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Cycloneophylplatinum Chemistry: A New Route to Platinum(II) Complexes and the Mechanism and Selectivity of Protonolysis of Platinum−Carbon Bonds

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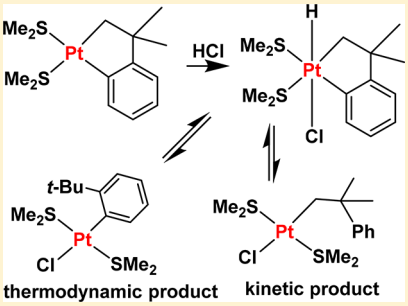
Supporting Information

ABSTRACT: A new route to cycloneophylplatinum(II) complexes is reported and the selectivity of protonolysis of the platinum−aryl and −alkyl bonds has been determined. Reaction of $[PtCl_2(SMe_2)_2]$ with neophylmagnesium chloride gives the binuclear cycloneophylplatinum(II) complex $[Pt_2(CH_2CMe_2C_6H_4)_2(\mu\text{-}SMe_2)_2]$, **1**, which is shown to exist as a mixture of *syn* and *anti* isomers. Complex **1** reacts reversibly with SMe_2 to give $[Pt(CH_2CMe_2C_6H_4)(SMe_2)_2]$, **2**, and irreversibly with bidentate ligands NN = 3,4,7,8-tetramethyl-1,10-phenanthroline (phen*) or 4,4′-di-*t*-butyl-2,2′bipyridine (bubipy) to give the corresponding complexes $[Pt(CH_2CMe_2C_6H_4)(phen^*)]$, **3**, and $[Pt(CH_2CMe_2C_6H_4)(bubipy)]$, **4**, respectively. Complex **2** reacts with HCl initially by cleavage of the aryl−platinum bond to give mostly *trans*-$[PtCl(CH_2CMe_2Ph)(SMe_2)_2]$, which then rearranges to an equilibrium mixture with *trans*-$[PtCl(C_6H_4\text{-}2\text{-}t\text{-}Bu)(SMe_2)_2]$, while **3** and **4** react to give $[PtCl(CH_2CMe_2Ph)(phen^*)]$ and $[PtCl(CH_2CMe_2Ph)(bubipy)]$, which do not undergo the isomerization reaction. The protonolysis reactions occur by way of a platinum(IV) hydride complex in each case, and the unusual reactivity of complex **2** is attributed to the ease of dissociation of the Me_2S ligands.



INTRODUCTION

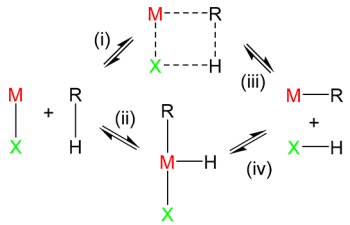
The practical activation and functionalization of the C−H bonds of alkanes and arenes is challenging and potentially very rewarding, and so it is important to understand the likely steps in proposed catalytic cycles and to be able to predict the selectivity of C−H activation reactions. Since platinum complexes are among the most promising for C−H bond activation, there has been much research on C−H bond activation at platinum(II), often known as Shilov chemistry after the pioneer of the field.[1] There are two established mechanisms of C−H bond activation, namely, the concerted mechanism (i) and the oxidative addition/reductive elimination mechanism (ii) shown in Scheme 1. The reverse reaction involves protonolysis of the metal−alkyl or metal−aryl bond and is often easier to study mechanistically. In studies of selectivity, the C−H bond activation may use reagents such as toluene, which contains both alkyl and aryl C−H bonds, while the reverse protonolysis may use organometallic reagents $L_nMR(R')$, containing both an alkyl and aryl group.[1] An alternative is to use cyclometalated complexes containing, for example, the cycloneophyl group $CH_2CMe_2\text{-}2\text{-}C_6H_4$, which contain both $M-CH_2$ and $M-C_6H_4$ groups.

