SUPPLEMENTARY INFORMATION for:

(κ^2-*P*,*S*)Pt(benzyl) Complexes Derived from 1/3-P^{i}Pr$_2$-2-S^{t}Bu-Indene: Facile Synthesis of Carbanion- and Borate-Containing Zwitterions

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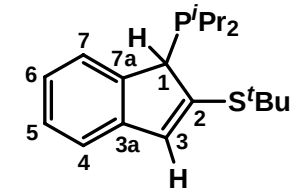
Contents:

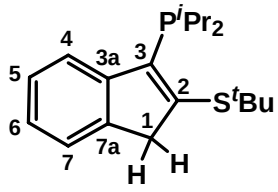
Experimental Section

General Considerations. All manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 ºC) and evacuated while hot prior to use. Celite® (Aldrich) was oven-dried for 5 d and then evacuated for 24 h prior to use. The non-deuterated solvents tetrahydrofuran, diethyl ether, dichloromethane, benzene, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system purchased from mBraun Inc. Tetrahydrofuran, diethyl ether and dichloromethane were purified over two alumina-packed columns, while benzene and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. $CDCl_3$ (Aldrich) was degassed by using three repeated freeze-pump-thaw cycles, dried over CaH_2 for 7 days, distilled in vacuo, and stored over 4 Å molecular sieves for 24 h prior to use. Benzene-d_6, methylene chloride-d_2 and toluene-d_8 (Cambridge Isotopes) were degassed by using three repeated freeze-pump-thaw cycles and then dried over 4 Å molecular sieves for 24 h prior to use. All solvents used within the glovebox were stored over activated 4 Å molecular sieves. 2-*tert*-Butylthioindene,[S1] (COD)Pt(η^1-benzyl)Cl (COD = η^4-1,5-cyclooctadiene),[S2] and $H(OEt_2)_2B(C_6F_5)_4$[S3] were prepared by using literature procedures, and were dried *in vacuo* for 24 h prior to use. $NaN(SiMe_3)_2$ (Aldrich) and $B(C_6F_5)_3$ (Boulder Scientific) were dried in vacuo for 24 h prior to use. All other reagents were obtained from Aldrich and were used as received. Variable-temperature NMR experiments were conducted on a Bruker AC-250 spectrometer. Otherwise, ^1H, ^{13}C, ^{29}Si, ^{11}B and ^{31}P NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, 99.4, 160.5 and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^1H, ^{13}C, and ^{29}Si), 85% H_3PO_4 in D_2O (for ^{31}P), or BF_3 in diethyl ether (for ^{11}B). ^1H and ^{13}C NMR chemical shift assignments are given on the basis of data obtained from ^{13}C-DEPT, ^1H-^1H COSY, ^1H-^{13}C HSQC,

and ^{1}H-^{13}C HMBC NMR experiments. In some cases slightly fewer than expected independent ^{1}H or ^{13}C NMR resonances were observed (despite prolonged data acquisition times), and ^{13}C NMR resonances associated with $B(C_6F_5)_4^-$ were not assigned. ^{29}Si NMR chemical shift assignments are given on the basis of data obtained from ^{1}H-^{29}Si HMQC NMR experiments. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada.



