A Zwitterionic Transition-Metal Complex: Platinum−*closo*-Borate Coordination Synthesis, Structure, and DFT Calculations

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Summary: A zwitterionic platinum(IV) complex comprising a cationic transition-metal center and an anionic heteroborate cluster was synthesized and structurally characterized. On the basis of DFT calculations a dipole moment of 29.8 D was determined for this polar molecule.

Introduction

With regard to reactive cationic transition-metal complexes cation−anion interactions are of special interest. For the stabilization of these electrophilic centers, weakly coordinating anions play an important role.[1] Perfluorinated borates such as $[B(C_6F_5)_4]^-$ and cluster borates are prominent anions in these salts. An intramolecular combination of weakly coordinating anions and the reactive cation is realized in single-component catalysts.[2] A considerable amount of attention has been focused on the zwitterionic compounds of group 4 metals. These dipoles consist of a cationic transition-metal center and an anionic group in the periphery of the ligand system. The other group of zwitterionic complexes features an anionic transition-metal fragment in combination with cationic ligands. These complexes have been the subject of a very recent review article.[3]

So far, borane clusters have not been introduced in the chemistry of transition-metal zwitterions. In one part of our project we focus our work on the direct linkage of an anionic *closo*-borate at cationic transition-metal centers. Recently we have shown that the stanna-*closo*-dodecaborate dianion[4] serves as a nucleophile in reactions with transition-metal halides.[5] One charge of the stanna-*closo*-dodecaborate dianion is compensated in reaction with electrophiles, resulting in formation of monoanions of the type $[L_nM-SnB_{11}H_{11}]^-$. The remaining charge in these complexes is located on the cluster sphere. From Wade's cluster rules the substituted *closo* cluster with $2n + 2$ cluster electrons of the type $L_nM-SnB_{11}H_{11}$ has to carry one negative charge on the cluster skeleton.[6] This charge can be regarded to be chemically inert in the sense of substitution chemistry.

We have systematically studied zwitterionic *closo*-borate complexes in order to investigate their physical and chemical properties. In this paper we present the synthesis together with the structural characterization and density functional (DFT)[13] calculations of an intramolecular combination of a cationic platinum complex and an anionic stanna-*closo*-borate.

Results and Discussion

Synthesis and Characterization of the Zwitterionic Complex 5. Our strategy for the synthesis of zwitterionic complexes started with the linkage of the anionic stanna-*closo*-dodecaborate cluster and a platinum halide complex. The nucleophilic substitution (Scheme 1) is straightforward, and the resulting anionic transition-metal complex **3** was isolated as a yellow, crystalline, air-stable material in almost quantitative yield.

The second step in our reaction sequence is an oxidative addition of benzyl bromide to the platinum(II) complex (Scheme 2). After several hours of reaction time the octahedrally coordinated Pt(IV) complex was isolated in 92% yield. Crystallization from a mixture of dichloromethane and hexane resulted in orange-brown crystals of **4**. Finally the zwitterion **5** was formed by abstraction of the halide with silver tetrafluoroborate and addition of *tert*-butyl isocyanide as the neutral