The cyclometalation of neophylplatinum complexes, by *δ*-CH bond activation, was first investigated by Young and co-workers.[2−4] They prepared 1,5-cyclooctadiene complex **A**, which could then undergo ligand substitution to give a range of other dineophylplatinum(II) complexes **B** with monodentate or bidentate ligands (Scheme 2). On heating, these complexes underwent *δ*-CH bond activation, with loss of *t*-butylbenzene, to give cycloneophyl complexes **C**. In one case, isomerization of a neophylplatinum group to give a *t*-butylphenylplatinum group was observed (**D**, Scheme 2).[2]

The reactions to give **C** and **D** (Scheme 2) were proposed to occur by way of hydridoplatinum(IV) complexes, formed after loss of one ligand L (Scheme 3).[2−4]

Since these pioneering studies, there has been intensive research into related nickel(II) and palladium(II) complexes, leading to impressive advances in understanding selectivity and mechanism in C−H bond activation and in electrophilic

Scheme 1. Two Basic Mechanisms of C−H Bond Activation[a]



[a](i) Concerted or Σ-CAM (variations are known depending on the presence of other functional groups), (ii) stepwise or oxidative addition/reductive elimination and of M−C bond bond protonolysis, (iii) S_E2, and (iv) S_Eox (R = alkyl or aryl, X = anionic ligand).

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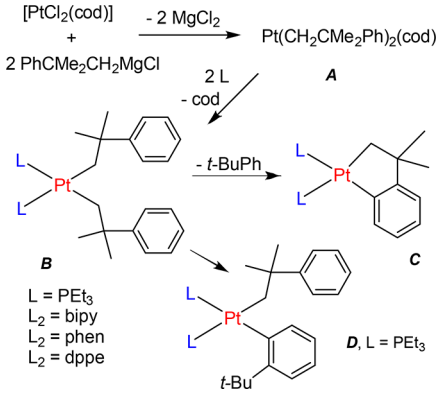
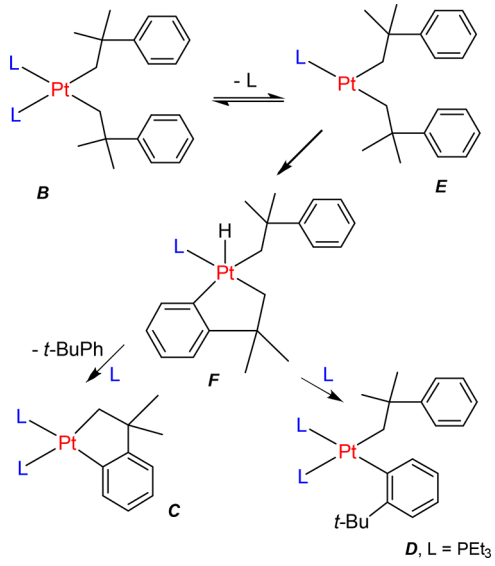
Scheme 2. Known Chemistry of Dineophyl and Cycloneophyl Complexes of Platinum(II)[a]



[a]cod = 1,5-cyclooctadiene, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, dppe = 1,2-*bis*(diphenylphosphino)ethane.

Scheme 3. Proposed Mechanism of Formation of Complexes C and D via Intermediates E and F

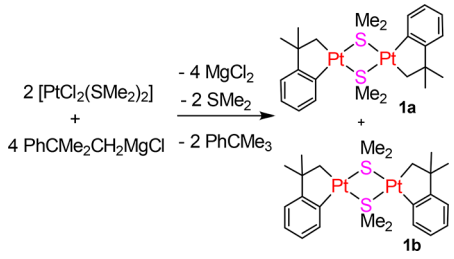


cleavage of the metal−carbon bonds of cycloneophyl complexes, but there has not been further research into the analogous platinum(II) complexes.[5−13] This article describes a new approach to synthesis of cycloneophylplatinum(II) complexes, using labile dimethyl sulfide complexes, and a study of the mechanism and selectivity of metal−carbon bond protonolysis. The research gives new insights into the mechanisms of protonolysis of Pt−C bonds and of the microscopic reverse reaction involving C−H bond activation at platinum(II).

RESULTS AND DISCUSSION

The reaction of $[PtCl_2(SMe_2)_2]$ with neophylmagnesium chloride gave the cycloneophylplatinum(II) complex $[Pt_2(CH_2CMe_2C_6H_4)_2(\mu\text{-}SMe_2)_2]$, **1**, in a single step according to Scheme 4. The facile cyclometalation compared to other platinum(II) complexes (Scheme 2) is presumably a result of the presence of labile dimethyl sulfide ligands which gives easy access to the coordinatively unsaturated intermediates analogous to those in Scheme 3.[1−4] Complex **1** exists as a mixture of *anti* and *syn* isomers **1a** and **1b**, in a ratio of **1a**/**1b** =

Scheme 4. Synthesis of Cycloneophyl Complexes 1a and 1b, with K_{eq} = 1a/1b = 1.5[a]



[a]The yield of **1a**/**1b** was 65%.