1-P^{i}Pr$_2$-2-S^{t}Bu-indene

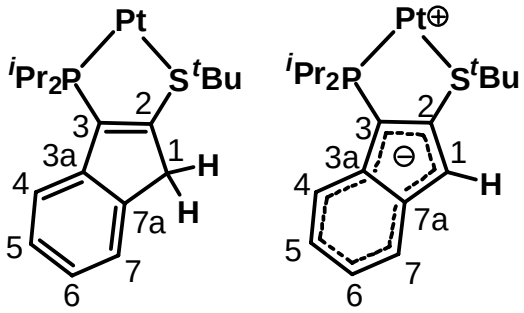


3-P^{i}Pr$_2$-2-S^{t}Bu-indene

Synthesis of 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene. A Schlenk tube containing 2-*tert*-butylthioindene (6.10 g, 29.9 mmol) in diethyl ether (10 mL) was cooled to -78 ^{o}C, followed by initiation of magnetic stirring and dropwise addition of a 2.9 M solution of *n*-BuLi in hexanes (10.3 mL, 29.9 mmol). The resulting solution was left to stir and warm to ambient temperature. After 3 h, the reaction mixture was cooled to -78 ^{o}C with subsequent addition of ^{i}Pr$_2$PCl (4.7 mL, 29.9 mmol) which effected the precipitation of a white solid. The reaction mixture was left to stir and warm to ambient temperature over 16 h, followed by filtration by use of a Schlenk filter stick to remove the white precipitate. The solvent and other volatile materials were removed *in vacuo*, affording 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene (the isomeric ratio can vary from 1:10 to 10:1 on the basis of NMR data) as an analytically pure, light brown oil (8.33 g, 26.0 mmol, 87%). Anal. Calcd for $C_{19}H_{29}PS$: C 71.21; H 9.12; N 0.00. Found: C 71.09; H 9.15; N <0.3. **3-P^{i}Pr$_2$-2-S^{t}Bu-indene**: ^{1}H NMR (C_6D_6): δ 7.72 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, C4-H or C7-H), 7.26-7.19 (m, 2H, Ar-H), 7.11 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, C5-H or C6-H), 3.58 (s, 2H, C1(H)$_2$), 2.62 (m, 2H, P(C*H*Me$_a$Me$_b$)), 1.20 (s, 9H, C(C*H*$_3$)$_3$), 1.22 (d of d, $^{3}J_{PH}$ = 18.5 Hz, $^{3}J_{HH}$ = 7.0 Hz, 6H, P(CH*Me$_a$*Me$_b$)), 1.01 (d of d, $^{3}J_{PH}$ =12.0 Hz, $^{3}J_{HH}$ = 7.0 Hz, 6H, P(CHMe$_a$*Me$_b$*)); ^{13}C{^{1}H} NMR (C_6D_6): δ 154.1 (d, $^{2}J_{PC}$

= 24.5 Hz, C2), 147.1 (C3a or C7a), 143.7 (d, J_{PC} = 2.0 Hz, C3a or C7a), 143.2 (d, $^{1}J_{PC}$ = 25.5 Hz, C3), 126.7 (Ar-C), 124.7 (Ar-C), 123.5 (Ar-C), 121.8 (d, J_{PC} = 3.8 Hz, C4 or C7), 46.7 (d, $^{3}J_{PC}$ = 3.1 Hz, C1), 46.5 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 24.3 (d, $^{1}J_{PC}$ = 12.1 Hz, P(CHMe$_a$Me$_b$)), 22.2 (d, $^{2}J_{PC}$ = 25.4 Hz, P(CH*Me$_a$*Me$_b$)), 21.3 (d, $^{2}J_{PC}$ = 11.8 Hz, P(CHMe$_a$*Me$_b$*)); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ -4.8. **1-P^{i}Pr$_2$-2-S^{t}Bu-indene**: ^{1}H NMR (C_6D_6): δ 7.29 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, C4-H or C7-H), 7.23 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, C7-H or C4-H), 7.17 (t, $^{3}J_{HH}$ = 7.0 Hz, 1H, C5-H or C6-H), 7.08 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, C6-H or C5-H), 6.86 (s, 1H, C3-H), 4.03 (s, 1H, C1-H), 2.00 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.87 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.30 (s, 9H, C(CH_3)$_3$), 1.11-0.96 (m, 9H, P(CH*Me$_a$*Me$_b$) and P(CH*Me$_c$Me$_d$*)), 0.79 (d of d, $^{3}J_{PH}$ = 11.5 Hz, $^{3}J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)); $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 145.5 (C3a or C7a), 144.1 (d, $^{2}J_{PC}$ = 21.0 Hz, C2), 143.2 (C3a or C7a), 132.6 (C3), 125.5 (C5 or C6), 123.4 (C5 or C6), 122.8 (d, J_{PC} = 5.3 Hz, C4 or C7), 119.8 (C4 or C7), 64.8 ($C(CH_3)_3$), 51.7 (d, $^{1}J_{PC}$ = 32.2 Hz, C1), 30.3 ($C(CH_3)_3$), 21.1-19.9 (m, P(*C*H*Me$_a$*Me$_b$) and P(*C*H*Me$_c$Me$_d$*)), 19.3 (d, $^{2}J_{PC}$ = 13.5 Hz, P(CHMe$_a$*Me$_b$*)); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 21.4.