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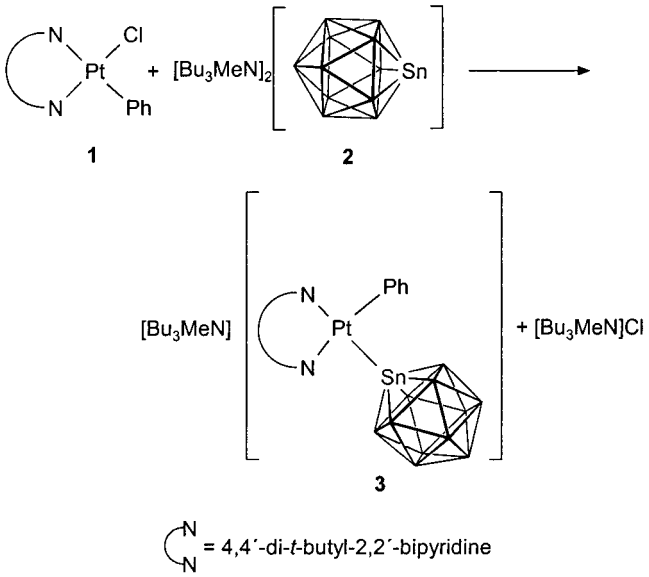
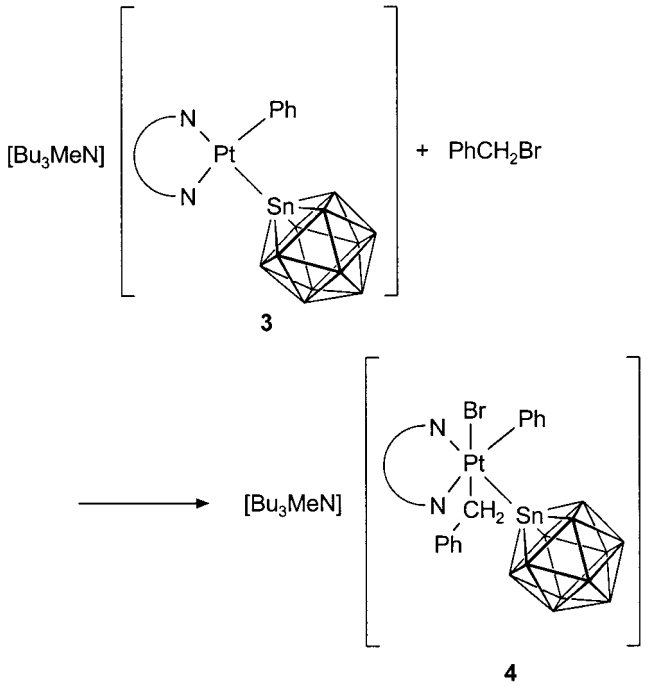
Scheme 1



Scheme 2



donor ligand (Scheme 3). The betaine is inert toward moisture and only soluble in polar solvents such as dichloromethane, acetone, and dimethyl sulfoxide. Single crystals were obtained by slow diffusion of hexane into a dichloromethane solution of the platinum complex. The zwitterion crystallizes with inclusion of 2 equiv of dichloromethane as yellow rods in the monoclinic space group $P2_1/n$. Figure 1 shows an ORTEP plot of the molecule **5**, and Table 1 summarizes selected interatomic distances and angles. The geometry around the transition metal can be described as nearly octahedral. The *closo* cluster is coordinated at the platinum center with an interatomic distance (Pt−Sn) of 2.554(1) Å. This can be compared with Pt−Sn bond lengths of coordinated $SnCl_3$ or $SnMe_3$ groups in [*trans*-$(Ph_3P)_2Pt(H)SnCl_3$] (Pt−Sn = 2.601(1) Å)[7] or [$Pt(bipy)(Me)_2(SnMe_3)I$] (Pt−Sn = 2.547(5) Å).[8] The bipyridine ligand is coordi-

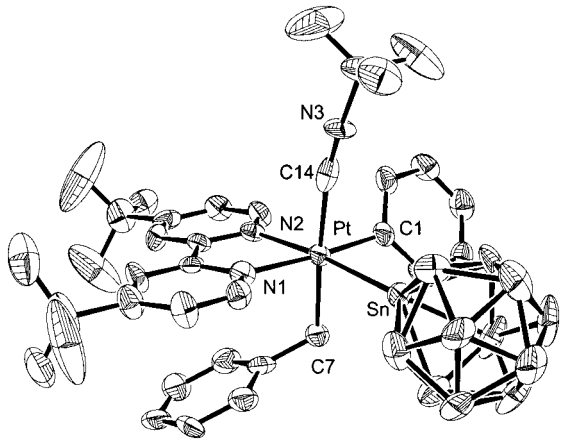


Figure 1. Structure of **5** in the crystal (PLATON representation ellipsoids at the 30% probability level).

