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# Synthesis and Reactions of Palladium and Platinum Complexes Bearing Diphosphinidenecyclobutene Ligands. A Thermally Stable Catalyst for Ethylene Polymerization

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## Experimental Section

**General Procedure and Materials.** All manipulations were carried out under a nitrogen atmosphere using conventional Schlenk techniques. Nitrogen gas was dried by passing through $P_2O_5$ (Merck, SICAPENT). NMR spectra were recorded on JEOL JNM-A400 and Varian Mercury 300 spectrometers. Chemical shifts are reported in $\delta$ (ppm), referred to $^1H$ (of residual protons) and $^{13}C$ signals of the deuterated solvents or to the $^{31}P$ signal of an external 85% $H_3PO_4$ standard. GPC analysis was performed on a Waters 150C syetem using polyethylene standards (1,2,4-trichlorobenzene, 145 °C). $Et_2O$ and pentane were dried over sodium benzophenone ketyl and distilled prior to use. $CH_2Cl_2$ and $CH_3CN$ were dried over $CaH_2$ and distilled prior to use. $CD_2Cl_2$ and $CDCl_3$ were purified by passing through a short $Al_2O_3$ column and stored under a nitrogen atmosphere. Diphosphinidenecyclobutene ligands,[1] [$PdMe_2$(tmeda)],[2] [$PdMe_2$(cod)],[3] [$Pt_2Me_4(SMe_2)_2$],[4] and $H(OEt_2)_2BAr_4$ (Ar = 3,5-$(CF_3)_2C_6H_3$)[5] were synthesized according to the literatures. All other compounds were obtained from commercial sources and used without further purification.

**Preparation of 1 and 4.** A typical procedure for synthesizing **1** was as follows. To a solution of [$PdMe_2$(tmeda)] (100 mg, 0.396 mmol) in $Et_2O$ (6 mL) was added the phenyl group-substituted diphosphinidene ligand (329 mg, 0.436 mmol). On stirring the mixture, an orange precipitate was gradually separated from the solution. After 12 h at room temperature, the precipitate was collected by filtration, washed with $Et_2O$ (2 mL), and dried under vacuum (333 mg, 94%), which was analytically pure without further purification. Complex **4** was prepared in almost the same procedure using $[Pt_2Me_4(SMe_2)_2]$ in place of $[PdMe_2(tmeda)]$, and isolated as red crystals suitable for single-crystal X-ray diffraction analysis in 89% yield after recrystallization from toluene.

**1:** $^1$H NMR (300 MHz, $CD_2Cl_2$, 20 °C): $\delta = 0.55$ ($A_3A'_3XX'$, 6H, PdMe), 1.44 (s, 18H, *p*-*t*Bu), 1.59 (s, 36H, *o*-*t*Bu), 6.75 (d, $J_{HH}$ = 8.5 Hz, 4H, *o*-Ph), 6.89 (t, $J_{HH}$ = 7.9 Hz, 4H, *m*-Ph), 7.11 (t, $J_{HH}$ = 7.5 Hz, 2H, *p*-Ph), 7.56 (d, $J_{PH}$ = 2.1 Hz, 4H, PAr); $^{13}C\{^1H\}$ NMR (100 MHz, $CD_2Cl_2$, 20 °C): $\delta$ = 2.2 (dd, $J_{PC}$ = 121, 8 Hz, PdMe), 31.6 (s, *p*-C*Me*$_3$), 33.6 (s, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 39.0 (s, *o*-*C*Me$_3$), 123.2 (s, *m*-PAr), 128.1 (d, $J_{PC}$ = 32 Hz, *ipso*-PAr), 128.2, 128.5 (each s, *o* or *m*-Ph), 129.4 (s, *p*-Ph), 131.5 (s, *ipso*-Ph), 151.0 (dd, $J_{PC}$ = 55, 36 Hz, P=*C*–C), 153.0 (s, *p*-PAr), 156.9 (s, *o*-PAr), 172.6 (dd, $J_{PC}$ = 26, 21 Hz, P=C–*C*); $^{31}P\{^1H\}$ NMR (121 MHz, $CD_2Cl_2$, 20 °C): $\delta$ 164.0 (s); elementary analysis calcd for $C_{54}H_{74}P_2Pd$: C 72.75, H 8.37; found: C 72.50, H 8.26.

