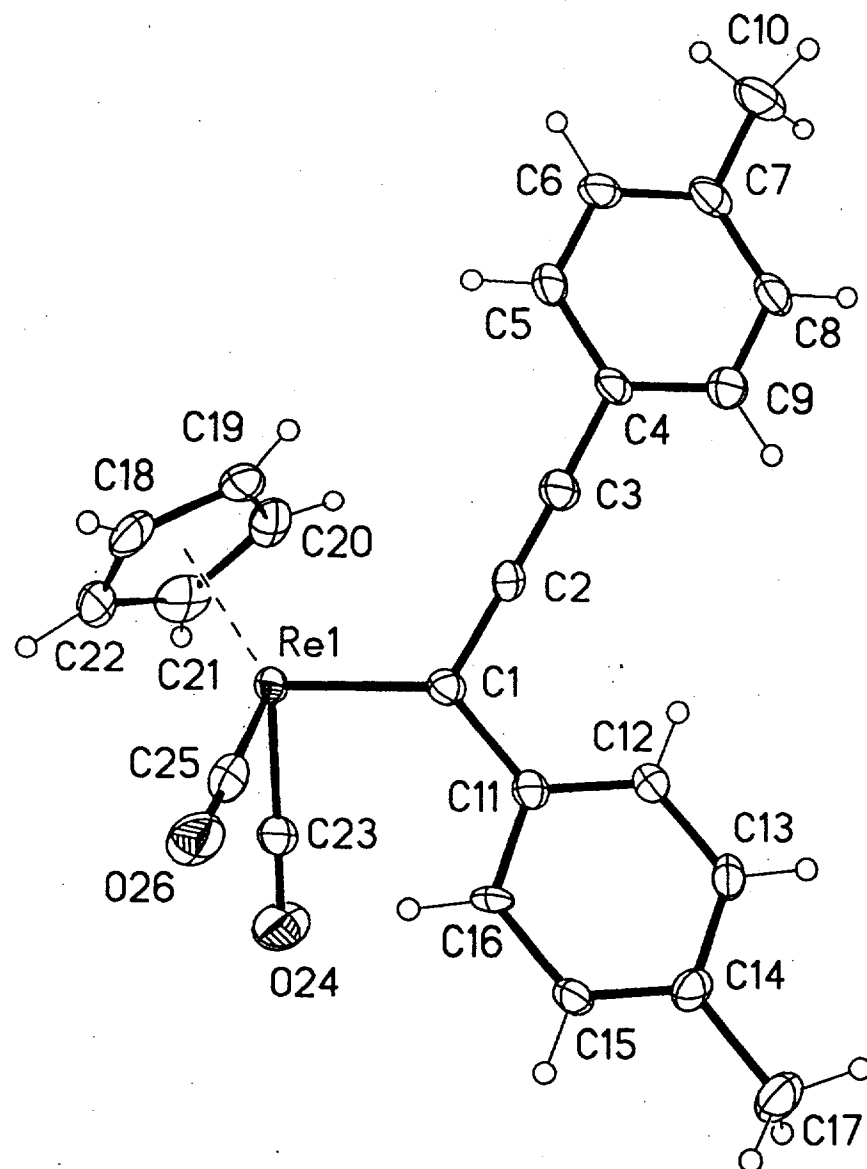


Figure 2. X-ray crystal structure of Cp(CO)₂Re=C(Tol)(C≡CTol) (**3**). The displacement ellipsoids are drawn at the 50% probability level.

Table 1. Crystal data and structure refinement for $\text{Cp}(\text{CO})_2\text{Re}=\text{C}(\text{Tol})(\text{C}\equiv\text{CTol})$ (**3**).

Empirical formula	$\text{C}_{24} \text{H}_{19} \text{O}_2 \text{Re}$	
Formula weight	525.59	
Crystal system	Monoclinic	
Space group	$P2(1)/n$	
Unit cell dimensions	$a = 10.7934(3) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 8.2280(3) \text{ \AA}$	$\beta = 99.665(2)^\circ$
	$c = 21.9941(7) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$1925.53(11) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.813 Mg/m^3	
Wavelength	$0.71073 \text{ \AA}$	
Temperature	$133(2) \text{ K}$	
$F(000)$	1016	
Absorption coefficient	6.326 mm^{-1}	
Absorption correction	Empirical	
Max. and min. transmission	0.3554 and 0.1094	
Theta range for data collection	1.88 to 27.79°	
Reflections collected	7369	
Independent reflections	3713 [$R(\text{int}) = 0.0227$]	
Data / restraints / parameters	3713 / 0 / 244	
$wR(F^2 \text{ all data})$	$wR = 0.1041$	
$R(F \text{ obsd data})$	$R = 0.0389$	
Goodness-of-fit on F^2	1.155	
Observed data [$I > 2\sigma(I)$]	3533	
Largest and mean shift / s.u.	0.001 and 0.000	
Largest diff. peak and hole	2.202 and $-3.042 \text{ e/\AA}^3$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for **3**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Re(1)	0.81308(2)	0.89065(2)	0.099528(9)	0.01926(11)
C(1)	0.7994(4)	0.6702(6)	0.1366(2)	0.0184(10)
C(2)	0.6811(5)	0.5897(6)	0.1233(3)	0.0216(11)
C(3)	0.5785(5)	0.5249(6)	0.1127(3)	0.0243(11)
C(4)	0.4528(5)	0.4615(6)	0.1028(3)	0.0214(10)
C(5)	0.3627(5)	0.5205(7)	0.0546(3)	0.0264(12)
C(6)	0.2384(5)	0.4672(7)	0.0482(3)	0.0295(12)
C(7)	0.2026(5)	0.3545(7)	0.0895(3)	0.0276(12)
C(8)	0.2928(5)	0.2930(7)	0.1362(3)	0.0279(12)
C(9)	0.4166(5)	0.3448(7)	0.1427(3)	0.0268(12)
C(10)	0.0674(5)	0.2997(8)	0.0834(3)	0.0371(15)
C(11)	0.8923(5)	0.5761(6)	0.1816(2)	0.0195(10)
C(12)	0.8524(5)	0.4548(7)	0.2199(2)	0.0228(10)
C(13)	0.9364(5)	0.3719(6)	0.2627(3)	0.0243(12)
C(14)	1.0673(6)	0.4036(6)	0.2702(3)	0.0232(11)
C(15)	1.1063(5)	0.5189(6)	0.2315(3)	0.0223(11)
C(16)	1.0223(5)	0.6060(6)	0.1891(3)	0.0238(12)
C(17)	1.1589(6)	0.3123(8)	0.3171(3)	0.0328(13)
C(18)	0.7162(6)	0.9937(8)	0.0041(3)	0.0353(15)
C(19)	0.6321(6)	0.8830(7)	0.0251(3)	0.0282(13)
C(20)	0.5983(5)	0.9454(8)	0.0803(3)	0.0301(12)
C(21)	0.6654(6)	1.0954(7)	0.0947(4)	0.037(2)
C(22)	0.7349(6)	1.1247(8)	0.0462(4)	0.039(2)
C(23)	0.9176(5)	0.9641(7)	0.1723(3)	0.0277(12)
O(24)	0.9834(5)	1.0086(6)	0.2168(2)	0.0482(13)
C(25)	0.9711(6)	0.8530(7)	0.0745(3)	0.0290(12)
O(26)	1.0678(4)	0.8374(7)	0.0591(2)	0.0415(11)

Table 3. Bond lengths [Å] and angles [°] for **3**.