Scheme 3

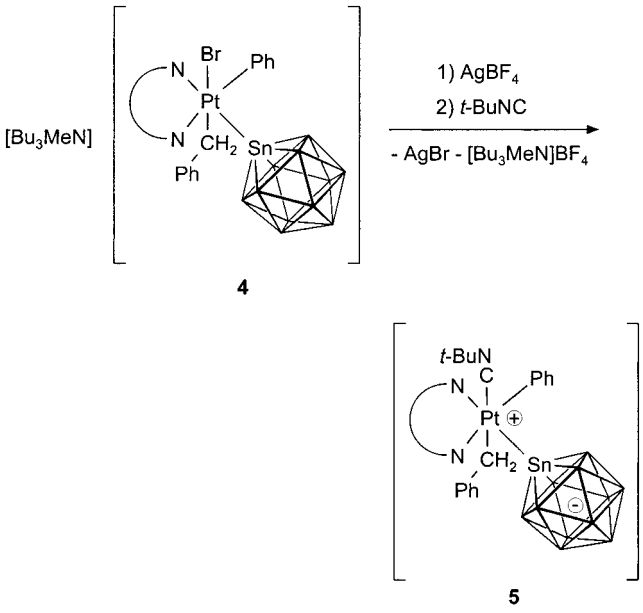


Table 1. Selected Interatomic Distances (Å) and Bond Angles (deg) for [(bipy′)Pt(Bz)(Ph)(*t*-Bu-NC)($SnB_{11}H_{11}$)] (5)

Pt−Sn	2.554(1)	C14−N3	1.164(10)
Pt−C1	2.064(8)	Sn−B1	2.309(11)
Pt−C7	2.145(8)	Sn−B2	2.316(10)
Pt−C14	2.063(9)	Sn−B3	2.332(9)
Pt−N1	2.159(7)	Sn−B4	2.286(9)
Pt−N2	2.154(6)	Sn−B5	2.272(10)
Sn−Pt−N2	174.0(2)	Sn−Pt−N1	99.3(2)
N1−Pt−C1	174.4(3)	Sn−Pt−C1	86.2(2)
C14−Pt−C7	176.5(3)	Sn−Pt−C14	88.1(2)
Sn−Pt−C7	89.3(2)	Pt−C14−N3	171.2(7)

nated at the platinum center with Pt−N distances of 2.159(7) and 2.154(6) Å. These relatively long distances are a good reflection of the fact that the phenylide and stannaborate ligands exhibit similarly large trans influences. Examples for bipyridine platinum(IV) complexes are as follows: $[Pt(bipy)Cl_4]$, Pt−N = 2.038(8), 2.044(9) Å;[9] $[Pt(Me)_2(I)(OPh)(bipy)]$, Pt−N(*trans*-Me) = 2.106(6)

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Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) for [(bipy′)Pt(Bz)(Ph)(*t*-Bu-NC)($SnB_{11}H_{11}$)] Calculated with DFT Methods[a]

Pt−Sn	2.650	C14−N3	1.177
Pt−C1	2.078	Sn−B1	2.315
Pt−C7	2.168	Sn−B2	2.330
Pt−C14	2.076	Sn−B3	2.335
Pt−N1	2.243	Sn−B4	2.320
Pt−N2	2.277	Sn−B5	2.310
Sn−Pt−N2	173.2	Sn−Pt−N1	99.9
N1−Pt−C1	172.9	Sn−Pt−C1	87.1
C14−Pt−C7	175.3	Sn−Pt−C14	85.3
Sn−Pt−C7	90.0	Pt−C14−N3	172.9

[a] The numbering of the atoms is the same as for experimentally observed compound **5**.

Å, Pt−N(*trans*-OPh) = 2.018(6) Å;[10] [Pt(bipy)(CH_2CH_2-CH_2)Cl_2], Pt−N(*trans*-alkyl) = 2.20(3) Å;[11] [Pt(bipy)-$(Me)_2(SnMe_3)I$], Pt−N(*trans*-Me) = 2.140(18) Å.[8]