1.5, which can be identified by their NMR spectra. Thus, **1a** and **1b** have effective C_{2h} and C_{2v} symmetry, respectively. Each gives a single set of cycloneophyl resonances: **1a** gives only one dimethyl sulfide resonance, while **1b** gives two, in either the ^{1}H or ^{13}C NMR spectrum. For example, in the ^{1}H NMR spectrum, complex **1a** gave one resonance at $\delta(Me_2S)$ 3.11, $^3J_{PtH}$ = 16 Hz, while **1b** gave two resonances at $\delta(Me_2S)$ 3.26, $^3J_{PtH}$ = 16 Hz, and 2.99, $^3J_{PtH}$ = 18 Hz. A feature of the cycloneophyl resonances is the large coupling constant $^2J_{PtH}$ for the $PtCH_2$ group, which was 92 Hz in **1a** and 98 Hz in **1b**. Crystallization of the mixture of isomers gave **1a** selectively, but redissolution gave back the equilibrium mixture of isomers, showing that the isomerization is rapid at room temperature. The structure of complex **1a** was determined and is shown in Figure 1. There is a crystallographic inversion center at the

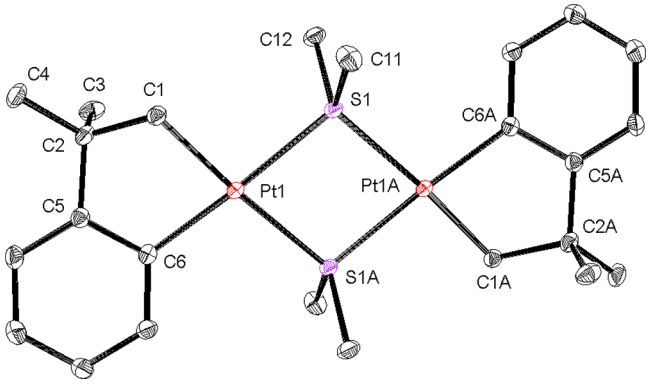


Figure 1. Structure of complex **1a**, showing 30% probability ellipsoids. Selected bond parameters: Pt(1)C(1) 2.035(3), Pt(1)C(6) 2.011(3), Pt(1)S(1) 2.3511(9), Pt(1)S(1A) 2.3718(9) Å; C(1)Pt(1)C(6) 81.31(11), S(1)Pt(1)S(1A) 80.22(2)°. Symmetry equivalent atoms: *x*, *y*, *z*; 4/3 − *x*; 5/3 − *y*; 2/3 − *z*.

center of the Pt_2S_2 ring. The distance pf Pt(1)S(1), 2.3511(9) Å, is slightly shorter than that of Pt(1)S(1A), 2.3718(9) Å, which could be taken to reflect a slightly lower *trans*-influence of the aromatic compared to the aliphatic carbon donor.[14] However, in $[Pt_2R_4(\mu\text{-}SMe_2)_2]$ the corresponding distances PtS = 2.354(3) Å when R = Me but 2.377(4) and 2.388(4) when R = Ph.[15a] The bite angle at the cycloneophyl group [C(1)Pt(1)C(6) = 81.31(11)°] is similar to those in related compounds.[1−13,15b]

Complex **1** is a useful precursor to other cycloneophylplatinum(II) complexes (Scheme 5). The reversible reaction with dimethyl sulfide gave the monomeric complex $[Pt(CH_2CMe_2C_6H_4)(SMe_2)_2]$, **2**, which could not be isolated because it easily reverted back to complex **1**, but which