Atomic numbering scheme employed for the metal complexes (by convention, the *sp*^{3}-C on the indene unit is labeled as C1):



Synthesis of 1. A solution of 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene (0.603 g, 1.88 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a suspension of (COD)Pt(η^1-benzyl)Cl (0.819 g, 1.88 mmol) in CH_2Cl_2 (2 mL) followed by magnetic stirring for 16 h at ambient temperature. ^{31}P NMR analysis of the reaction mixture indicated the quantitative formation of **1**. The CH_2Cl_2 and other volatiles were removed *in vacuo* and the resulting solid was washed with diethyl ether (3 x 5 mL). Removal of the residual solvent afforded **1** as an analytically pure, pale yellow solid (0.832 g, 1.27 mmol, 68 %). Anal. Calcd for $C_{26}H_{36}ClPPtS$: C 48.62; H 5.65; N 0.00. Found: C 48.57; H 5.42; N < 0.3. ^{1}H NMR ($CDCl_3$): δ 7.45 (m, 1H, C4 or C7), 7.43 (m, 2H, aryl-H), 7.32 (m, 1H, C7 or C4), 7.21 (m, 2H, C5 or C6 and aryl-H), 7.04 (m, 2H, aryl-H), 6.91 (m, 1H, C6 or C5), 4.04 (s, 2H, C1(H)$_2$), 3.69 (d, $^3J_{PH}$ = 3.0 Hz with ^{195}Pt satellites $^2J_{PtH}$ = 70.0 Hz, 2H, benzyl-CH_2), 3.14 (m, 2H, P(C*H*Me$_a$Me$_b$)$_2$), 2.11 (s, 9H, C(CH_3)$_3$) , 1.73 (d of d, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 6.0 Hz, 6H, P(CH*Me*$_a$Me$_b$)$_2$), 1.69 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 8.0 Hz, 6H, P(CHMe$_a$*Me*$_b$)$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.9 (d, $^2J_{PC}$ = 13.1 Hz, C2), 149.1 (d, J_{PC} = 6.0 Hz, C3a or C7a), 148.5 (d, $^1J_{PC}$ = 44.9 Hz, C3), 147.1 (aryl-C), 139.2 (d, J_{PC} = 3.8 Hz, C7a or C3a), 130.1 (aryl-C), 127.3 (aryl-C), 126.9 (C5 or C6), 126.6 (aryl-C), 125.0 (C7 or C4), 123.5 (C6 or C5), 122.6 (C4 or C7), 57.8 (d, J_{PC} = 0.8 Hz, *C*(CH$_3$)$_3$), 43.1 (d, $^3J_{PC}$ = 9.8 Hz, C1), 32.4 (C(*C*H$_3$)$_3$), 24.8 (d, $^1J_{PC}$ = 35.3 Hz, P(*C*HMe$_a$Me$_b$)), 19.6 (d, $^2J_{PC}$ = 1.4 Hz, P(CH*Me*$_a$Me$_b$)), 19.0 (d, $^2J_{PC}$ = 1.9 Hz, P(CHMe$_a$*Me*$_b$)), 14.2 (d, $^2J_{PC}$ = 5.3 Hz, benzyl-*C*H$_2$); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 38.3 (s with ^{195}Pt satellites $^1J_{PtP}$ = 3848 Hz). Crystals suitable for X-ray crystallographic analysis were grown by vapor diffusion of pentane into a concentrated solution of **1** in benzene at ambient temperature.