**4:** $^1$H NMR (300 MHz, $CDCl_3$, 20 °C): $\delta = 1.06$ ($A_3A'_3XX'$, $J_{PtH}$ = 80.3 Hz, 6H, PtMe), 1.43 (s, 18H, *p*-*t*Bu), 1.62 (s, 36H, *o*-*t*Bu), 6.81 (d, $J_{HH}$ = 7.8 Hz, 4H, *o*-Ph), 6.86 (t, $J_{HH}$ = 8.0 Hz, 4H, *m*-Ph), 7.11 (t, $J_{HH}$ = 7.2 Hz, 2H, *p*-Ph), 7.57 (d, $J_{PH}$ = 1.6 Hz, 4H, PAr); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 20 °C): $\delta = -1.9$ (dd, $J_{PC}$ = 126, 9 Hz, $J_{PtC}$ = 723 Hz, PtMe), 31.5 (s, *p*-C*Me*$_3$), 33.5 (s, *o*-C*Me*$_3$), 35.4 (s, *p*-*C*Me$_3$), 38.8 (s, *o*-*C*Me$_3$), 122.8 (s, *m*-PAr), *ca.* 127 (m, the coupling pattern and exact chemical shift were obscure due to overlap with the Ph signals, *ipso*-PAr), 127.4, 128.1 (each s, *o*- or *m*-Ph), 128.6 (s, *p*-Ph), 131.8 (s, *ipso*-Ph), 147.8 (dd, $J_{PC}$ = 60, 40 Hz, P=*C*–C), 152.6 (s, *p*-PAr), 156.9 (s, *o*-PAr), 170.7 (dd, $J_{PC}$ = 36, 30 Hz, P=C–*C*); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 20 °C): $\delta = 171.6$ (s, $J_{PtP}$ = 1590 Hz); elementary analysis calcd for $C_{54}H_{74}P_2Pt$: C 66.17, H 7.61; found: C 65.64, H 7.31.

**Preparation of 2 and 3.** Complex **2** was synthesized as follows. To a solution of $[PdMe_2(cod)]$ (43.0 mg, 0.176 mmol) in $Et_2O$ (3 mL) was added the trimethylsilyl group-substituted diphosphinidene ligand (135 mg, 0.181 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 30 min. The color of the solution turned to greenish yellow, which was filtered through a short Celite column. The filtrate was concentrated to *ca.* 1 mL and cooled to –78 °C. Pentane (1mL) was slowly added with stirring, leading to the separation of a yellow precipitate, which was collected by filtration, washed with pentane (1 mL), and dried under vacuum (109 mg, 70%). Complex **3** was similarly prepared in 60% isolated yield. Complex **2** could be synthesized from [$PdMe_2$(tmeda)] instead of [$PdMe_2$(cod)] in 63% yield, while an elongated reaction time (17 h) was needed. Attempts for recrystallization of **2** and **3** from toluene or dichloromethane were unsuccessful due to partial decomposition.

**2:** $^1H$ NMR (300 MHz, $CD_2Cl_2$, 20 °C): $\delta = -0.28$ (s, 18H, $SiMe_3$), 0.38 ($A_3A'_3XX'$, 6H, PdMe), 1.34 (s, 18H, *p-t*Bu), 1.64 (s, 36H, *o-t*Bu), 7.54 (s, 4H, PAr); $^{13}C\{^1H\}$ NMR (100 MHz, $CD_2Cl_2$, 20 °C): $\delta$ –0.42 (s, $SiMe_3$), 2.45 (dd, $J_{PC}$ = 119, 7 Hz, PdMe), 31.2 (s, *p*-C*Me*$_3$), 33.7 (s, *o*-C*Me*$_3$), 35.5 (s, *p*-*C*Me$_3$), 39.0 (s, *o*-*C*Me$_3$), 123.4 (s, *m*-PAr), 127.8 (d, $J_{PC}$ = 30 Hz, *ipso*-PAr), 152.7 (s, *p*-PAr), 156.4 (s, *o*-PAr), 173.3 (dd, $J_{PC}$ = 46, 31 Hz, P=*C*–C), 178.3 (dd, $J_{PC}$ = 23, 15 Hz, P=C–*C*); $^{31}P\{^1H\}$ NMR (121 MHz, $CD_2Cl_2$, 20 °C): $\delta$ = 170.8 (s); elementary analysis calcd for $C_{48}H_{82}P_2Si_2Pd$: C 65.24, H 9.35; found: C 64.89, H 8.87.