DFT Calculations on Complex 5. To explain the poor solubility of **5** in most organic solvents, quantum chemical investigations were carried out by employing the program system TURBOMOLE.[12,18] The calculations were performed with DFT methods[13] that have been sufficiently proven in the past to be very suitable for the theoretical description of transition-metal-element compounds. For the simultaneous optimization of the electronic and geometric structures, the experimentally found structural data were used as starting vectors in C_1 symmetry. Relevant interatomic distances of the calculated molecule are given in Table 2. A comparison of Tables 1 and 2 shows only slight deviations of the geometry parameters for the calculated structure with regard to the distances and angles of the X-ray analysis result. All distances are calculated somewhat too large, which is typical for the employment of DFT methods that do not consider dispersion interactions explicitly. Therefore, the most noticeable differences (to a maximum of ca. 0.12 Å) are found for interactomic contacts whose binding interactions feature the most significant dispersion contributions: the Pt−Sn bond and the Pt−N donor contacts. Experimentally observed and computed angles differ by only 0.6−2.8°. By calculating the expectation value of the dipole operator in the DFT wave function (i.e. the electronic part of the dipole moment) and the electrostatic moment caused by the nuclei, a resulting dipole moment of 28.9 D was computed for the optimized structure of [(bipy′)Pt(Bz)(Ph)(*t*-Bu-NC)-($SnB_{11}H_{11}$)]. The result is in good agreement with the experimental observation of highly polar solvents being required for a solution of compound **5**. A dipole moment that was calculated for the experimental observed structure amounts to 31.4 D; this value is about 2.5 D (i.e. ca. 8%) larger than the dipole moment that is calculated for the DFT minimum structure after the geometry optimization with about ca. 4% enlarged Pt−Sn and Pt−N bonds. Although we are aware of an investigation carried out with a nonminimum structure, this could still be a hint for the development of the dipole moment. Possibly, elongation of even the weaker Pt−element bonds causes reduction of the polarity of the complex. Comparable dipole moments for zwitterions have been observed by AM1 calculations for tetraalkylammonium−aryl−borate dipoles ($Me_3N-C_6H_4-BnBu_3$, 20.0 D).[14]

Conclusion

The stanna-*closo*-dodecaborate cluster can be used as a ligand, providing the platinum complex with a negative charge. A zwitterionic molecule with a high dipole moment results after replacement of a halide anion with a neutral donor ligand.

Experimental Section

General Considerations. All manipulations were carried out under dry N_2 in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under N_2. NMR: Bruker AC 200 (^{1}H, 200 MHz, internal TMS; $^{13}C\{^1H\}$, 50 MHz, internal TMS; $^{11}B\{^1H\}$, 64 MHz, external $BF_3{\cdot}Et_2O$). Elemental analysis: Institut für Anorganische Chemie der Universität zu Köln, Heraeus C,H,N,O-Rapid elemental analyzer. (bipy′)Pt(Cl)(Ph) (bipy′ = 4,4′-di-*tert*-butyl-2,2′-bipyridine) was prepared by the method reported in the literature.[15]

[(bipy′)Pt(Ph)($SnB_{11}H_{11}$)][Bu_3NMe] (3). At room temperature 0.52 g (M_r = 576.05 g/mol, 0.90 mmol) of (bipy′)Pt(Cl)-Ph dissolved in 20 mL of CH_2Cl_2 was treated with a solution of 0.58 g (M_r = 649.48, 0.90 mmol) of $[Bu_3NMe]_2[SnB_{11}H_{11}]$[4b] in 20 mL of CH_2Cl_2. After the mixture was stirred for 24 h, the solvent was removed in vacuo and the residue was washed with 60 mL of water to remove [Bu_3NMe]Cl. The remaining yellow product was isolated by filtration, dried in vacuo, and recrystallized from CH_2Cl_2 by slow diffusion of hexane at +8 °C to give 0.78 g (88% yield) of **3**. ^{1}H NMR (CD_2Cl_2): δ 0.98 (t, 9H, ^3J = 7.2 Hz, $-CH_2CH_3$), 1.37−1.46 (m, 24H, $-CH_2CH_2$-CH_3, $-C(CH_3)_3$), 1.65 (m, 6H, $-CH_2CH_2CH_2-$), 3.12 (s, 3H, $-NCH_3$), 3.29 (m, 6H, $-NCH_2CH_2-$), 6.90 (d, 1H, C*H* (Pt−C_6H_5)), 7.03 (m, 2H, C*H* (Pt−C_6H_5)), 7.37 (d, 2H, C*H* (Pt−C_6H_5)), 7.47 (d, 1H, C*H* (bipy′)), 7.49 (s, 1H, C*H* (bipy′)), 7.58 (d, 1H, C*H* (bipy′)), 7.89 (d, 1H, C*H* (bipy′)), 8.07 (s, 1H, C*H* (bipy′)), 9.70 (d, 1H, C*H* (bipy′)). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −10.8 (s, B12), −15.5 (s, B2/B3/B4/B5/B6, B7/B8/B9/B10/B11). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 13.8 (s, $-CH_2CH_3$), 0.0 (s, $-CH_2CH_2$-CH_3), 24.6 (s, $-CH_2CH_2CH_2-$), 30.3 (s, $-C(CH_3)_3$), 36.0 (s, $-C(CH_3)_3$), 36.1 (s, $-C(CH_3)_3$), 49.3 (s, NCH_3), 61.8 (s, NCH_2-CH_2-), 119.6 (s, *C*H (bipy′)), 119.8 (s, *C*H (bipy′)), 123.1 (s, *C*H (Pt−C_6H_5)), 125.0 (s, *C*H (bipy′)), 126.2 (s, *C*H (bipy′)), 128.1 (s, *C*H (Pt−C_6H_5)), 130.8 (s, C_{ipso} (Pt−C_6H_5)), 139.6 (s, *C*H (Pt−C_6H_5)), 147.7 (s, *C*H (bipy′)), 153.3 (s, *C*-H (bipy′)), 155.9/156.7 (s, *C2*/*C2*′ (bipy′)), 163.7/164.5 (s, *C4*/*C4*′ (bipy′)). Anal. Calcd for $C_{37}H_{70}B_{11}N_3PtSn$ (989.7): C, 44.87; H, 7.12; N, 4.24. Found: C, 45.32; H, 7.65; N, 4.25.