Re(1)-C(23)	1.896(6)	C(7)-C(10)	1.512(8)
Re(1)-C(25)	1.904(6)	C(8)-C(9)	1.387(8)
Re(1)-C(1)	2.004(5)	C(11)-C(16)	1.407(7)
Re(1)-C(21)	2.310(6)	C(11)-C(12)	1.419(7)
Re(1)-C(19)	2.329(6)	C(12)-C(13)	1.375(8)
Re(1)-C(20)	2.330(5)	C(13)-C(14)	1.419(8)
Re(1)-C(22)	2.338(6)	C(14)-C(15)	1.386(8)
Re(1)-C(18)	2.341(6)	C(14)-C(17)	1.505(8)
C(1)-C(2)	1.425(7)	C(15)-C(16)	1.386(8)
C(1)-C(11)	1.500(7)	C(18)-C(22)	1.413(11)
C(2)-C(3)	1.216(8)	C(18)-C(19)	1.416(9)
C(3)-C(4)	1.436(7)	C(19)-C(20)	1.422(9)
C(4)-C(5)	1.399(8)	C(20)-C(21)	1.440(9)
C(4)-C(9)	1.401(8)	C(21)-C(22)	1.425(11)
C(5)-C(6)	1.395(8)	C(23)-O(24)	1.168(7)
C(6)-C(7)	1.397(9)	C(25)-O(26)	1.157(8)
C(7)-C(8)	1.388(9)		
C(23)-Re(1)-C(25)	82.0(3)	C(23)-Re(1)-C(22)	105.9(3)
C(23)-Re(1)-C(1)	91.1(2)	C(25)-Re(1)-C(22)	104.7(3)
C(25)-Re(1)-C(1)	95.8(2)	C(1)-Re(1)-C(22)	154.8(2)
C(23)-Re(1)-C(21)	96.6(2)	C(21)-Re(1)-C(22)	35.7(3)
C(25)-Re(1)-C(21)	138.6(3)	C(19)-Re(1)-C(22)	58.7(2)
C(1)-Re(1)-C(21)	125.6(2)	C(20)-Re(1)-C(22)	59.0(2)
C(23)-Re(1)-C(19)	155.8(2)	C(23)-Re(1)-C(18)	139.0(3)
C(25)-Re(1)-C(19)	118.6(2)	C(25)-Re(1)-C(18)	95.0(2)
C(1)-Re(1)-C(19)	98.7(2)	C(1)-Re(1)-C(18)	129.8(2)
C(21)-Re(1)-C(19)	59.8(2)	C(21)-Re(1)-C(18)	59.6(3)
C(23)-Re(1)-C(20)	121.6(2)	C(19)-Re(1)-C(18)	35.3(2)
C(25)-Re(1)-C(20)	153.1(2)	C(20)-Re(1)-C(18)	59.1(2)
C(1)-Re(1)-C(20)	96.3(2)	C(22)-Re(1)-C(18)	35.2(3)
C(21)-Re(1)-C(20)	36.1(2)	C(2)-C(1)-C(11)	111.8(4)
C(19)-Re(1)-C(20)	35.5(2)	C(2)-C(1)-Re(1)	117.5(4)

C(11)-C(1)-Re(1)	130.5(4)	C(13)-C(14)-C(17)	120.9(5)
C(3)-C(2)-C(1)	178.0(5)	C(14)-C(15)-C(16)	122.3(5)
C(2)-C(3)-C(4)	174.7(6)	C(15)-C(16)-C(11)	121.0(5)
C(5)-C(4)-C(9)	118.7(5)	C(22)-C(18)-C(19)	107.8(6)
C(5)-C(4)-C(3)	120.6(5)	C(22)-C(18)-Re(1)	72.3(4)
C(9)-C(4)-C(3)	120.6(5)	C(19)-C(18)-Re(1)	71.9(3)
C(6)-C(5)-C(4)	120.1(5)	C(18)-C(19)-C(20)	108.5(6)
C(5)-C(6)-C(7)	120.6(5)	C(18)-C(19)-Re(1)	72.8(3)
C(8)-C(7)-C(6)	119.1(5)	C(20)-C(19)-Re(1)	72.3(3)
C(8)-C(7)-C(10)	120.2(6)	C(19)-C(20)-C(21)	107.8(5)
C(6)-C(7)-C(10)	120.6(6)	C(19)-C(20)-Re(1)	72.2(3)
C(9)-C(8)-C(7)	120.6(6)	C(21)-C(20)-Re(1)	71.2(3)
C(8)-C(9)-C(4)	120.7(5)	C(22)-C(21)-C(20)	106.8(6)
C(16)-C(11)-C(12)	116.7(5)	C(22)-C(21)-Re(1)	73.2(4)
C(16)-C(11)-C(1)	122.0(5)	C(20)-C(21)-Re(1)	72.7(3)
C(12)-C(11)-C(1)	121.2(5)	C(18)-C(22)-C(21)	109.0(6)
C(13)-C(12)-C(11)	121.6(5)	C(18)-C(22)-Re(1)	72.5(3)
C(12)-C(13)-C(14)	121.2(5)	C(21)-C(22)-Re(1)	71.1(3)
C(15)-C(14)-C(13)	117.0(5)	O(24)-C(23)-Re(1)	179.1(6)
C(15)-C(14)-C(17)	122.0(5)	O(26)-C(25)-Re(1)	177.0(6)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2hk a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re(1)	17(1)	12(1)	27(1)	3(1)	-2(1)	0(1)
C(1)	17(2)	16(2)	21(2)	-2(2)	1(2)	-1(2)
C(2)	27(3)	7(2)	29(3)	1(2)	-2(2)	3(2)
C(3)	23(3)	16(3)	32(3)	-1(2)	0(2)	1(2)
C(4)	20(2)	11(2)	32(3)	-4(2)	-2(2)	-2(2)
C(5)	27(3)	14(3)	36(3)	3(2)	-1(2)	-2(2)
C(6)	22(3)	18(3)	42(3)	0(2)	-11(2)	0(2)
C(7)	23(3)	15(3)	43(3)	-6(2)	1(3)	-3(2)
C(8)	26(3)	16(3)	40(3)	-1(2)	2(2)	-6(2)
C(9)	25(3)	21(3)	33(3)	1(2)	-1(2)	0(2)
C(10)	22(3)	33(4)	54(4)	-7(3)	-1(3)	-8(2)
C(11)	20(2)	12(2)	25(2)	-2(2)	1(2)	0(2)
C(12)	20(2)	18(3)	29(3)	3(2)	0(2)	-3(2)
C(13)	25(3)	17(3)	31(3)	7(2)	5(2)	-1(2)
C(14)	25(3)	17(3)	27(3)	0(2)	0(2)	6(2)
C(15)	13(2)	17(3)	35(3)	2(2)	1(2)	-2(2)
C(16)	10(2)	24(3)	34(3)	4(2)	-7(2)	-3(2)
C(17)	29(3)	32(3)	36(3)	10(3)	1(3)	10(2)
C(18)	26(3)	41(4)	36(3)	20(3)	-5(3)	6(3)
C(19)	20(3)	24(3)	37(3)	5(2)	-6(3)	3(2)
C(20)	20(3)	33(3)	38(3)	12(3)	8(2)	8(2)
C(21)	34(3)	23(3)	50(4)	-5(3)	-3(3)	17(2)
C(22)	24(3)	26(3)	62(5)	23(3)	-7(3)	2(2)
C(23)	26(3)	12(3)	41(3)	1(2)	-6(3)	1(2)
O(24)	60(3)	24(2)	49(3)	-8(2)	-23(2)	-3(2)
C(25)	29(3)	25(3)	31(3)	11(2)	0(3)	2(2)
O(26)	22(2)	58(3)	44(3)	18(2)	7(2)	8(2)

