Experimental Section

General Data. All reactions were conducted under N_2 or H_2 atmospheres. Chemicals were treated as follows: THF and hexane, distilled from Na/benzophenone; acetone, distilled from $CaCl_2$; CH_2Cl_2, distilled from $CaCl_2$ (for reactions) or simple distillation (chromatography); hexane (for chromatography), methanol, and PCl_3 (Merck), simple distillation; C_6D_6, $CDCl_3$, toluene-d_8, C_6D_5Cl, CD_2Cl_2 (5 × Acros), Grubbs' catalyst $Ru(=CHPh)(PCy_3)_2(Cl)_2$ (Aldrich), PtO_2 (Acros), $[(COD)Rh(\mu\text{-}Cl)]_2$ (Johnson Matthey), NaI (Rienst, 99%), KSCN (Fluka, 98%), $CBrCl_3$ (Acros, 97%), used as received. The $P((CH_2)_6CH=CH_2)_3$ and $CDFCl_2$ were prepared by literature procedures.[1,2] Other materials not listed were used as received from common commercial sources.

NMR spectra were obtained on Bruker 300 or 400 MHz spectrometers. IR and mass spectra were recorded on ASI React-IR 1000 and Micromass Zabspec instruments, respectively. DSC and TGA data were obtained with a Mettler-Toledo DSC-821 instrument and treated by standard methods.[3] Microanalyses were conducted with a Carlo Erba EA1110 instrument.

***trans*-$Rh(CO)(Cl)[P((CH_2)_6CH=CH_2)_3]_2$ (1).** A Schlenk flask was charged with $P((CH_2)_6CH=CH_2)_3$ (1.495 g, 4.10 mmol), CH_2Cl_2 (20 mL), hexane (20 mL), and $[(COD)Rh(\mu\text{-}Cl)]_2$ (0.493 g, 1.00 mmol), and flushed with CO. The orange solution was stirred, and turned deep yellow. After 2 h, the solvent was removed by oil pump vacuum. The tan oil was chromatographed on silica gel (2.5 × 7.0 cm column) with hexane/CH_2Cl_2 (2:1 v/v). The solvent was removed from the product-containing fractions by oil pump vacuum to give **1** as a yellow oil (1.306 g, 1.458 mmol, 73%). Anal. Calcd. for $C_{49}H_{90}ClOP_2Rh$: C, 65.72; H, 10.13. Found: C, 65.28; H, 9.70.

NMR (δ, $CDCl_3$): ^1H 5.93-5.71 (m, 6H, $CH=$), 4.98-4.96 (m, 12H, $=CH_2$), 2.00 (q, J_{HH} = 6.8 Hz, 12H, $CH_2CH=$), 1.80-1.70 (m, 12H, CH_2), 1.52-1.49 (m, 12H, CH_2), 1.40-1.25 (m, 36H, CH_2); $^{13}C\{^1H\}$ 187.9 (dt, J_{RhC} = 75.6 Hz, J_{PC} = 15.7 Hz, CO), 138.7 (s, $CH=$), 114.1 (s, $=CH_2$), 33.5 (s, CH_2), 32.0 (virtual t,[4] J_{CP} = 6.5 Hz, CH_2), 28.6 (s, CH_2), 28.5 (s, CH_2), 24.6 (virtual t, J_{CP} = 12.8 Hz, CH_2), 24.4 (s, CH_2); $^{31}P\{^1H\}$ 17.6 (d, J_{RhP} = 115.0 Hz).

IR (cm^{-1}, powder film): 2980 (m), 2926 (s), 2856 (m), 1953 (s, ν_{CO}), 1640 (w), 1463 (w), 1440 (w), 1417 (w), 992 (m), 907 (s), 722 (m).