[(bipy′)Pt(Br)(Bz)(Ph)($SnB_{11}H_{11}$)][Bu_3NMe] (4). To a solution of 0.50 g (M_r = 989.67, 0.51 mmol) of [(bipy′)Pt(Ph)-$SnB_{11}H_{11}$][Bu_3NMe] (**3**) in 20 mL of acetone was added 0.5 mL (M_r = 171.04, 0.72 g, 4.2 mmol) of benzyl bromide. After it was stirred overnight, the reaction mixture was evaporated in vacuo and the resulting brown residue was recrystallized from CH_2Cl_2 by slow diffusion of hexane at +8 °C to give 0.55 g (92% yield) of **4**. ^{1}H NMR (CD_2Cl_2): δ 0.97 (t, 9H, ^3J = 7.1

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Hz, $-CH_2CH_3$), 1.37−1.46 (m, 24H, $-CH_2CH_2CH_3$, $-C(CH_3)_3$), 1.57 (m, 6H, $-CH_2CH_2CH_2-$), 2.90 (s, 3H, $-NCH_3$), 3.09 (m, 6H, $-NCH_2CH_2-$), 3.28 (d, 1H, ^2J = 9.1 Hz, $^2J_{H-Pt}$ = 98.3 Hz, Pt−CH_2Ph), 4.73 (d, 1H, ^2J = 9.0 Hz, $^2J_{H-Pt}$ = 72.7 Hz, Pt−CH_2Ph), δ 6.33 (d, 2H, *C*H (Pt−Bz)), 6.50 (t, 2H, *C*H (Pt−Bz)), 6.72 (d, 1H, *C*H (Pt−Bz)), 7.34 (d, 1H, *C*H (Pt−C_6H_5)), 7.48 (d, 2H, *C*H (Pt−C_6H_5)), 7.61 (d, 2H, *C*H (Pt−C_6H_5)), 7.74 (m, 2H, *C*H (bipy′)), 7.96 (s, br, 1H, *C*H (bipy′)), 8.27 (m, 1H, *C*H (bipy′)), 8.53 (m, 1H, *C*H (bipy′)), 8.61 (m, 1H, *C*H (bipy′)). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −13.8 (s, B12), −16.8 (s, B2/B3/B4/B5/B6, B7/B8/B9/B10/B11). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 13.9 (s, $-CH_2CH_3$), 20.0 (s, $-CH_2CH_2CH_3$), 22.9 (s, $^1J_{C-Pt}$ = 505 Hz, Pt−CH_2Ph), 24.6 (s, $-CH_2CH_2CH_2-$), 30.4 (s, $-C(CH_3)_3$), 30.5 (s, $-C(CH_3)_3$), 35.8 (s, $-C(CH_3)_3$), 36.0 (s, $-C(CH_3)_3$), 49.6 (s, NCH_3), 62.1 (s, NCH_2CH_2-), 119.9 (s, $^1J_{C-Pt}$ = 720 Hz, C_{ipso} (Pt−C_6H_5)), 120.4 (s, *C*H (bipy′)), 121.2 (s, *C*H (bipy′)), 124.5 (s, *C*H (bipy′)), 124.9−126.0 (s, *C*H (Pt−C_6H_5)), 125.3 (s, *C*H (bipy′)), 125.6 (s, *C*H (Pt−Bz)), 128.0 (s, *C*H (Pt−Bz)), 128.9 (s, *C*H (Pt−C_6H_5)), 129.2 (s, *C*H (Pt−Bz)), 140.0 (s, *C*H (Pt−C_6H_5)), 140.8 (s, *C*H (Pt−C_6H_5)), 142.7 (s, $^2J_{C-Pt}$ = 47.2 Hz, C_{ipso} (−C_6H_5)), 146.3 (s, *C*H (bipy′)), 153.5 (s, *C*H (bipy′)), 154.0/155.4 (s, *C2*/*C2′* (bipy′)), 163.8/165.5 (s, *C4*/*C4′* (bipy′)). Anal. Calcd for $C_{44}H_{77}B_{11}BrN_3PtSn$ (1160.7): C, 45.53; H, 6.69; N, 3.62. Found: C, 45.63; H, 6.61; N, 3.51.