Table 5. Hydrogen coordinates and isotropic displacement parameters for **3**.

	x	y	z	U(eq)
H(5)	0.3861(5)	0.5971(7)	0.0263(3)	0.032
H(6)	0.1777(5)	0.5078(7)	0.0154(3)	0.035
H(8)	0.2696(5)	0.2147(7)	0.1640(3)	0.034
H(9)	0.4775(5)	0.3007(7)	0.1747(3)	0.032
H(10A)	0.0454(5)	0.2859(8)	0.1246(3)	0.056
H(10B)	0.0568(5)	0.1960(8)	0.0612(3)	0.056
H(10C)	0.0123(5)	0.3816(8)	0.0605(3)	0.056
H(12)	0.7654(5)	0.4303(7)	0.2158(2)	0.027
H(13)	0.9064(5)	0.2919(6)	0.2878(3)	0.029
H(15)	1.1938(5)	0.5389(6)	0.2341(3)	0.027
H(16)	1.0530(5)	0.6871(6)	0.1647(3)	0.029
H(17A)	1.1339(6)	0.1978(8)	0.3173(3)	0.049
H(17B)	1.1591(6)	0.3594(8)	0.3581(3)	0.049
H(17C)	1.2433(6)	0.3202(8)	0.3065(3)	0.049
H(18)	0.7533(6)	0.9819(8)	-0.0319(3)	0.042
H(19)	0.6033(6)	0.7839(7)	0.0056(3)	0.034
H(20)	0.5415(5)	0.8968(8)	0.1035(3)	0.036
H(21)	0.6637(6)	1.1621(7)	0.1299(4)	0.044
H(22)	0.7857(6)	1.2174(8)	0.0427(4)	0.047

Table 6. Torsion angles [°] for **3**

C(23)-Re(1)-C(1)-C(2)	142.0(4)	C(16)-C(11)-C(12)-C(13)	0.7(8)
C(25)-Re(1)-C(1)-C(2)	-135.9(4)	C(1)-C(11)-C(12)-C(13)	-177.8(5)
C(21)-Re(1)-C(1)-C(2)	43.1(5)	C(11)-C(12)-C(13)-C(14)	-0.4(9)
C(19)-Re(1)-C(1)-C(2)	-15.8(4)	C(12)-C(13)-C(14)-C(15)	-1.4(8)
C(20)-Re(1)-C(1)-C(2)	20.0(4)	C(12)-C(13)-C(14)-C(17)	-180.0(6)
C(22)-Re(1)-C(1)-C(2)	8.7(8)	C(13)-C(14)-C(15)-C(16)	2.9(8)
C(18)-Re(1)-C(1)-C(2)	-34.5(5)	C(17)-C(14)-C(15)-C(16)	-178.5(6)
C(23)-Re(1)-C(1)-C(11)	-32.5(5)	C(14)-C(15)-C(16)-C(11)	-2.6(9)
C(25)-Re(1)-C(1)-C(11)	49.6(5)	C(12)-C(11)-C(16)-C(15)	0.7(8)
C(21)-Re(1)-C(1)-C(11)	-131.3(5)	C(1)-C(11)-C(16)-C(15)	179.2(5)
C(19)-Re(1)-C(1)-C(11)	169.8(5)	C(23)-Re(1)-C(18)-C(22)	-25.1(6)
C(20)-Re(1)-C(1)-C(11)	-154.5(5)	C(25)-Re(1)-C(18)-C(22)	-108.6(4)
C(22)-Re(1)-C(1)-C(11)	-165.7(6)	C(1)-Re(1)-C(18)-C(22)	149.6(4)
C(18)-Re(1)-C(1)-C(11)	151.0(4)	C(21)-Re(1)-C(18)-C(22)	36.7(4)
C(11)-C(1)-C(2)-C(3)	116.6(181)	C(19)-Re(1)-C(18)-C(22)	116.3(6)
Re(1)-C(1)-C(2)-C(3)	-58.8(183)	C(20)-Re(1)-C(18)-C(22)	79.0(4)
C(1)-C(2)-C(3)-C(4)	0.4(233)	C(23)-Re(1)-C(18)-C(19)	-141.3(4)
C(2)-C(3)-C(4)-C(5)	76.7(67)	C(25)-Re(1)-C(18)-C(19)	135.1(4)
C(2)-C(3)-C(4)-C(9)	-100.3(65)	C(1)-Re(1)-C(18)-C(19)	33.3(5)
C(9)-C(4)-C(5)-C(6)	2.0(8)	C(21)-Re(1)-C(18)-C(19)	-79.6(4)
C(3)-C(4)-C(5)-C(6)	-175.1(5)	C(20)-Re(1)-C(18)-C(19)	-37.3(4)
C(4)-C(5)-C(6)-C(7)	-0.1(9)	C(22)-Re(1)-C(18)-C(19)	-116.3(6)
C(5)-C(6)-C(7)-C(8)	-1.6(9)	C(22)-C(18)-C(19)-C(20)	0.1(7)
C(5)-C(6)-C(7)-C(10)	178.5(6)	Re(1)-C(18)-C(19)-C(20)	63.9(4)
C(6)-C(7)-C(8)-C(9)	1.3(9)	C(22)-C(18)-C(19)-Re(1)	-63.8(4)
C(10)-C(7)-C(8)-C(9)	-178.8(6)	C(23)-Re(1)-C(19)-C(18)	92.5(7)
C(7)-C(8)-C(9)-C(4)	0.7(9)	C(25)-Re(1)-C(19)-C(18)	-53.2(5)
C(5)-C(4)-C(9)-C(8)	-2.3(9)	C(1)-Re(1)-C(19)-C(18)	-154.7(4)
C(3)-C(4)-C(9)-C(8)	174.8(5)	C(21)-Re(1)-C(19)-C(18)	79.0(4)
C(2)-C(1)-C(11)-C(16)	162.4(5)	C(20)-Re(1)-C(19)-C(18)	116.6(5)
Re(1)-C(1)-C(11)-C(16)	-22.9(8)	C(22)-Re(1)-C(19)-C(18)	37.2(4)
C(2)-C(1)-C(11)-C(12)	-19.2(7)	C(23)-Re(1)-C(19)-C(20)	-24.1(7)
Re(1)-C(1)-C(11)-C(12)	155.5(4)	C(25)-Re(1)-C(19)-C(20)	-169.8(4)