***trans*-$\overline{Rh(CO)(Cl)[P((CH_2)_6CH=CH(CH_2)_6)_3P}]$ (2).** A Schlenk flask was charged with **1** (1.306 g, 1.458 mmol), Grubbs' catalyst (ca. half of 0.180 g, 0.220 mmol, 15 mol%), and CH_2Cl_2

(800 mL; the resulting solution is 0.0018 M in **1**), and fitted with a condenser. The solution was stirred. After 24 h, the remaining catalyst was added. The solution was refluxed, and aliquots were periodically monitored by ^{1}H and ^{31}P NMR. After 48 h, the $\mathrm{CH{=}CH_2}$ signals had disappeared. The solvent was removed by oil pump vacuum. The residue was chromatographed on silica gel (2.5 × 10 cm column) with hexane/$\mathrm{CH_2Cl_2}$ (2:1 v/v). The fractions were monitored by TLC. The solvent was removed from those containing only **2** by oil pump vacuum. This gave **2** as a mixture of C=C isomers and a pale yellow oil (0.890 g, 1.09 mmol, 75%; ^{31}P and ^{13}C NMR spectra showed trace impurities that may be dimers or oligomers).

NMR (δ, $\mathrm{C_6D_6}$, mixture of *E*/*Z* isomers): ^{1}H 5.40-5.34 (m, 6H, $\mathrm{C}H{=}$), 2.04-2.00 (m, 24H, $\mathrm{C}H_2$), 1.70-1.67 (m, 12H, $\mathrm{C}H_2$), 1.34-1.30 (m, 36H, $\mathrm{C}H_2$); ^{13}C{^{1}H} 188.3 (dt, $J_{\mathrm{RhC}} = 74.7$ Hz, $J_{\mathrm{PC}} = 15.6$ Hz, *C*O), 130.5 (s, $C\mathrm{H}{=}$), 31.8 (s, $C\mathrm{H_2}$), 31.1 (virtual t,[4] $J_{\mathrm{CP}} = 6.9$ Hz, $C\mathrm{H_2}$), 28.6 (s, $C\mathrm{H_2}$), 27.7 (s, $C\mathrm{H_2}$), 26.9 (virtual t, $J_{\mathrm{CP}} = 12.6$ Hz, $C\mathrm{H_2}$), 25.7 (s, $C\mathrm{H_2}$); ^{31}P{^{1}H} 23.8 (d, $J_{\mathrm{RhP}} = 118.3$ Hz, 70%), 22.0 (d, $J_{\mathrm{RhP}} = 124.4$ Hz, 30%).

***trans*-$\mathrm{Rh(CO)(Cl)[P((CH_2)_{14})_3P]}$ (3).** A Fischer-Porter bottle was charged with **2** (0.890 g, 1.09 mmol), $\mathrm{PtO_2}$ (0.037 g, 0.16 mmol, 15 mol%), THF (15 mL), and $\mathrm{H_2}$ (4 atm). The mixture was stirred for 12 h. The solvent was removed by oil pump vacuum. The residue was chromatographed on silica gel (2.5 × 9.0 cm column) with hexane/$\mathrm{CH_2Cl_2}$ (3:1 v/v). The solvent was removed from the yellow fraction by oil pump vacuum to give **3** as yellow powder (0.479 g, 0.586 mmol, 54%). DSC ($T_i/T_e/T_p/T_c/T_f$): endotherm, 40.0/55.4/69.6/76.27/76.28 °C; endotherm, 103.5/126.7/134.8/139.2/145.8 °C. TGA: onset of mass loss, 277.6 °C (T_e). Anal. Calcd. for $\mathrm{C_{43}H_{84}ClOP_2Rh}$: C, 63.18; H, 10.36. Found: C, 62.84; H, 10.00.