[(bipy′)Pt(Bz)(Ph)(*t*-Bu-NC)($SnB_{11}H_{11}$)] (5). To an ice-cooled suspension of 0.09 g (M_r = 194.68, 0.45 mmol) of $AgBF_4$ in 20 mL of acetone was added a solution of 0.52 g (M_r = 1160.71, 0.45 mmol) of [(bipy′)Pt(Br)(Bz)(Ph)($SnB_{11}H_{11}$)][Bu_3NMe] (**4**) in 20 mL of acetone, and AgBr was formed immediately. After the mixture was stirred for 5 min, the precipitate was filtered off and to the filtrate was added 0.2 mL (M_r = 83.13, 0.15 g, 1.80 mmol) of *tert*-butyl isocyanide. The yellow solution was stirred for 1 h before it was evaporated in vacuo. The residue was properly washed with water to separate the formed [Bu_3NMe][BF_4], and the yellow product was purified by crystallization from CH_2Cl_2 by slow diffusion of hexane at +8 °C to give 0.28 g (65% yield) of **5**. ^1H NMR (CD_2Cl_2): δ 1.37 (s, 9H, $-C(CH_3)_3$ (bipy′)), 1.39 (s, 9H, $-C(CH_3)_3$ (bipy′)), 1.51 (s, 9H, $-C(CH_3)_3$ (*t*-Bu-NC)), 2.80 (d, 1H, ^2J = 10.2 Hz, $^2J_{H-Pt}$ = 89.0 Hz, Pt−CH_2Ph), 4.50 (d, 1H, ^2J = 10.5 Hz, $^2J_{H-Pt}$ = 51.7 Hz, Pt−CH_2Ph), 6.15 (d, 2H, *C*H (Pt−Bz)), 6.53 (t, 2H, *C*H (Pt−Bz)), 6.73 (m, 1H, *C*H (Pt−Bz)), 7.30 (s, br, 2H, *C*H (bipy′)), 7.58 (m, br, 2H, *C*H (Pt−C_6H_5)), 7.67 (m, br, 2H, *C*H (Pt−C_6H_5)), 7.76 (m, br, 2H, *C*H (bipy′, Pt−C_6H_5)), 7.99 (s, br, 1H, *C*H (bipy′)), 8.45 (m, 1H, *C*H (bipy′)), 9.46 (m, 1H, *C*H (bipy′)). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −12.5 (s, B12), −16.6 (s, B2/B3/B4/B5/B6, B7/B8/B9/B10/B11). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 21.6 (s, $^1J_{C-Pt}$ = 420 Hz, Pt-CH_2Ph), 29.8 (s, $-C(CH_3)_3$ (*t*-Bu-NC)), 30.3 (s, $-C(CH_3)_3$ (bipy′)), 30.5 (s, $-C(CH_3)_3$ (bipy′)), 36.1 (s, $-C(CH_3)_3$ (bipy′)), 36.3 (s, $-C(CH_3)_3$ (bipy′)), 61.2 (s, $-C(CH_3)_3$ (*t*-Bu-NC)), 116.2 (s, $^1J_{C-Pt}$ = 680 Hz, C_{ipso} (Pt−C_6H_5)), 120.2 (s, *C*H (bipy′)), 121.8 (s, *C*H (bipy′)), 125.4 (s, *C*H (Pt−C_6H_5)), 125.9 (s, *C*H (bipy′)), 126.6 (s, *C*H (bipy′)), 127.3 (s, *C*H (Pt−Bz)), 128.0 (s, *C*-H (Pt−Bz)), 129.2 (s, *C*H (Pt−Bz)), 129.9 (s, *C*H (Pt−C_6H_5)), 131.0 (s, *C*H (Pt−C_6H_5)), 138.7 (s, *C*H (Pt−C_6H_5)), 139.3 (s, *C*H (Pt−C_6H_5)), 141.5 (s, C_{ipso} (−C_6H_5)), 147.0 (s, *C*H (bipy′)), δ = 152.8 (s, *C*-H (bipy′)), δ = 153.9/155.2 (s, *C2*/*C2′* (bipy′)), 165.8/167.0 (s, *C4*/*C4′* (bipy′)). Anal. Calcd for $C_{36}H_{56}B_{11}N_3PtSn$ (963.5): C, 44.86; H, 5.86; N, 4.36. Found: C, 45.38; H, 6.32; N, 4.00.