**3:** $^1H$ NMR (300 MHz, $CD_2Cl_2$, –20 °C): $\delta = 0.47$ ($A_3A'_3XX'$, 6H, PdMe), 1.32 (s, 18H, *p-t*Bu), 1.58 (s, 36H, *o-t*Bu), 6.75 (pseudo t, $J_{PH}$ = 2.7 Hz, 2H, P=C–C*H*), 7.49 (d, $J_{PH}$ = 1.8 Hz, 4H, PAr); $^{13}C\{^1H\}$ NMR (100 MHz, $CD_2Cl_2$, –20 °C): $\delta$ = 1.2 (dd, $J_{PC}$ = 118, 10 Hz, PdMe), 31.0 (s, *p*-C*Me*$_3$), 33.0 (s, *o*-C*Me*$_3$), 35.2 (s, *p*-*C*Me$_3$), 38.3 (s, *o*-*C*Me$_3$), 122.3 (s, *m*-PAr), 126.3 (d, $J_{PC}$ = 28 Hz, *ipso*-PAr), 144.7 (dd, $J_{PC}$ = 52, 35 Hz, P=*C*–C), 152.0 (s, *p*-PAr), 156.2 (s, *o*-PAr), 174.7 (dd, $J_{PC}$ = 25 Hz, P=C–*C*); $^{31}P\{^1H\}$ NMR (121 MHz, $CD_2Cl_2$, –20 °C): $\delta$ 165.8 (s); elementary analysis calcd for $C_{42}H_{66}P_2Pd$: C 68.23, H 8.99; found: C 67.87, H 8.42.

**Ethylene Polymerization** (run 1, Table 1). Complex **1** (9.31 mg, 10.4 μmol) and $H(OEt_2)_2BAr_4$ (10.7 mg, 10.6 μmol) were placed in a Schlenk tube, and dissolved in chlorobenzene (5 mL) at room temperature. The solution was transferred by cannulation into a 150 mL pressure bottle and diluted with chlorobenzene (15 mL). Ethylene gas was charged and the mixture was mechanically stirred at 60 °C for 1 h under a constant pressure (10 kgf $cm^{-2}$). The mixture was poured into MeOH (80 mL), and the resulting precipitate was collected by filtration and dried under vacuum to give a white solid of polyethylene (0.90 g). $^1$H NMR (400 MHz, 1,2,4-trichlorobenzene/$C_6D_6$, 130 °C): δ = 0.90 (m, C*H*$_3$, 2% of total H), 1.33 (C*H*$_2$, 95% of total H), 2.01 (m, allylic H, 1% of total H), 4.94 (m, terminal vinyl H), 5.40 (m, internal vinyl H), 5.78 (m, terminal vinyl H); $^{13}$C{$^1$H} NMR (100 MHz, 1,2,4-trichlorobenzene/$C_6D_6$, 130 °C): δ = 14.1 (s, *C*H$_3$), 30.0 (s, *C*H$_2$), 32.8, 33.9 (each s, allylic C).

**Reaction of 1 and H(OEt$_2$)$_2$BAr$_4$.** Complex **1** (13.6 mg, 15.3 μmol) and H(OEt$_2$)$_2$BAr$_4$ (15.5 mg, 15.3 μmol) were placed in an NMR sample tube equipped with a rubber septum cap, and the system was replaced with argon gas at room temperature. $CD_2Cl_2$ (0.7 mL) was added at 0 °C, and the contents were dissolved at this temperature. The sample was examined by NMR spectroscopy at 20 °C, showing the formation of monomethylpalladium complex **5**.

**5:** $^1$H NMR (300 MHz, $CD_2Cl_2$, 20 °C): δ = 1.24 (br, 12H, OEt$_2$), *ca.* 1.4 (m, the coupling pattern and exact chemical shift were obscure due to overlap with the *t*-Bu signals, PdMe), 1.43, 1.45, 1.61, 1.61, 1.63, 1.64 (each s, each 9H, *t*-Bu), 3.57 (br, 8H, OEt$_2$), 6.78 (d, $J_{HH}$ = 7.8 Hz, 2H, *o*-Ph), 6.83 (d, $J_{HH}$ = 8.1 Hz, 2H, *o*-Ph), 6.97 (t, $J_{HH}$ = 7.8 Hz, 2H, *m*-Ph), 6.98 (t, $J_{HH}$ = 8.1 Hz, 2H, *m*-Ph), 7.25 (t, $J_{HH}$ = 7.5 Hz, 2H, *p*-Ph), 7.57 (s, 4H, *p*-BAr), 7.61 (d, $J_{PH}$ = 2.7 Hz, 2H, PAr), 7.73 (d, $J_{PH}$ = 4.2 Hz, 2H, PAr), 7.74 (s, 8H, *o*-BAr); $^{31}$P{$^1$H} NMR (121 MHz, $CD_2Cl_2$, 20 °C): δ = 126.6, 157.7 (each br).