NMR (δ, $\mathrm{CD_2Cl_2}$): ^{1}H 1.81-1.79 (m, 12H, $\mathrm{C}H_2$), 1.67-1.63 (m, 12H, $\mathrm{C}H_2$), 1.46-1.42 (m, 12H, $\mathrm{C}H_2$), 1.33-1.30 (m, 48H, $\mathrm{C}H_2$); ^{13}C{^{1}H} 188.7 (dt, $J_{\mathrm{CRh}} = 75.0$ Hz, $J_{\mathrm{CP}} = 16.0$ Hz, *C*O), 30.7 (virtual t,[4] $J_{\mathrm{CP}} = 6.5$ Hz, $C\mathrm{H_2}$), 28.4 (s, $C\mathrm{H_2}$), 27.7 (s, $C\mathrm{H_2}$), 27.4 (s, $C\mathrm{H_2}$), 27.3 (s, $C\mathrm{H_2}$), 25.6 (virtual t, $J_{\mathrm{CP}} = 12.9$ Hz, $C\mathrm{H_2}$), 24.5 (s, $C\mathrm{H_2}$); ^{31}P {^{1}H} 19.5 (d, $J_{\mathrm{RhP}} = 118.0$ Hz). NMR (δ, $\mathrm{CDFCl_2}$, −20 °C): ^{1}H 1.82-1.79 (m, 12H, $\mathrm{C}H_2$), 1.67-1.63 (m, 12H, $\mathrm{C}H_2$), 1.47-1.42 (m, 12H, $\mathrm{C}H_2$), 1.33-1.28 (m, 48H, $\mathrm{C}H_2$); ^{13}C{^{1}H}[5] 30.4 (virtual t,[4] $J_{\mathrm{CP}} = 6.5$ Hz, $C\mathrm{H_2}$), 28.1 (s, $C\mathrm{H_2}$), 27.4 (s, $C\mathrm{H_2}$), 27.2 (s, $C\mathrm{H_2}$), 26.9 (s, $C\mathrm{H_2}$), 25.3 (virtual t, $J_{\mathrm{CP}} = 12.6$ Hz, $C\mathrm{H_2}$), 24.2 (s, $C\mathrm{H_2}$); ^{31}P{^{1}H} 20.2 (d, $J_{\mathrm{RhP}} = 117.4$ Hz).

IR (cm^{-1}, powder film): 2926 (s), 2853 (m), 1949 (s, ν_{CO}), 1459 (w), 1262 (w), 1089 (w), 1023 (w), 799 (w), 726 (w). MS:[6] 816 ([**M** – 1]$^+$, 20%), 789 ([**M** – CO]$^+$, 95%), 781 ([**M** – Cl]$^+$, 100%), 747 (90%).

***trans*-Rh(CO)(I)(P(CH$_2$)$_{14}$)$_3$P) (4). A.** An NMR tube was charged with **3** (0.020 g, 0.025 mmol), NaI (0.015 g, 0.10 mmol), and CD_2Cl_2 (0.8 mL). The mixture was vigorously stirred for 8 h under N_2, and filtered to remove a white solid. The solvent was removed from the filtrate by oil pump vacuum to give **4** as a yellow oil (0.022 g, 0.024 mmol, >95%). The oil was dissolved in CD_2Cl_2 and the solution was layered with MeOH. After one week, the yellow crystals of **4** were isolated by filtration (0.010 g, 0.0154 mmol, 45%). DSC ($T_i/T_e/T_p/T_c/T_f$): endotherm, 88.0/102.3/ 104.7/106.4/110.0 °C. TGA: onset of mass loss, 263.8 °C (T_e). Anal. Calcd. for $C_{43}H_{84}IOP_2Rh$: C, 56.82; H, 9.32. Found: C, 56.13; H, 9.87.[7] **B**. Complex **6** was prepared in an NMR tube as described below. Then N_2 was aspirated through the sample for 1 h. A ^{31}P NMR spectrum showed complete conversion to **4**. Then CO was aspirated through the sample for 1 h. A ^{31}P NMR spectrum showed ≥98% conversion to **6**.