Synthesis of 2. To a magnetically stirred suspension of **1** (0.510 g, 0.780 mmol) in benzene (5 mL) was added solid NaN(SiMe$_3$)$_2$ (0.157 g, 0.854 mmol). The resulting solution turned deep red and an orange precipitate formed. The mixture was magnetically stirred at ambient temperature for 16 h followed by removal of all volatiles *in vacuo*. The resulting orange solid was extracted into CH_2Cl_2 (5 mL) followed

by filtration through Celite, which afforded a deep red supernatant solution. The supernatant was evaporated to dryness *in vacuo* and the resulting solid was washed with pentane (3 x 3 mL) followed by drying *in vacuo* to afford **2** as an analytically pure, orange solid (0.316 g, 0.522 mmol, 67 %). Anal Calcd. for $C_{26}H_{35}PPtS$: C 51.54; H 5.83; N 0.00. Found: C 51.67; H 6.01; N < 0.3. The ^{1}H NMR spectrum of **2** at 300 K exhibited very broad features, possibly attributable to dynamic behavior arising due to slow inversion at sulfur as well as η^1-η^3 dynamics of the coordinated benzyl ligand.[S4,S5] Upon cooling to 273 K some diagnostic ^{1}H NMR signals associated with **2** could be assigned qualitatively; however, further cooling provided no gains in spectral resolution. ^{1}H NMR (toluene-d_8): δ 6.23 (s, C1-H), 2.69 (m, P(C*H*Me$_2$)$_2$), 2.52 (s, benzyl-C*H*$_2$), 1.02-1.26 (m, P(CH*Me*$_2$)$_2$), 0.88 (s, C(C*H*$_3$)$_3$). The ^{31}P{^{1}H} NMR resonance for **2** remained sharp between 273-300 K; ^{31}P{^{1}H} NMR (toluene-d_8): δ 55.5 (s with ^{195}Pt satellites $^{1}J_{PPt}$ = 5012 Hz).

Synthesis of 2·DMAP. A magnetically stirred suspension of **2** (0.219 g, 0.361 mmol) in THF (5 mL) was treated with solid 4-dimethylaminopyridine (DMAP; 0.044 g, 0.361 mmol). The homogeneous solution was magnetically stirred at ambient temperature for 16 h during which time an off-white precipitate formed. All solvent and other volatiles were removed *in vacuo* and the resulting off-white solid was washed with diethyl ether (4 x 2 mL). The remaining off-white solid (**2·DMAP**) was dried *in vacuo* and isolated (0.215 g, 0.296 mmol, 82 %). Anal Calcd. for $C_{33}H_{45}N_2PPtS$: C 54.44; H 6.24; N 3.85. Found: C 54.40; H 6.49; N 3.59. The ^{1}H NMR spectrum of **2·DMAP** over the temperature range of 185-300 K exhibited very broad features, possibly attributable in part to dynamic processes associated with slow inversion at sulfur. Although NMR line-shape changes were noted over this temperature range, definitive chemical shift assignments for **2·DMAP** could not be made unequivocally. The ^{31}P{^{1}H} NMR resonance for **2·DMAP** remained sharp over this temperature range; ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 24.1 (s with ^{195}Pt satellites $^{1}J_{PPt}$ = 3755 Hz). Crystals suitable for X-ray

crystallographic analysis were grown by vapor diffusion of diethyl ether into a concentrated solution of **2·DMAP** in CH_2Cl_2 at ambient temperature.