Crystal Data for 5: $C_{38}H_{60}B_{11}Cl_4N_3PtSn$; formula mass 1133.38 g/mol; monoclinic space group $P2_1/n$ (No. 14); a = 11.283(2) Å, b = 25.283(3) Å, c = 17.109(3) Å, β = 93.18(2)°, V = 4873 (1) Å^3, Z = 4, d_{calcd} = 1.545 g cm^{-3}, μ(Mo Kα) = 2.953 mm^{-1}; image plate diffractometer (IPDS, Stoe); Mo Kα radiation (graphite monochromator, λ = 71.07 pm); data collection at 170 K on a single crystal of dimensions 0.2 × 0.3 × 0.4 mm, 1.9 ≤ θ ≤ 24.2°; 7329 independent reflections measured, 5479 "observed" ($I > 2\sigma(I)$); data corrections Lorentz and polarization factors, numerical absorption with programs X-RED and X-Shape (Stoe Darmstadt, 1994);[16] structure solution by direct methods and difference Fourier synthesis, F^2 refinement;[17] anisotropic parameters for non-hydrogen atoms. Hydrogen atoms were placed in calculated positions or found. All hydrogens were refined with isotropic thermal parameters. Convergence was obtained for 580 variables with wR2(all data) = 0.113, $R1$(all data) = 0.064, and GOF = 0.986. The maximum/minimum residual density was +2.17 e Å^{-3} (1.06 Å from Pt)/ −1.1 e Å^{-3} (0.64 Å from Cl2). Further details on the crystal structure determination are available on request from the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 144784. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, + 44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

Methods of the Theoretical Investigations. The program system TURBOMOLE[12,18] was employed to carry out the density functional theory (DFT)[13] investigations using the efficient RIDFT program[18] with the Becke−Perdew (B−P) functional[19] and the grid size m3. The RIDFT program has been developed on the basis of the DFT program,[20] approximating the coulomb part of the two electron interactions. Basis sets were of SV(P) quality (SV(P) = split valence plus polarization for all non-hydrogen atoms, split valence for hydrogen atoms).[21] The Sn and the Pt atoms were treated with effective core potentials (ECP) that serve as approximations for inner electrons considering relativistic effects. For Sn, an ECP-46 describing 46 core electrons was used; for Pt, we employed an ECP-60 describing 60 core electrons.[22] The dipole moment of **5** was calculated by means of the program MOLOCH being equally implemented within TURBOMOLE.

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Supporting Information Available: Listings of all fractional atomic coordinates and equivalent isotropic displacement parameters, interatomic distances, and angles, and anisotropic displacement parameters for **5** and listings of the Cartesian coordinates of the calculated geometry of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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