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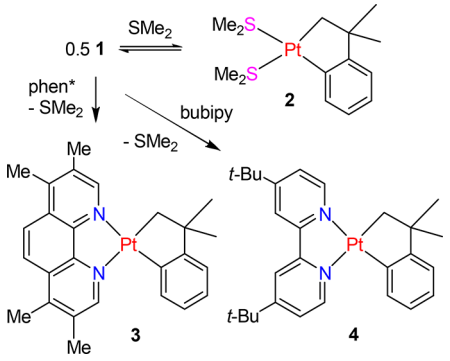
Scheme 5. Synthesis of Cycloneophylplatinum(II) Complexes from Complex 1



was identified by its NMR spectra in solution. The dimethyl sulfide ligands are nonequivalent and gave separate resonances in the ^{1}H NMR spectrum at δ 2.49, $^2J_{PtH}$ = 25 Hz, and 2.48, $^2J_{PtH}$ = 20 Hz, while the $PtCH_2$ resonance was observed at δ 2.17, $^2J_{PtH}$ = 96 Hz. The reaction of complex **1** with 3,4,7,8-tetramethyl-1,10-phenanthroline (phen*) or 4,4′-di-*t*-butyl-2,2′-bipyridine (bubipy) gave corresponding complexes **3** and **4** by displacement of the dimethyl sulfide ligands. Complex **3** was characterized by a structure determination (Figure 2). The cycloneophylplatinum group is similar to that

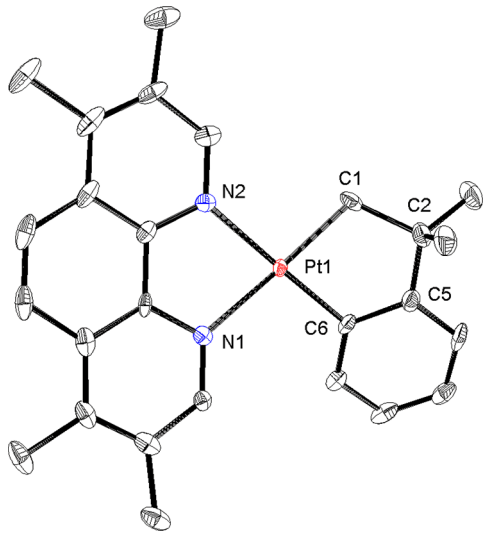
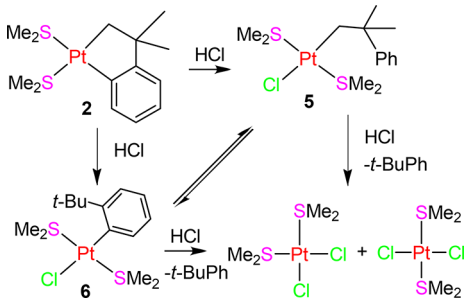


Figure 2. Structure of complex **3**, showing 30% probability ellipsoids. Selected bond parameters: Pt(1)C(1) 2.029(11), Pt(1)C(6) 1.989(11), Pt(1)N(1) 2.131(9), Pt(1)N(2) 2.099(9) Å; C(1)Pt(1)-C(6) 80.6(5), N(1)Pt(1)N(2) 78.1(4)°.

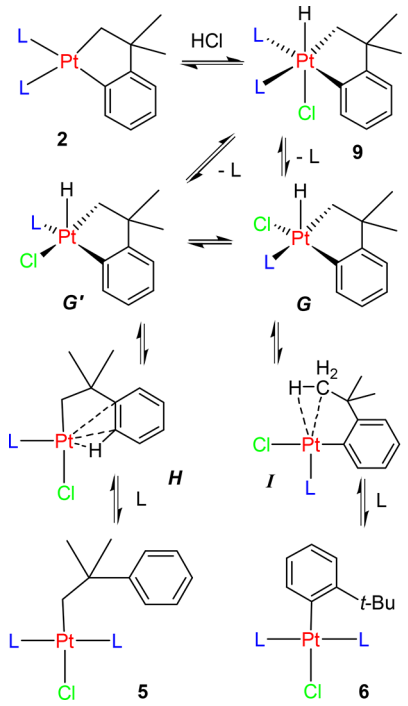
in **1a** (Figure 1), but it is twisted out of the plane of the Pt(phen*) group, probably to avoid a close contact between the adjacent ortho protons of the aromatic C_6H_4 and phen* groups. This route to cycloneophylplatinum(II) complexes by way of labile dimethyl sulfide complex **1** is much simpler and more convenient than the procedure used in the early research.[1−4]