Synthesis of 2·B(C$_6$F$_5$)$_3$. To a vial containing solid $B(C_6F_5)_3$ (0.089 g, 0.173 mmol) was added a solution of **2** (0.105 g, 0.173 mmol) in benzene (2 mL). The vial was manually shaken for several minutes, affording initially a darkly colored homogeneous solution, followed by the precipitation of an off-white solid. The vial was left at ambient temperature without stirring for 1 h upon which time the supernatant was removed by using a Pasteur pipette and the precipitate was washed with pentane (4 x 1 mL). Drying of the solid *in vacuo* afforded **2·B(C$_6$F$_5$)$_3$** as an analytically pure, orange solid (0.131 g, 0.118 mmol, 68 %). Anal. Calcd for $C_{44}H_{35}BF_{15}PPtS$: C 47.26; H 3.16; N 0.00. Found: C 47.64; H 3.40; N < 0.3. Resonances observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **2·B(C$_6$F$_5$)$_3$** at 300 K were broadened modestly, thereby precluding the definitive assignment of peak multiplicities. Such broadness may possibly be attributable to the dynamic features associated with slow inversion at sulfur as well as η^1-η^3 dynamics of the coordinated benzyl ligand.[S4,S5] ^{1}H NMR (CD_2Cl_2): δ 7.83-7.52 (br m, 3H, aryl-H), 7.44-7.28 (br m, 2H, aryl-H), 7.21-7.07 (br m, 2H, aryl-H), 7.04-6.58 (br m, 2H, aryl-H), 5.53 (br s, 1H, C1-H), 3.48 (br s, 1H, benzyl-CH_aH$_b$), 3.10 (m, 1H, P(CHMe$_a$Me$_b$)), 2.79 (br s, 1H, benzyl-CH$_a$$H_b$), 2.61 (m, 1H, P(C$HMe_cMe_d$)), 1.48 (d of d, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe_cMe$_d$)), 1.37 (d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CHMe_aMe$_b$)), 1.26 (d of d, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHMe$_c$$Me_d$)), 1.07 (s, 9H, C(C$H_3$)$_3$), 0.99 (d of d, $^3J_{PH}$ = 19.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$$Me_b$)); ^{13}C{^{1}H} NMR ($CD_2Cl_2$): δ 158.0 (Ar-C), 156.9 (Ar-C), 148.7 (Ar-C), 137.3 (Ar-C), 134.3 (Ar-C), 128.3 (Ar-C), 127.1 (Ar-C), 125.5 (Ar-C), 124.1 (Ar-C), 121.2 (Ar-C), 119.3 (Ar-C), 115.4 (Ar-C), 61.2 (-C(CH$_3$)$_3$), 53.4 (C1-H), 31.2 (-C(CH_3)$_3$), 29.8 (P(CHMe$_c$Me$_d$)), 29.5 (benzyl-CH$_2$), 24.9 (P(CHMe$_a$Me$_b$)), 20.6 (P(CHMe$_c$$Me_d$)), 19.3 (P(CH$Me_cMe_d$)), 18.5 (P(CH$Me_aMe_b$)), 18.3 (P(CHMe$_a$$Me_b$)); ^{31}P{^{1}H} NMR ($CD_2Cl_2$): δ 59.6 (s with ^{195}Pt satellites $^1J_{PtP}$ =

5264 Hz); ^{11}B NMR (CD_2Cl_2): δ -11.2. Crystals of **2·B(C$_6$F$_5$)$_3$**(C_7H_8) suitable for X-ray crystallographic analysis were grown by vapor diffusion of pentane into a concentrated solution of **2·B(C$_6$F$_5$)$_3$** in toluene at ambient temperature.