NMR (δ, CD_2Cl_2): ^{1}H 1.96-1.94 (m, 12H, $\mathrm{C}H_2$), 1.62-1.61 (m, 12H, $\mathrm{C}H_2$), 1.45-1.41 (m, 12H, $\mathrm{C}H_2$), 1.32-1.29 (m, 48H, $\mathrm{C}H_2$); ^{13}C{^{1}H} 186.5 (dt, J_{CRh} = 75.0 Hz, J_{CP} = 15.0 Hz, $C\mathrm{O}$), 30.7 (virtual t,[4] J_{CP} = 6.5 Hz, $C\mathrm{H}_2$), 28.4 (s, $C\mathrm{H}_2$), 28.0 (virtual t, J_{CP} = 13.5 Hz, $C\mathrm{H}_2$), 27.9 (s, $C\mathrm{H}_2$), 27.6 (s, $C\mathrm{H}_2$), 27.5(s, $C\mathrm{H}_2$), 24.7 (s, $C\mathrm{H}_2$); ^{31}P{^{1}H} 15.8 (d, J_{RhP} = 113.0 Hz).

IR (cm^{-1}, powder film): 2926 (s), 2853 (m), 1949 (s, ν_{CO}), 1459 (w), 1262 (w), 1089 (w), 1046 (w), 780 (w), 718 (w). MS:[6] 910 ([**M** + 1]$^+$, 35%), 880 ([**M** – CO + 1]$^+$, 90%), 781 ([**M** – I]$^+$, 100%), 747 (90%).

***trans*-Rh(CO)$_2$(I)(P((CH$_2$)$_{14}$)$_3$P) (6).** A NMR tube was charged with **3** (0.020 g, 0.025 mmol), NaI (0.015 mg, 0.1 mmol), and CD_2Cl_2 (0.8 mL), and fitted with a septum. The tube was purged with CO, and stirred for 4 h under a balloon pressure of CO. NMR spectra were periodically recorded. After conversion was complete, the sample was filtered under CO to remove a white solid. The filtrate was saturated with CO and layered with CO-saturated methanol. After 24 h, yellow crystals of **6** had formed, some of which were collected from the walls of the tube and immediately used for IR spectra.

NMR (δ, CD_2Cl_2, 25 °C): ^{1}H 1.96 (br m, 12H, $\mathrm{C}H_2$), 1.62 (br m, 12H, $\mathrm{C}H_2$), 1.41 (m, 12H,

CH_2), 1.34-1.30 (m, 48H, CH_2); $^{13}C\{^1H\}$ 193.0 (br signal, CO), 30.6 (virtual t,[4] J_{CP} = 6.5 Hz, CH_2), 30.0 (br m, CH_2), 28.2 (s, CH_2), 28.0 (s, CH_2), 27.2 (s, CH_2), 27.0 (br s, CH_2), 24.8 (s, CH_2); $^{31}P\{^1H\}$ 25.2 (d, J_{RhP} = 85.4 Hz). NMR (δ, CD_2Cl_2, –40 °C): ^1H 1.98 (br m, 8H, CH_2), 1.69 (br m, 4H, CH_2), 1.54 (br m, 4H, CH_2), 1.37 (m, 8H, CH_2), 1.16 (m, 60H, CH_2); $^{13}C\{^1H\}$ 192.3 (dt, J_{CRh} = 71.5 Hz, J_{CP} = 16.0 Hz, CO), 30.7 (br m, CH_2), 29.8 (virtual t,[4] J_{CP} = 5.6 Hz, CH_2),[8] 29.3 (virtual t, J_{CP} = 15.6 Hz, CH_2),[8] 28.3 (virtual t, J_{CP} = 15.6 Hz, CH_2), 27.6 (s, CH_2),[8] 27.4 (s, CH_2), 27.2 (s, 2CH_2),[9] 26.1 (s, CH_2),[8] 26.0 (s, CH_2),[8] 25.9 (s, CH_2), 24.9 (s, CH_2), 24.2 (s, CH_2), 24.0 (s, CH_2); $^{31}P\{^1H\}$ 26.2 (d, J_{RhP} = 85.0 Hz). NMR (δ, CD_2Cl_2, –70 °C): ^1H 2.00 (br m, 8H, CH_2), 1.72 (br m, 4H, CH_2), 1.57 (br m, 4H, CH_2), 1.40 (m, 8H, CH_2), 1.14 (m, 60H, CH_2); $^{13}C\{^1H\}$[5] 30.6 (br m, CH_2), 29.4 (br m, CH_2),[8] 28.5 (virtual t,[4] J_{CP} = 16.1 Hz, CH_2),[8] 27.9 (virtual t, J_{CP} = 16.1 Hz, CH_2), 27.3 (s, CH_2), 27.1 (s, CH_2),[8] 26.9 (s, CH_2), 26.8 (s, CH_2),[8] 25.5 (s, CH_2),[8] 25.3 (s, CH_2), 25.2 (s, CH_2),[8] 24.8 (s, CH_2), 23.7 (s, CH_2),[8] 23.2 (s, CH_2); $^{31}P\{^1H\}$ 25.8 (d, J_{RhP} = 85.2 Hz).