C(1)-Re(1)-C(19)-C(20)	88.7(4)	C(19)-C(18)-C(22)-Re(1)	63.5(4)
C(21)-Re(1)-C(19)-C(20)	-37.6(4)	C(20)-C(21)-C(22)-C(18)	-2.4(7)
C(22)-Re(1)-C(19)-C(20)	-79.4(4)	Re(1)-C(21)-C(22)-C(18)	63.0(4)
C(18)-Re(1)-C(19)-C(20)	-116.6(5)	C(20)-C(21)-C(22)-Re(1)	-65.4(4)
C(18)-C(19)-C(20)-C(21)	-1.6(6)	C(23)-Re(1)-C(22)-C(18)	163.2(4)
Re(1)-C(19)-C(20)-C(21)	62.7(4)	C(25)-Re(1)-C(22)-C(18)	77.5(4)
C(18)-C(19)-C(20)-Re(1)	-64.3(4)	C(1)-Re(1)-C(22)-C(18)	-66.0(8)
C(23)-Re(1)-C(20)-C(19)	168.6(3)	C(21)-Re(1)-C(22)-C(18)	-118.0(6)
C(25)-Re(1)-C(20)-C(19)	20.1(7)	C(19)-Re(1)-C(22)-C(18)	-37.3(4)
C(1)-Re(1)-C(20)-C(19)	-96.2(4)	C(20)-Re(1)-C(22)-C(18)	-79.1(4)
C(21)-Re(1)-C(20)-C(19)	116.7(5)	C(23)-Re(1)-C(22)-C(21)	-78.8(4)
C(22)-Re(1)-C(20)-C(19)	78.3(4)	C(25)-Re(1)-C(22)-C(21)	-164.6(4)
C(18)-Re(1)-C(20)-C(19)	37.0(3)	C(1)-Re(1)-C(22)-C(21)	51.9(8)
C(23)-Re(1)-C(20)-C(21)	52.0(5)	C(19)-Re(1)-C(22)-C(21)	80.6(4)
C(25)-Re(1)-C(20)-C(21)	-96.6(7)	C(20)-Re(1)-C(22)-C(21)	38.9(4)
C(1)-Re(1)-C(20)-C(21)	147.2(4)	C(18)-Re(1)-C(22)-C(21)	118.0(6)
C(19)-Re(1)-C(20)-C(21)	-116.7(5)	C(25)-Re(1)-C(23)-O(24)	-7.5(301)
C(22)-Re(1)-C(20)-C(21)	-38.4(4)	C(1)-Re(1)-C(23)-O(24)	88.2(301)
C(18)-Re(1)-C(20)-C(21)	-79.6(4)	C(21)-Re(1)-C(23)-O(24)	-145.8(301)
C(19)-C(20)-C(21)-C(22)	2.5(7)	C(19)-Re(1)-C(23)-O(24)	-157.5(298)
Re(1)-C(20)-C(21)-C(22)	65.8(4)	C(20)-Re(1)-C(23)-O(24)	-173.7(1000)
C(19)-C(20)-C(21)-Re(1)	-63.3(4)	C(22)-Re(1)-C(23)-O(24)	-110.6(301)
C(23)-Re(1)-C(21)-C(22)	108.3(4)	C(18)-Re(1)-C(23)-O(24)	-95.9(301)
C(25)-Re(1)-C(21)-C(22)	22.9(6)	C(23)-Re(1)-C(25)-O(26)	-71.4(104)
C(1)-Re(1)-C(21)-C(22)	-155.7(4)	C(1)-Re(1)-C(25)-O(26)	-161.7(104)
C(19)-Re(1)-C(21)-C(22)	-77.3(4)	C(21)-Re(1)-C(25)-O(26)	19.4(106)
C(20)-Re(1)-C(21)-C(22)	-114.2(6)	C(19)-Re(1)-C(25)-O(26)	95.1(104)
C(18)-Re(1)-C(21)-C(22)	-36.1(4)	C(20)-Re(1)-C(25)-O(26)	81.9(105)
C(23)-Re(1)-C(21)-C(20)	-137.5(4)	C(22)-Re(1)-C(25)-O(26)	33.0(104)
C(25)-Re(1)-C(21)-C(20)	137.1(4)	C(18)-Re(1)-C(25)-O(26)	67.4(104)
C(1)-Re(1)-C(21)-C(20)	-41.5(5)		
C(19)-Re(1)-C(21)-C(20)	36.9(4)		
C(22)-Re(1)-C(21)-C(20)	114.2(6)		
C(18)-Re(1)-C(21)-C(20)	78.1(4)		
C(19)-C(18)-C(22)-C(21)	1.5(7)		
Re(1)-C(18)-C(22)-C(21)	-62.1(4)		

X-ray Crystal Structure Determination of
[Cp(CO)₂Re]₂{[Tol(²η-C≡C)](Ph)C=C(Ph)[(²η-C≡C)Tol]} (4). An orange prism-shaped crystal of dimensions 0.36 x 0.28 x 0.10 mm was selected for structural analysis. Intensity data for this compound were collected using a Bruker SMART ccd area detector¹⁴ mounted on a Bruker P4 goniometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073 \text{ \AA}$). The sample was cooled to 133(2) K. The intensity data, which nominally covered one and a half hemispheres of reciprocal space, were measured as a series of ϕ oscillation frames each of 0.4° for 60 sec / frame. The detector was operated in 512 x 512 mode and was positioned 5.00 cm from the sample. Coverage of unique data was 97.5 % complete to 25.00 degrees in θ . Cell parameters were determined from a non-linear least squares fit of 5366 peaks in the range $3.0 < \theta < 25.0^\circ$. The first 50 frames were repeated at the end of data collection and yielded 221 peaks showing a variation of -0.08 % during the data collection. A total of 8279 data were measured in the range $2.62 < \theta < 28.91^\circ$. The data were corrected for absorption by the empirical method¹⁵ giving minimum and maximum transmission factors of 0.181 and 0.297. The data were merged to form a set of 4114 independent data with $R(\text{int}) = 0.0388$.

The monoclinic space group $P2(1)/n$ was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods¹⁶ on F^2 . Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters. A total of 235 parameters were refined against 4114 data to give $wR(F^2) = 0.1087$ and $S = 1.056$ for weights of $w = 1/[\sigma^2(F^2) + (0.0582 P)^2]$, where $P = [F_o^2 + 2F_c^2] / 3$. The final $R(F)$ was 0.0505 for the 3159 observed, $[F > 4\sigma(F)]$, data. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 3.551 and -3.467 e/Å³, respectively.