Synthesis of 3. To a magnetically stirred solution of **2** (0.065 g, 0.106 mmol) in benzene (2 mL) was added solid $H(OEt_2)_2B(C_6F_5)_4$ (0.176 g, 0.213 mmol) which effected the separation of a red oil. After 2 h of magnetic stirring the benzene layer was removed by using a pipette, followed by washing of the remaining red oil with benzene (3 x 1 mL). Subsequent removal of the solvent and other volatiles *in vacuo* afforded **3** as an analytically pure, off-white solid (0.119 g, 0.093 mmol, 88 %). Anal. Calcd for $C_{50}H_{36}BF_{20}PPtS$: C 46.68; H 2.82; N 0.00. Found: C 46.55; H 3.06; N < 0.3. ^{1}H NMR ($CDCl_3$): δ 7.78-7.68 (m, 2H, aryl-H), 7.60-7.48 (m, 3H, aryl-H), 7.46-7.41 (m, 2H, aryl-H), 6.98-6.89 (m, 2H, aryl-H), 3.87 (s, 2H, C1(H)$_2$), 3.15-2.84 (m, 4H, P(C*H*Me$_a$Me$_b$)$_2$ and benzyl-C*H*$_2$), 1.40 (d of d, $^3J_{PH}$ = 19.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CH*Me*$_a$Me$_b$)$_2$), 1.18-1.10 (m, 15H, P(CHMe$_a$*Me*$_b$)$_2$ and C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.6 (Ar-C), 149.1 (Ar-C), 148.6 (Ar-C), 143.4 (Ar-C), 137.3 (Ar-C), 134.9 (Ar-C), 132.6 (Ar-C), 128.3 (Ar-C), 128.1 (Ar-C), 127.9 (Ar-C), 125.8 (Ar-C), 121.7 (Ar-C), 60.7 (*C*(CH$_3$)$_3$), 42.2 (d, $^3J_{PC}$ = 9.2 Hz, C1), 31.6 (benzyl-*C*H$_2$), 28.2 (d, $^1J_{PC}$ = 36.0 Hz, P(*C*HMe$_a$Me$_b$)$_2$), 20.0 (P(CHMe$_a$*Me*$_b$)$_2$), 19.5 (P(CH*Me*$_a$Me$_b$)$_2$), 14.3 (C(*C*H$_3$)$_3$); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 62.7 (s with ^{195}Pt satellites $^1J_{PPt}$ = 5317 Hz). Crystals suitable for X-ray crystallographic analysis were grown from slow evaporation of a concentrated diethyl ether solution of **3** at ambient temperature.

Crystallographic Solution and Refinement Details

Crystallographic Characterization of 1. Crystallographic data for **1** was obtained at 173(±2) K on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Cell parameters were initially retrieved by using the COLLECT

software (Nonius), and refined with the HKL DENZO and SCALEPACK software.[S6a] Data reduction and absorption correction (multi-scan) were also performed with the HKL DENZO and SCALEPACK software. The structures were solved by using the direct methods package in SIR-97,[S6b] and refined by use of the SHELXL97-2 program,[S7] employing full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms. Otherwise, all hydrogen atoms were added at calculated positions and refined by using a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Additional crystallographic information for **1** is provided in the deposited CIF (CCDC 687093). The ORTEP diagram of **1** featured in the manuscript was prepared by use of ORTEP-3 for Windows version 1.074.[S8]

Crystallographic Characterization of 2·DMAP, 2·B(C_6F_5)$_3$(C_7H_8), and 3. In each case, crystallographic data were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, data reduction, and absorption correction (including SAINT and SADABS) were supplied by Bruker. The structures of **2·DMAP** and **2·B(C_6F_5)$_3$**(C_7H_8) were solved by using a Patterson search/structure expansion, while **3** was solved by use of the direct methods package in SIR-97.[S6b] The structures were refined by use of the SHELXL97-2 program,[S7] employing full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms. All hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Additional crystallographic information is provided in the deposited CIFs (CCDC 687090 for

2·DMAP; CCDC 687091 for **2·B(C_6F_5)$_3$**(C_7H_8); and CCDC 687092 for **3**). The ORTEP diagrams featured in the manuscript were prepared by use of ORTEP-3 for Windows version 1.074.[S8]

References

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S2. M. Janka, G. K. Anderson and N. P. Rath, *Organometallics* 2000, **19**, 5071.

S3. P. Jutzi, C. Müller, A. Stammler and H.-G. Stammler, *Organometallics* 2000, **19**, 1442.

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