IR (cm^{-1}, powder film): 2926 (s), 2853 (m), 1988 (m, ν_{CO}), 1930 (s, ν_{CO}), 1459 (m), 718 (m).

***trans*-Rh(CO)(NCS)[P((CH_2)$_{14}$)$_3$P] (5).** A Schlenk tube was charged with **3** (0.050 g, 0.060 mmol), KSCN (0.030 g, 0.30 mmol), and acetone (5 mL). The mixture was stirred for 0.5 h, and filtered through a Celite plug over sintered glass. Most of acetone was removed from the filtrate by oil pump vacuum. The sample was cooled to –20 °C and layered with methanol (2 mL). After 24 h, the precipitate was isolated by filtration, washed with methanol, and dried by oil pump vacuum to give **5** as a yellow powder (0.0368 g, 0.044 mmol, 73%). DSC ($T_i/T_e/T_p/T_c/T_f$): endotherm, 62.3/86.2/92.6/95.6/102.9 °C; exotherm, 191.0/215.3/232.6/246.6/259.5 °C. TGA: onset of mass loss, 176.4 °C (T_e). Anal. Calcd. for $C_{44}H_{84}NOP_2SRh$: C, 62.91; H, 10.08, N, 1.67; S, 3.82. Found: C, 62.66; H, 9.91; N, 1.48; S, 3.13.

NMR (δ, toluene-d_8) ^1H 1.90-1.60 (m, 12H, PCH_2), 1.55-1.25 (m, 72H, CH_2); $^{13}C\{^1H\}$[10] 31.3 (virtual t, J_{CP} = 6.5 Hz, CH_2), 30.4 (virtual t,[4] J_{CP} = 6.5 Hz, CH_2), 28.6 (s, CH_2), 28.3 (s, CH_2),[8] 28.2 (s, 2CH_2),[9] 27.7 (s, CH_2), 27.6 (s, CH_2), 27.5 (s, CH_2),[8] 27.1 (virtual t, J_{CP} = 12.7 Hz, CH_2), 26.9 (s, CH_2),[8] 26.8 (virtual t, J_{CP} = 12.7 Hz, CH_2),[8] 25.5 (s, CH_2),[8] 24.0 (s, CH_2); $^{31}P\{^1H\}$ 21.0 (d, J_{RhP} = 115.4 Hz).

IR (cm^{-1}, powder film): 2926 (s), 2853 (s), 2084 (vs, ν_{NCS}), 1953 (vs, ν_{CO}), 1459 (s), 1262 (m), 1092 (s), 1015 (s). MS:[6] 841 ([**M** + 2]$^+$, 49%), 811 ([**M** – CO]$^+$, 28%), 781 ([**M** – NCS]$^+$, 30%), 747 (15%), 136 (100%).