The reactions of **2**−**4** with HCl were studied in order to determine the selectivity and mechanism of protonolysis of the metal−carbon bonds and structures of products **6**−**8** were obtained (Schemes 6 and 7). In order to control the stoichiometry in small scale reactions, HCl or DCl was

Scheme 6. Products of Reaction of Complex 2 with HCl



Scheme 7. Proposed Mechanism of Formation of Complexes 5 and 6 and the Equilibrium between Them[a]



[a] K_{eq} = [**6**]/[**5**] = 9, L = SMe_2.

generated by hydrolysis of Me_3SiCl with H_2O or D_2O, respectively. The reactions with complex **2** are shown in Scheme 6. By comparison with related palladium chemistry, the selective cleavage of the arylplatinum bond was expected to occur, which would give neophylplatinum complex **5**.[5,6,13] However, in the initial reaction, the product mixture was recrystallized and the product, isolated in low yield, was identified crystallographically (Figure 3) as 2-*t*-butylphenylplatinum(II) complex **6**, which is the expected product of protonolysis of the alkylplatinum bond. In the structure, the methylsulfur groups are oriented away from the bulky *t*-butylphenyl group. There is a mirror plane containing the C_6H_4PtCl atoms and perpendicular to the S(1)S(1A) axis. Thus, the two dimethyl sulfide groups are equivalent, but the two methyl groups on each individual ligand are not (Figure 3).

The reaction of complex **2** with HCl in acetone-d_6 solution was monitored by ^{1}H NMR spectroscopy, with the HCl added at −60 °C and spectra recorded as the sample warmed to room temperature, following an established protocol.[16−18] At −60 °C, a transient PtH resonance was observed at δ −18.80, $^1J_{PtH}$

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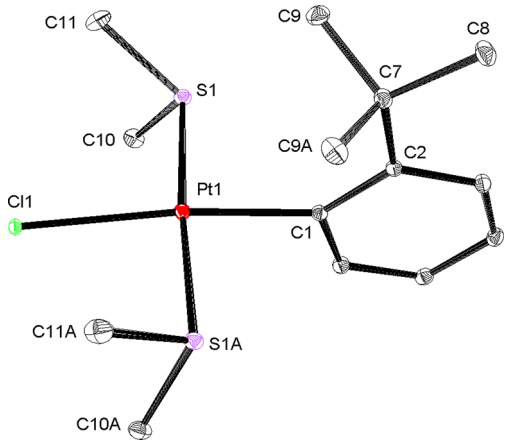


Figure 3. Structure of complex **6**, showing 30% probability ellipsoids. Selected bond parameters: Pt(1)C(1) 2.031(3), Pt(1)S(1) 2.3022(10), Pt(1)Cl(1) 2.4558(8) Å; S(1)Pt(1)S(1A) 175.82(3), C(1)Pt(1)Cl(1) 170.38(8)°. Symmetry equivalent atoms: *x*, *y*, *z*; *x*, 1/2 − *y*, *z*.

= 1473 Hz, in the range expected for a platinum(IV) hydride, such as the expected $[PtHCl(CH_2CMe_2C_6H_4)(SMe_2)_2]$, **9**,[16−18] but the concentration was not high enough to assign the associated resonances. It was not observed at all when the sample was warmed to −50 °C. In the similar reaction with DCl, the complex $[PtDCl(CH_2CMe_2C_6H_4)(SMe_2)_2]$, **9**-$d_1$, was longer-lived, indicating a significant kinetic isotope effect on the reductive elimination step, and was detected at −50 °C [δ(PtD) −18.83, $^1J_{PtD}$ = 226 Hz] but had decayed at −25 °C (Figure 4). NMR analysis indicated that at room temperature