Complex **5** thus formed gradually decomposed in solution. However, in the presence of added $CH_3CN$ (3 molar amounts) or in neat $Et_2O$, this complex was stable for a few days. The acetonitrile adduct of **5** could be isolated as described below.

**Preparation of 5·(MeCN).** To a suspension of **1** (84.3 mg, 0.0946 mmol) in $CH_2Cl_2$ (3 mL) was added a $CH_2Cl_2$ (2 mL) solution of H(OEt$_2$)$_2$BAr$_4$ (95.8 mg, 0.0946 mmol) at 0 °C. The mixture instantly turned into an orange solution. $CH_3CN$ (25 μL, 0.48 mmol) was then added, and the solution was stirred at room temperature for 30 min. The solution was filtered and the solvent was removed by pumping, giving a brown solid (159 mg, 94%).

**5·(MeCN):** $^1$H NMR (300 MHz, $CD_2Cl_2$, 20 °C): δ = 1.39 (dd, $J_{PH}$ = 9.3, 3.3 Hz, 3H, PdMe), 1.44, 1.45, 1.59, 1.60, 1.60, 1.61 (each s, each 9H, *t*Bu), 2.30 (s, 3H, MeCN), 6.78 (d,

$J_{HH}$ = 7.8 Hz, 2H, *o*-Ph), 6.84 (d, $J_{HH}$ = 8.1 Hz, 2H, *o*-Ph), 6.97 (t, $J_{HH}$ = 8.1 Hz, 2H, *m*-Ph), 6.98 (t, $J_{HH}$ = 7.8 Hz, 2H, *m*-Ph), 7.24 (t, $J_{HH}$ = 7.8 Hz, 2H, *p*-Ph), 7.57 (s, 4H, *p*-BAr), 7.61 (d, $J_{PH}$ = 2.7 Hz, 2H, PAr), 7.71 (d, $J_{PH}$ = 4.2 Hz, 2H, PAr), 7.73 (s, 8H, *o*-BAr); $^{13}C\{^1H\}$ NMR (75 MHz, $CD_2Cl_2$, 20 °C): δ = 3.4 (s, *Me*CN), 14.5 (dd, $J_{PC}$ = 94, 3 Hz, PdMe), 31.3, 31.5, 33.8, 33.8, 34.1, 34.1 (each s, C*Me*$_3$), 35.8, 36.0, 38.7, 38.7, 39.8, 39.9 (each s, *C*Me$_3$), 117.8 (septets, $J_{FC}$ = 4 Hz, *p*-BAr), 120.7 (d, $J_{PC}$ = 23 Hz, *ipso*-PAr), 122.7 (s, N*C*Me), 125.9 (d, $J_{PC}$ = 23 Hz, *ipso*-PAr), 123.6, 123.6, 124.9, 125.0 (each s, *m*-PAr), 125.0 (q, $J_{FC}$ = 273 Hz, $CF_3$), 128.4, 128.4, 128.4, 128.5, 129.0, 129.0, 129.0, 129.1 (each s, *o* or *m*-Ph), 129.6 (q, $J_{FC}$ = 32 Hz, *m*-BAr), 131.4, 131.5 (s, *ipso*-Ph), 131.5 (s, *p*-Ph), 135.2 (s, *o*-BAr), 153.6 (dd, $J_{PC}$ = 57, 34 Hz, P=*C*–C), 154.9 (dd, $J_{PC}$ = 53, 31 Hz, P=C–*C*), 155.1, 156.4 (each s, *p*-PAr), 157.5 (s, *o*-PAr), 162.1 (q, $J_{BC}$ = 50 Hz, *ipso*-BAr), 170.7 (dd, $J_{PC}$ = 28, 13 Hz, P=C–*C*), 171.5 (dd, $J_{PC}$ = 58, 35 Hz, P=*C*–C); $^{31}P\{^1H\}$ NMR (121 MHz, $CD_2Cl_2$, 20 °C): δ = 133.6, 159.9 (each d, $J_{PP}$ = 30 Hz); elementary analysis calcd for $C_{87}H_{86}BF_{24}NP_2Pd$: C 58.68; H 4.87; N 0.79. found: C 58.25; H 4.75; N, 0.73.

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