***trans*-Rh(CO)(Cl)(Br)(CCl$_3$)[P((CH$_2$)$_{14}$)$_3$P] (7).** An NMR tube was charged with **3** (0.049 g, 0.067 mmol), $CBrCl_3$ (0.034 mL, 0.34 mmol), and benzene-d_6 (1.0 mL). The mixture was stirred for 1 h. The volatiles were removed by oil pump vacuum and the residue was washed with methanol to give **7** as a pale yellow solid (0.066 g, 0.065 mol, 97%). DSC: no phase transition below 102.5 °C. TGA: onset of mass loss, 102.5 °C (T_e). Anal. Calcd. for $C_{44}H_{84}BrCl_4OP_2Rh$: C, 52.04; H, 8.28. Found: C, 52.01; H, 8.07.

NMR (δ, C_6D_6) ^{1}H 3.10 -2.90 (br m, 2H, CH_2), 2.80-2.60 (br m, 2H, CH_2), 2.50-2.35 (br m, 4H, CH_2), 2.30-1.95 (br m, 6H, CH_2), 1.85-1.65 (br m, 2H, CH_2), 1.73-1.31 (m, 68H, CH_2); $^{13}C\{^1H\}$ 183.0 (dt, J_{RhC} = 62.0 Hz, J_{CP} = 6.9 Hz, *C*O), 87.9 (dt, J_{RhC} = 46.6 Hz, J_{PC} = 4.0 Hz, *C*Cl$_3$), 30.9 (virtual t,[4] J_{CP} = 6.3 Hz, *C*H$_2$), 30.49 (virtual t, J_{CP} = 4.1 Hz, *C*H$_2$), 30.43 (virtual t, J_{CP} = 6.4 Hz, *C*H$_2$), 30.0 (s, *C*H$_2$), 29.8 (s, *C*H$_2$), 29.2 (s, *C*H$_2$), 29.1 (s, *C*H$_2$), 29.0 (s, *C*H$_2$), 28.9 (s, *C*H$_2$), 28.7 (s, *C*H$_2$), 28.4 (s, *C*H$_2$), 28.3 (s, *C*H$_2$), 28.2 (s, *C*H$_2$), 27.8 (s, *C*H$_2$), 27.2 (s, *C*H$_2$), 26.0 (virtual t, J_{CP} = 12.8 Hz, *C*H$_2$), 25.2 (virtual t, J_{CP} = 15.6 Hz, *C*H$_2$), 23.9 (s, *C*H$_2$), 23.6 (s, *C*H$_2$), 23.3 (s, *C*H$_2$), 22.8 (virtual t, J_{CP} = 12.6 Hz, *C*H$_2$); $^{31}P\{^1H\}$ 15.6 (d, J_{RhP} = 83.3 Hz). NMR (toluene-d_8) $^{13}C\{^1H\}$ 183.0 (d,[11] J_{RhC} = 62.0 Hz, CO), 87.9 (dt, J_{RhC} = 46.7 Hz, J_{PC} = 4.3 Hz, CCl$_3$), 30.8 (virtual t,[4] J_{CP} = 6.0 Hz, *C*H$_2$), 30.4 (virtual t, J_{CP} = 5.1 Hz, *C*H$_2$), 30.1 (virtual t, J_{CP} = 5.0 Hz, *C*H$_2$), 29.8 (s, *C*H$_2$), 29.7 (s, *C*H$_2$), 29.11 (s, *C*H$_2$), 29.05 (s, *C*H$_2$), 28.97 (s, *C*H$_2$), 28.8 (s, *C*H$_2$), 28.4 (s, *C*H$_2$), 28.3 (s, *C*H$_2$), 28.2 (s, *C*H$_2$), 28.1 (s, *C*H$_2$), 27.6 (s, *C*H$_2$), 27.1 (s, *C*H$_2$), 25.9 (virtual t, J_{CP} = 12.8 Hz, *C*H$_2$), 25.1 (virtual t, J_{CP} = 15.5 Hz, *C*H$_2$), 23.8 (s, *C*H$_2$), 23.5 (s, *C*H$_2$), 23.2 (s, *C*H$_2$), 22.6 (virtual t, J_{CP} = 12.8 Hz, *C*H$_2$).