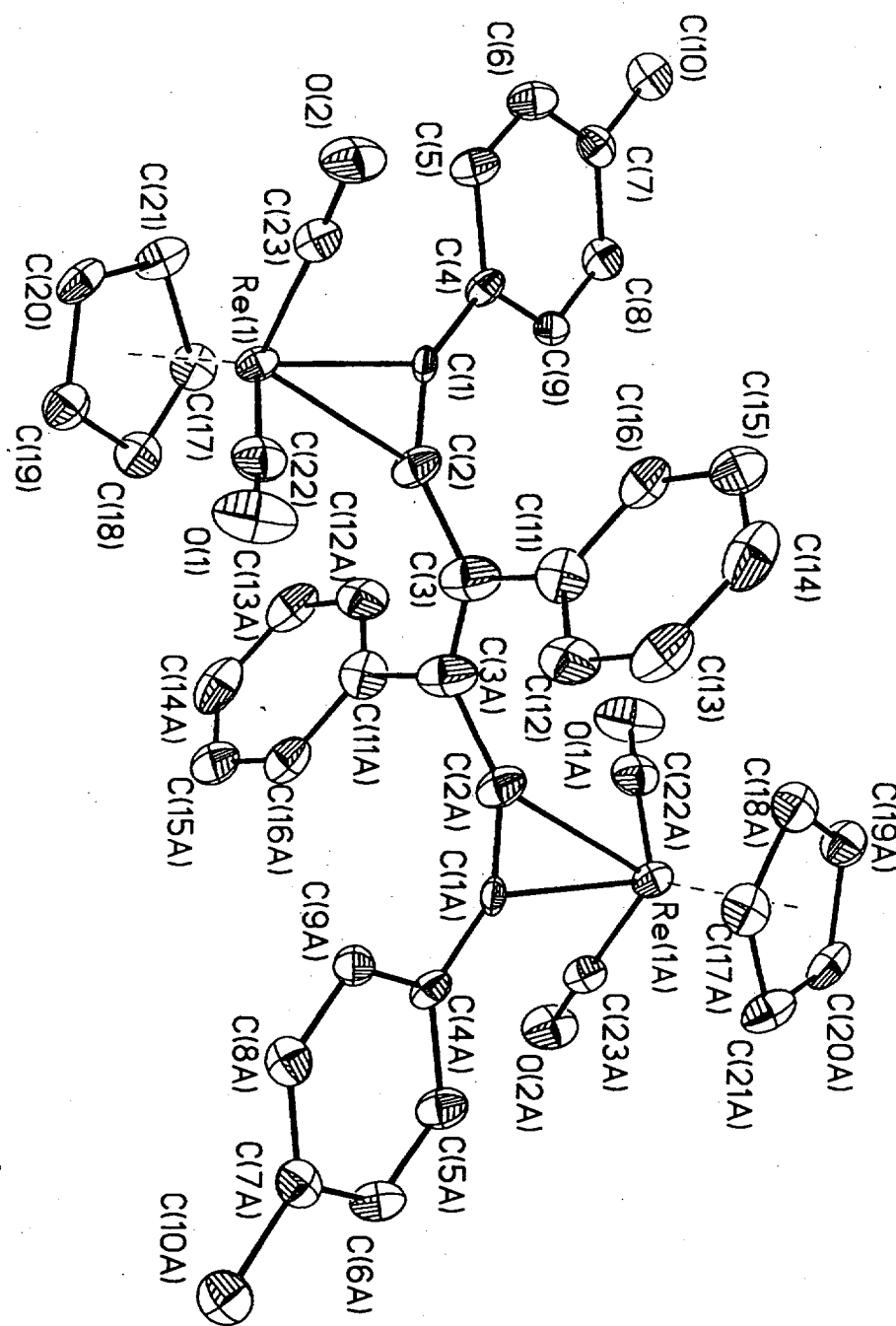


Figure 3. X-ray crystal structure of $[\text{Cp}(\text{CO})_2\text{Re}]_2\{[\text{Tol}(\eta^2\text{-C}\equiv\text{C})](\text{Ph})\text{C}=\text{C}(\text{Ph})[(\eta^2\text{-C}\equiv\text{C})\text{Tol}]\}$ (**4**) with atom labeling. The displacement ellipsoids are drawn at the 50% probability level.

Table 7. Crystal data and structure refinement for **4**.

Empirical formula	$\text{C}_{46}\text{H}_{34}\text{O}_4\text{Re}_2$	
Formula weight	1023.13	
Crystal system	Monoclinic	
Space group	p2(1)/n	
Unit cell dimensions	$a = 10.5996(9) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 11.4974(8) \text{ \AA}$	$\beta = 94.222(2)^\circ$
	$c = 14.7550(10) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$1793.3(2) \text{ \AA}^3$	
Z	2	
Density (calculated)	1.895 Mg/m^3	
Wavelength	$0.71073 \text{ \AA}$	
Temperature	$133(2) \text{ K}$	
$F(000)$	984	
Absorption coefficient	6.790 mm^{-1}	
Absorption correction	Empirical	
Max. and min. transmission	0.297 and 0.181	
Theta range for data collection	2.62 to 28.91°	
Reflections collected	8279	
Independent reflections	4114 [$R(\text{int}) = 0.0388$]	
Data / restraints / parameters	4114 / 0 / 235	
$wR(F^2_{\text{all data}})$	$wR2 = 0.1087$	
$R(F_{\text{obsd data}})$	$R1 = 0.0505$	
Goodness-of-fit on F^2	1.056	
Observed data [$I > 2\sigma(I)$]	3159	
Largest and mean shift / s.u.	0.001 and 0.000	
Largest diff. peak and hole	3.551 and $-3.467 \text{ e/\AA}^3$	

Table 8. Atomic coordinates and equivalent isotropic displacement parameters for **4**.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Re(1)	0.61947(2)	0.740490(19)	0.665086(17)	0.01959(10)
O(1)	0.6490(5)	0.5011(5)	0.7563(5)	0.0471(17)
O(2)	0.9075(5)	0.7397(4)	0.7061(4)	0.0363(13)
C(1)	0.6514(6)	0.7342(5)	0.5206(4)	0.0181(13)
C(2)	0.5911(7)	0.6403(6)	0.5344(5)	0.0269(16)
C(3)	0.5589(8)	0.5175(7)	0.5107(6)	0.037(2)
C(4)	0.7017(7)	0.8106(5)	0.4556(4)	0.0211(14)
C(5)	0.7985(7)	0.8924(6)	0.4827(5)	0.0274(16)
C(6)	0.8454(7)	0.9651(6)	0.4180(5)	0.0284(17)
C(7)	0.7988(7)	0.9629(6)	0.3264(5)	0.0249(15)
C(8)	0.7027(7)	0.8828(6)	0.3017(5)	0.0254(15)
C(9)	0.6571(6)	0.8073(6)	0.3647(5)	0.0216(14)
C(10)	0.8486(7)	1.0460(6)	0.2574(5)	0.0329(18)
C(11)	0.6694(7)	0.4310(6)	0.5095(5)	0.0296(17)
C(12)	0.6719(8)	0.3199(7)	0.5479(5)	0.0339(19)
C(13)	0.7755(9)	0.2489(6)	0.5451(6)	0.0373(19)
C(14)	0.8795(8)	0.2845(7)	0.5017(6)	0.042(2)
C(15)	0.8804(8)	0.3957(7)	0.4639(6)	0.037(2)
C(16)	0.7770(8)	0.4675(6)	0.4694(5)	0.0317(17)
C(17)	0.4684(7)	0.8801(6)	0.6184(5)	0.0273(16)
C(18)	0.4079(7)	0.7981(7)	0.6717(5)	0.0301(16)
C(19)	0.4692(7)	0.8010(6)	0.7610(5)	0.0297(16)
C(20)	0.5677(7)	0.8867(6)	0.7622(5)	0.0286(17)
C(21)	0.5687(7)	0.9366(6)	0.6741(5)	0.0274(17)
C(22)	0.6376(7)	0.5888(6)	0.7198(6)	0.0300(17)
C(23)	0.7987(7)	0.7405(5)	0.6880(5)	0.0248(14)

Table 9. Bond lengths [Å] and angles [°] for **4**.