IR (cm^{-1}, powder film): 2922 (s), 2853 (s), 2069 (vs, ν_{CO}), 1459 (s), 1262 (m), 1089 (s), 1019 (s), 772 (s), 722 (vs). MS:[6] 951 ([**M** – CO – Cl]$^+$, 28%), 907 ([**M** – CO – Br]$^+$, 30%), 869 ([**M** – CO – CCl$_3$]$^+$ 78%), 823 (100%).

Crystallography. An NMR tube was charged under N_2 with a solution of **4** (0.010 g) in benzene/CH_2Cl_2 (1:1 v/v; 0.2 mL), and layered methanol (2.0 mL). After two weeks, the yellow prisms were taken directly to a Nonius KappaCCD area detector for data collection as outlined in

Table 1. Cell parameters were obtained from 10 frames using a 10° scan and refined with 10410 reflections. Lorentz, polarization, and absorption corrections[12] were applied. The space group was determined from systematic absences and subsequent least-squares refinement. The structure was solved by direct methods. The parameters were refined with all data by full-matrix-least-squares on F^2 using SHELXL-97.[13] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. Scattering factors were taken from literature.[14] The I-Rh-CO moiety was disordered, with two orientations differing by ca. 180°. The iodine atoms refined to a 89:11 occupancy ratio (I1/I1'), but the CO associated with the minor rotamer (coincident with the iodine of the major rotamer) could not be resolved. The atom C54 was also disordered, and could be refined to a 65:35 occupancy ratio (C54/C54'). The anisotropic displacement parameters of neighboring atoms (e.g., C55, C56) indicated further disorder that could not be resolved.

Table 1. Summary of crystallographic data for **4**

Empirical formula	$C_{43}H_{84}IOP_2Rh$	
Formula weight	908.85	
Temperature of Collection	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.4154(4) Å	α= 90°
	b = 12.3194(3) Å	β= 109.066(1)°
	c = 34.0731(8) Å	γ = 90°
Volume	9289.7(4) $Å^3$	
Z	8	
Density (calculated)	1.300 Mg/m^3	
Absorption coefficient	1.130 mm^{-1}	
F(000)	3824	
Crystal size	0.20 × 0.20 × 0.10 mm^3	
Θ range for data collection	1.26 to 27.49°	
Range/indices (*h,k,l*)	–30;30, –15;15, –44;44	
Reflections collected	18326	
Independent reflections	10641 [R(int) = 0.0562]	
Reflections [$I>2\sigma(I)$]	5767	
Completeness to Θ = 27.49°	99.8%	
Absorption correction	Empirical (Scalepack)	
Max. and min. transmission	0.8954 and 0.8056	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10641 / 3 / 447	
Goodness-of-fit on F^2	0.947	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0494, wR_2 = 0.1051	
R indices (all data)	R_1 = 0.1181, wR_2 = 0.1433	
Largest diff. peak and hole	0.711 and –00.647 $eÅ^{-3}$	

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[4] Hersh, W. H. *J. Chem. Educ.* **1997**, *74*, 1485. The J values given represent the apparent coupling between adjacent peaks of the triplet.

[5] The *C*O signal was not observed.

[6] FAB, 3-NBA, *m*/*z* (relative intensity, %); the most intense peak of isotope envelope is given.

[7] Although a few compounds did not give satisfactory microanalyses, the best available data are given.

[8] These signals were more intense than the others (ca. 2:1).

[9] The signal represents two overlapping carbons of the unique bridge.

[10] The *C*O and N*C*S signals were not observed.

[11] The J_{PC} coupling was not observed.

[12] (a) "Collect" data collection software, Nonius B.V., 1998. (b) "Scalepack" data processing software: Otwinowski, Z.; Minor, W. in *Methods in Enzymology* **1997**, *276* (Macromolecular Crystallography, Part A), 307.

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Fig. S2 Variable temperature ^{13}C NMR spectra of **6** in CD_2Cl_2 under CO (1 atm); observed and simulated $PCH_2\boldsymbol{C}H_2$ signals (the peak * is from another CH_2 group).