Re(1)-C(23)	1.905(8)	C(4)-C(5)	1.427(9)
Re(1)-C(22)	1.925(7)	C(5)-C(6)	1.388(10)
Re(1)-C(1)	2.184(6)	C(6)-C(7)	1.404(10)
Re(1)-C(2)	2.247(7)	C(7)-C(8)	1.401(10)
Re(1)-C(20)	2.301(7)	C(7)-C(10)	1.519(10)
Re(1)-C(19)	2.314(8)	C(8)-C(9)	1.384(10)
Re(1)-C(21)	2.324(6)	C(11)-C(16)	1.388(11)
Re(1)-C(17)	2.336(6)	C(11)-C(12)	1.397(10)
Re(1)-C(18)	2.348(7)	C(12)-C(13)	1.371(12)
O(1)-C(22)	1.146(9)	C(13)-C(14)	1.379(13)
O(2)-C(23)	1.164(9)	C(14)-C(15)	1.395(12)
C(1)-C(2)	1.278(9)	C(15)-C(16)	1.379(11)
C(1)-C(4)	1.433(9)	C(17)-C(18)	1.413(11)
C(2)-C(3)	1.488(10)	C(17)-C(21)	1.449(9)
C(3)-C(3)#1	1.327(16)	C(18)-C(19)	1.426(10)
C(3)-C(11)	1.538(11)	C(19)-C(20)	1.435(10)
C(4)-C(9)	1.390(9)	C(20)-C(21)	1.421(11)
C(23)-Re(1)-C(22)	81.8(3)	C(23)-Re(1)-C(21)	102.8(3)
C(23)-Re(1)-C(1)	87.1(3)	C(22)-Re(1)-C(21)	150.6(3)
C(22)-Re(1)-C(1)	111.2(3)	C(1)-Re(1)-C(21)	98.1(3)
C(23)-Re(1)-C(2)	102.8(3)	C(2)-Re(1)-C(21)	122.0(2)
C(22)-Re(1)-C(2)	84.2(3)	C(20)-Re(1)-C(21)	35.8(3)
C(1)-Re(1)-C(2)	33.5(2)	C(19)-Re(1)-C(21)	60.1(3)
C(23)-Re(1)-C(20)	99.8(3)	C(23)-Re(1)-C(17)	134.9(3)
C(22)-Re(1)-C(20)	114.9(3)	C(22)-Re(1)-C(17)	142.3(3)
C(1)-Re(1)-C(20)	133.9(3)	C(1)-Re(1)-C(17)	83.5(3)
C(2)-Re(1)-C(20)	152.3(3)	C(2)-Re(1)-C(17)	93.1(3)
C(23)-Re(1)-C(19)	127.9(3)	C(20)-Re(1)-C(17)	59.5(3)
C(22)-Re(1)-C(19)	93.9(3)	C(19)-Re(1)-C(17)	59.1(3)
C(1)-Re(1)-C(19)	140.4(3)	C(21)-Re(1)-C(17)	36.2(2)
C(2)-Re(1)-C(19)	128.6(3)	C(23)-Re(1)-C(18)	159.4(3)
C(20)-Re(1)-C(19)	36.2(3)	C(22)-Re(1)-C(18)	107.7(3)

C(1)-Re(1)-C(18)	105.5(3)	C(16)-C(11)-C(12)	117.2(7)
C(2)-Re(1)-C(18)	96.5(3)	C(16)-C(11)-C(3)	117.4(7)
C(20)-Re(1)-C(18)	59.7(3)	C(12)-C(11)-C(3)	125.3(7)
C(19)-Re(1)-C(18)	35.6(2)	C(13)-C(12)-C(11)	121.6(8)
C(21)-Re(1)-C(18)	59.9(3)	C(12)-C(13)-C(14)	120.4(7)
C(17)-Re(1)-C(18)	35.1(3)	C(13)-C(14)-C(15)	119.2(8)
C(2)-C(1)-C(4)	147.1(6)	C(16)-C(15)-C(14)	119.7(8)
C(2)-C(1)-Re(1)	76.0(4)	C(15)-C(16)-C(11)	121.7(7)
C(4)-C(1)-Re(1)	136.5(4)	C(18)-C(17)-C(21)	109.1(7)
C(1)-C(2)-C(3)	150.8(8)	C(18)-C(17)-Re(1)	72.9(4)
C(1)-C(2)-Re(1)	70.5(4)	C(21)-C(17)-Re(1)	71.5(4)
C(3)-C(2)-Re(1)	134.5(5)	C(17)-C(18)-C(19)	107.7(7)
C(3)#1-C(3)-C(2)	122.7(10)	C(17)-C(18)-Re(1)	72.0(4)
C(3)#1-C(3)-C(11)	120.3(9)	C(19)-C(18)-Re(1)	70.9(4)
C(2)-C(3)-C(11)	117.0(7)	C(18)-C(19)-C(20)	108.0(7)
C(9)-C(4)-C(5)	118.4(6)	C(18)-C(19)-Re(1)	73.5(4)
C(9)-C(4)-C(1)	120.8(6)	C(20)-C(19)-Re(1)	71.4(4)
C(5)-C(4)-C(1)	120.8(6)	C(21)-C(20)-C(19)	108.7(6)
C(6)-C(5)-C(4)	119.4(7)	C(21)-C(20)-Re(1)	73.0(4)
C(5)-C(6)-C(7)	122.2(7)	C(19)-C(20)-Re(1)	72.4(4)
C(8)-C(7)-C(6)	117.3(6)	C(20)-C(21)-C(17)	106.4(7)
C(8)-C(7)-C(10)	121.4(7)	C(20)-C(21)-Re(1)	71.2(4)
C(6)-C(7)-C(10)	121.2(6)	C(17)-C(21)-Re(1)	72.3(4)
C(9)-C(8)-C(7)	121.4(7)	O(1)-C(22)-Re(1)	176.7(8)
C(8)-C(9)-C(4)	121.3(6)	O(2)-C(23)-Re(1)	176.9(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, -z+1

Table 10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Re(1)	18(1)	19(1)	20(1)	-1(1)	-6(1)	0(1)
O(1)	33(3)	32(3)	74(5)	23(3)	-12(3)	1(2)
O(2)	19(3)	36(3)	53(4)	-1(2)	-11(2)	1(2)
C(1)	15(3)	23(3)	17(3)	-9(3)	5(2)	1(2)
C(2)	35(4)	24(3)	20(4)	-1(3)	-8(3)	-4(3)
C(3)	46(5)	34(4)	32(5)	8(3)	-8(4)	-11(3)
C(4)	29(4)	13(3)	20(4)	-1(3)	-1(3)	2(2)
C(5)	29(4)	25(3)	27(4)	0(3)	-7(3)	-5(3)
C(6)	28(4)	21(3)	35(5)	3(3)	-5(3)	-3(3)
C(7)	21(4)	25(3)	30(4)	3(3)	3(3)	6(3)
C(8)	24(4)	33(4)	18(4)	1(3)	-3(3)	1(3)
C(9)	16(4)	26(3)	22(4)	-5(3)	0(3)	-3(3)
C(10)	34(5)	34(4)	31(4)	6(3)	1(3)	3(3)
C(11)	25(4)	37(4)	25(4)	2(3)	-9(3)	7(3)
C(12)	29(5)	45(4)	26(4)	1(3)	-9(3)	-10(3)
C(13)	53(6)	26(4)	32(4)	-2(3)	-12(4)	4(3)
C(14)	39(5)	45(4)	40(5)	-17(4)	-16(4)	16(4)
C(15)	31(5)	48(5)	31(5)	-12(4)	-9(4)	-10(3)
C(16)	43(5)	26(3)	25(4)	-3(3)	-5(3)	2(3)
C(17)	21(4)	31(3)	29(4)	3(3)	-6(3)	9(3)
C(18)	18(4)	36(4)	35(4)	-5(3)	-4(3)	5(3)
C(19)	30(4)	31(4)	27(4)	-3(3)	-3(3)	0(3)
C(20)	27(4)	23(3)	34(4)	-12(3)	-8(3)	7(3)
C(21)	29(4)	16(3)	35(4)	0(3)	-14(3)	4(3)
C(22)	17(4)	33(4)	40(5)	1(3)	-3(3)	1(3)
C(23)	28(4)	22(3)	24(3)	0(3)	-2(3)	-2(3)

Table 11. Hydrogen coordinates and isotropic displacement parameters for **4**.

	x	y	z	U(eq)
H(5)	0.8307	0.8970	0.5444	0.033
H(6)	0.9111	1.0181	0.4362	0.034
H(8)	0.6681	0.8803	0.2405	0.030
H(9)	0.5941	0.7520	0.3453	0.026
H(10A)	0.9135	1.0963	0.2876	0.040
H(10B)	0.7789	1.0939	0.2308	0.040
H(10C)	0.8855	1.0014	0.2093	0.040
H(12)	0.6001	0.2929	0.5766	0.041
H(13)	0.7755	0.1747	0.5734	0.045
H(14)	0.9498	0.2340	0.4975	0.051
H(15)	0.9520	0.4219	0.4344	0.045
H(16)	0.7795	0.5439	0.4451	0.038
H(17)	0.4420	0.9003	0.5538	0.033
H(18)	0.3316	0.7508	0.6518	0.036
H(19)	0.4423	0.7573	0.8149	0.036
H(20)	0.6207	0.9128	0.8173	0.034
H(21)	0.6215	1.0037	0.6561	0.033

Table 12. Torsion angles [°] for **4**.

C(23)-Re(1)-C(1)-C(2)	118.6(5)	C(1)-C(2)-C(3)-C(3)#1	-122.3(16)
C(22)-Re(1)-C(1)-C(2)	38.5(5)	Re(1)-C(2)-C(3)-C(3)#1	94.4(12)
C(20)-Re(1)-C(1)-C(2)	-140.7(5)	C(1)-C(2)-C(3)-C(11)	56.1(17)
C(19)-Re(1)-C(1)-C(2)	-87.1(5)	Re(1)-C(2)-C(3)-C(11)	-87.2(10)
C(21)-Re(1)-C(1)-C(2)	-138.9(5)	C(2)-C(1)-C(4)-C(9)	19.8(16)
C(17)-Re(1)-C(1)-C(2)	-105.6(5)	Re(1)-C(1)-C(4)-C(9)	-148.7(6)
C(18)-Re(1)-C(1)-C(2)	-78.0(5)	C(2)-C(1)-C(4)-C(5)	-160.4(11)
C(23)-Re(1)-C(1)-C(4)	-67.9(7)	Re(1)-C(1)-C(4)-C(5)	31.1(11)
C(22)-Re(1)-C(1)-C(4)	-147.9(7)	C(9)-C(4)-C(5)-C(6)	-0.3(10)
C(2)-Re(1)-C(1)-C(4)	173.6(10)	C(1)-C(4)-C(5)-C(6)	179.9(7)
C(20)-Re(1)-C(1)-C(4)	32.9(9)	C(4)-C(5)-C(6)-C(7)	1.4(11)
C(19)-Re(1)-C(1)-C(4)	86.5(8)	C(5)-C(6)-C(7)-C(8)	-0.6(11)
C(21)-Re(1)-C(1)-C(4)	34.7(7)	C(5)-C(6)-C(7)-C(10)	178.0(7)
C(17)-Re(1)-C(1)-C(4)	67.9(7)	C(6)-C(7)-C(8)-C(9)	-1.2(10)
C(18)-Re(1)-C(1)-C(4)	95.6(7)	C(10)-C(7)-C(8)-C(9)	-179.8(7)
C(4)-C(1)-C(2)-C(3)	35(2)	C(7)-C(8)-C(9)-C(4)	2.3(11)
Re(1)-C(1)-C(2)-C(3)	-153.2(14)	C(5)-C(4)-C(9)-C(8)	-1.5(10)
C(4)-C(1)-C(2)-Re(1)	-171.9(12)	C(1)-C(4)-C(9)-C(8)	178.3(6)
C(23)-Re(1)-C(2)-C(1)	-64.1(5)	C(3)#1-C(3)-C(11)-C(16)	135.4(10)
C(22)-Re(1)-C(2)-C(1)	-144.3(5)	C(2)-C(3)-C(11)-C(16)	-43.1(10)
C(20)-Re(1)-C(2)-C(1)	79.8(7)	C(3)#1-C(3)-C(11)-C(12)	-46.7(15)
C(19)-Re(1)-C(2)-C(1)	125.4(5)	C(2)-C(3)-C(11)-C(12)	134.8(8)
C(21)-Re(1)-C(2)-C(1)	50.1(5)	C(16)-C(11)-C(12)-C(13)	-0.9(11)
C(17)-Re(1)-C(2)-C(1)	73.4(5)	C(3)-C(11)-C(12)-C(13)	-178.8(7)
C(18)-Re(1)-C(2)-C(1)	108.5(5)	C(11)-C(12)-C(13)-C(14)	-1.8(12)
C(23)-Re(1)-C(2)-C(3)	97.9(8)	C(12)-C(13)-C(14)-C(15)	2.8(12)
C(22)-Re(1)-C(2)-C(3)	17.7(8)	C(13)-C(14)-C(15)-C(16)	-0.9(12)
C(1)-Re(1)-C(2)-C(3)	162.0(11)	C(14)-C(15)-C(16)-C(11)	-1.9(11)
C(20)-Re(1)-C(2)-C(3)	-118.2(8)	C(12)-C(11)-C(16)-C(15)	2.8(11)
C(19)-Re(1)-C(2)-C(3)	-72.7(9)	C(3)-C(11)-C(16)-C(15)	-179.1(7)
C(21)-Re(1)-C(2)-C(3)	-147.9(7)	C(23)-Re(1)-C(17)-C(18)	-151.7(5)
C(17)-Re(1)-C(2)-C(3)	-124.6(8)	C(22)-Re(1)-C(17)-C(18)	12.4(7)
C(18)-Re(1)-C(2)-C(3)	-89.6(8)	C(1)-Re(1)-C(17)-C(18)	129.0(5)

C(2)-Re(1)-C(17)-C(18)	96.9(5)	C(21)-Re(1)-C(19)-C(18)	79.0(5)
C(20)-Re(1)-C(17)-C(18)	-79.7(5)	C(17)-Re(1)-C(19)-C(18)	36.8(4)
C(19)-Re(1)-C(17)-C(18)	-37.3(4)	C(23)-Re(1)-C(19)-C(20)	45.8(5)
C(21)-Re(1)-C(17)-C(18)	-117.7(7)	C(22)-Re(1)-C(19)-C(20)	128.5(5)
C(23)-Re(1)-C(17)-C(21)	-34.0(6)	C(1)-Re(1)-C(19)-C(20)	-101.0(5)
C(22)-Re(1)-C(17)-C(21)	130.1(6)	C(2)-Re(1)-C(19)-C(20)	-145.9(4)
C(1)-Re(1)-C(17)-C(21)	-113.3(5)	C(21)-Re(1)-C(19)-C(20)	-37.1(4)
C(2)-Re(1)-C(17)-C(21)	-145.5(5)	C(17)-Re(1)-C(19)-C(20)	-79.4(5)
C(20)-Re(1)-C(17)-C(21)	38.0(5)	C(18)-Re(1)-C(19)-C(20)	-116.1(6)
C(19)-Re(1)-C(17)-C(21)	80.4(5)	C(18)-C(19)-C(20)-C(21)	-0.4(8)
C(18)-Re(1)-C(17)-C(21)	117.7(7)	Re(1)-C(19)-C(20)-C(21)	64.4(5)
C(21)-C(17)-C(18)-C(19)	-0.4(8)	C(18)-C(19)-C(20)-Re(1)	-64.9(5)
Re(1)-C(17)-C(18)-C(19)	62.3(5)	C(23)-Re(1)-C(20)-C(21)	98.4(4)
C(21)-C(17)-C(18)-Re(1)	-62.7(5)	C(22)-Re(1)-C(20)-C(21)	-176.2(4)
C(23)-Re(1)-C(18)-C(17)	72.7(9)	C(1)-Re(1)-C(20)-C(21)	3.0(6)
C(22)-Re(1)-C(18)-C(17)	-172.1(5)	C(2)-Re(1)-C(20)-C(21)	-45.9(8)
C(1)-Re(1)-C(18)-C(17)	-53.3(5)	C(19)-Re(1)-C(20)-C(21)	-116.7(6)
C(2)-Re(1)-C(18)-C(17)	-86.1(5)	C(17)-Re(1)-C(20)-C(21)	-38.5(4)
C(20)-Re(1)-C(18)-C(17)	78.9(5)	C(18)-Re(1)-C(20)-C(21)	-79.4(5)
C(19)-Re(1)-C(18)-C(17)	116.8(6)	C(23)-Re(1)-C(20)-C(19)	-144.9(4)
C(21)-Re(1)-C(18)-C(17)	37.2(4)	C(22)-Re(1)-C(20)-C(19)	-59.5(5)
C(23)-Re(1)-C(18)-C(19)	-44.1(10)	C(1)-Re(1)-C(20)-C(19)	119.7(5)
C(22)-Re(1)-C(18)-C(19)	71.1(5)	C(2)-Re(1)-C(20)-C(19)	70.8(7)
C(1)-Re(1)-C(18)-C(19)	-170.1(4)	C(21)-Re(1)-C(20)-C(19)	116.7(6)
C(2)-Re(1)-C(18)-C(19)	157.0(4)	C(17)-Re(1)-C(20)-C(19)	78.2(5)
C(20)-Re(1)-C(18)-C(19)	-37.9(4)	C(18)-Re(1)-C(20)-C(19)	37.3(4)
C(21)-Re(1)-C(18)-C(19)	-79.6(5)	C(19)-C(20)-C(21)-C(17)	0.2(8)
C(17)-Re(1)-C(18)-C(19)	-116.8(6)	Re(1)-C(20)-C(21)-C(17)	64.2(5)
C(17)-C(18)-C(19)-C(20)	0.5(8)	C(19)-C(20)-C(21)-Re(1)	-64.0(5)
Re(1)-C(18)-C(19)-C(20)	63.5(5)	C(18)-C(17)-C(21)-C(20)	0.1(8)
C(17)-C(18)-C(19)-Re(1)	-63.0(5)	Re(1)-C(17)-C(21)-C(20)	-63.5(5)
C(23)-Re(1)-C(19)-C(18)	161.9(4)	C(18)-C(17)-C(21)-Re(1)	63.6(5)
C(22)-Re(1)-C(19)-C(18)	-115.4(5)	C(23)-Re(1)-C(21)-C(20)	-89.0(5)
C(1)-Re(1)-C(19)-C(18)	15.1(6)	C(22)-Re(1)-C(21)-C(20)	7.1(8)
C(2)-Re(1)-C(19)-C(18)	-29.7(6)	C(1)-Re(1)-C(21)-C(20)	-177.8(4)
C(20)-Re(1)-C(19)-C(18)	116.1(6)	C(2)-Re(1)-C(21)-C(20)	156.9(4)

C(19)-Re(1)-C(21)-C(20)	37.5(4)	C(20)-Re(1)-C(22)-O(1)	-17(12)
C(17)-Re(1)-C(21)-C(20)	115.0(7)	C(19)-Re(1)-C(22)-O(1)	-48(12)
C(18)-Re(1)-C(21)-C(20)	78.9(5)	C(21)-Re(1)-C(22)-O(1)	-22(12)
C(23)-Re(1)-C(21)-C(17)	156.0(5)	C(17)-Re(1)-C(22)-O(1)	-89(12)
C(22)-Re(1)-C(21)-C(17)	-107.9(6)	C(18)-Re(1)-C(22)-O(1)	-82(12)
C(1)-Re(1)-C(21)-C(17)	67.2(5)	C(22)-Re(1)-C(23)-O(2)	-58(10)
C(2)-Re(1)-C(21)-C(17)	41.9(6)	C(1)-Re(1)-C(23)-O(2)	-170(10)
C(20)-Re(1)-C(21)-C(17)	-115.0(7)	C(2)-Re(1)-C(23)-O(2)	-140(10)
C(19)-Re(1)-C(21)-C(17)	-77.4(5)	C(20)-Re(1)-C(23)-O(2)	56(10)
C(18)-Re(1)-C(21)-C(17)	-36.1(5)	C(19)-Re(1)-C(23)-O(2)	31(10)
C(23)-Re(1)-C(22)-O(1)	80(12)	C(21)-Re(1)-C(23)-O(2)	93(10)
C(1)-Re(1)-C(22)-O(1)	163(12)	C(17)-Re(1)-C(23)-O(2)	112(10)
C(2)-Re(1)-C(22)-O(1)	-177(100)	C(18)-Re(1)-C(23)-O(2)	62(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, -z+1

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- (8) This value is 20 ppm *downfield* from the shift in $\text{CpRe}(\text{CO})_3$ indicating a *reduced* electron density on the oxygen atom in **1** compared with $\text{CpRe}(\text{CO})_3$. ^{17}O NMR has been applied to related $\text{CpRe}(\text{CO})_2$ systems: Lyatfov, I. R.; Gulieva, G. I.; Babin, V. N.; Materikova, R. B.; Petrovskii, P. V.; Fedin, E. I. *J. Organomet. Chem.* **1987**, *326*, 93.
- (9) Prepared from $\text{C}_6\text{H}_5^{13}\text{C}\equiv\text{CH}$ and *n*-BuLi analogous to the synthesis of $\text{C}_6\text{H}_5\text{C}\equiv\text{CLi}$.⁴
- (10) Prepared from 4-(CH_3) $\text{C}_6\text{H}_4\text{C}\equiv\text{CH}$ and *n*-BuLi analogous to the synthesis of $\text{C}_6\text{H}_5\text{C}\equiv\text{CLi}$.⁴
- (11) The NMR tube was weighed after each addition of $\text{C}_6\text{D}_5\text{CD}_3$ at the beginning of each thermolysis and found to be constant within 0.5 mg. This ensured that the concentration during the thermolysis would not vary by more than 1%.

(12) **13** has also been prepared by a different route. Negishi, E.; Boardman, L. D.; Sawada, H.; Bagheri, V.; Stoll, A.T.; Tour, J. M.; Rand, C. L. *J. Am. Chem. Soc.* **1988**, *110*, 5383.

(13) Prepared from 2-(CH₂=CH-CH₂)C₆H₄C≡CH and *n*-BuLi analogous to the synthesis of C₆H₅C≡CLi.⁴

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