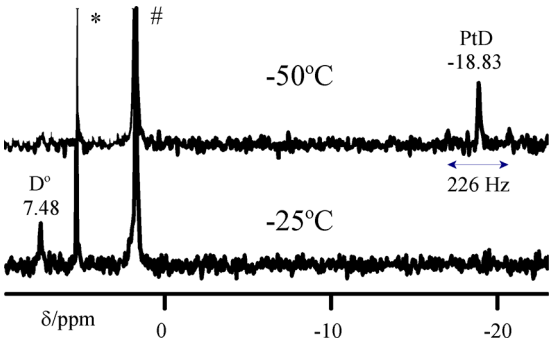


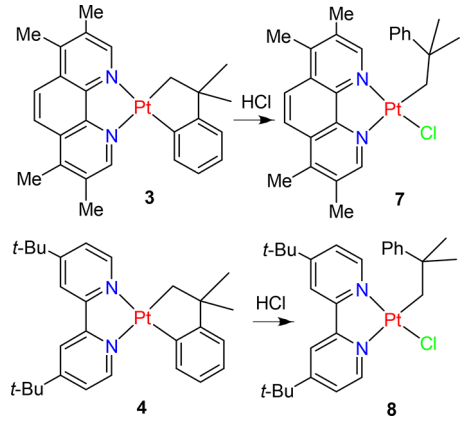
Figure 4. ^{2}H NMR spectra for the reaction of **2** with DCl in CH_2Cl_2; above at −50 °C, mostly $[PtDCl(CH_2CMe_2C_6H_4)(SMe_2)_2]$, **9**-$d_1$; below at −25 °C, mostly $[PtCl(CH_2CMe_2$-2-$C_6H_4D]$, **5**-d_1. The peaks labeled * and # are due to solvent and D_2O, respectively.

the major product from reaction of **2** with HCl was complex **5** formed along with **6**, *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$,[19] *t*-butylbenzene, and with some unreacted complex **2**. The initial ratio of products was **5**/**6** = ca. 10:1, but after 3 days it was ca. 1:9, indicating isomerization of **5** to **6** occurred in a way analogous to that for compounds **B** and **D** (Schemes 2 and 3). Similar results were obtained when the reaction was carried out in CD_2Cl_2 at room temperature. In this case, the ratio of **5**/**6** was approximately 2:1 initially but about 1:9 after 1 day. The equilibrium constant of K_{eq} = [**6**]/[**5**] = 9, corresponds to a difference in free energy of about 5 kJ mol^{-1}; no equilibrium constant was reported for the isomerization of **B** to **D**.[2−4] In terms of characterization by ^{1}H NMR spectroscopy, complex **5** in acetone-d_6 gives CH_2, CMe_2, and SMe_2 resonances at δ 1.98, $^2J_{PtH}$ = 90 Hz, 1.41 and 2.39, $^3J_{PtH}$ = 52 Hz, respectively, while complex **6** gives a characteristic resonance for the *ortho* aryl proton at δ 7.82, $^3J_{PtH}$ = 38 Hz, a *t*-butyl resonance at δ 1.62, and a broad SMe_2 resonance at δ 2.84, with no resolved coupling to ^{195}Pt. In CD_2Cl_2 solution, two broad MeS resonances were resolved for **6** at δ 2.79 and 2.82. The peak broadening is attributed to fluxionality, in which the two nonequivalent methyl groups of each Me_2S ligand (Figure 3) can exchange environments either by rotation of the bulky *t*-butylphenyl group about the Pt−C axis or by inversion at the pyramidal sulfur atoms.[2,20,21]

The above data indicate that complex **5** is the product of kinetic control while **6** is more stable thermodynamically (Scheme 6). The facile isomerization of **5** to **6** at room temperature was not anticipated but can be understood in terms of the lability of the dimethyl sulfide ligands, which allows access under mild conditions to the coordinatively unsaturated intermediates that are involved in C−H bond activation by oxidative addition and in C−H bond formation by reductive elimination.[1−13,17,18,22−24] A likely mechanism is shown in Scheme 7 (L = Me_2S). Proposed hydridoplatinum(IV) intermediate **9** can easily undergo loss of a ligand to give **G** or **G′**, which can undergo either aryl or alkyl C−H reductive elimination to give **H** or **I**, with formation of **H** favored kinetically. Coordination of dimethyl sulfide to **H** then gives kinetic product **5**. Reversal of these steps can regenerate **G′** and **G**, and this can give **I** and then thermodynamically more stable isomer **6** (Scheme 7), eventually giving an equilibrium mixture of **5** and **6**.

The major reactions of complexes **3** and **4** with HCl are shown in Scheme 8, and the structures of neophylplatinum(II)

Scheme 8. Formation of Neophylplatinum(II) Complexes 7 (Yield 59%) and 8 (Yield 64%)



complexes **7** and **8** are shown in Figure 5. In each case, the neophyl group is oriented so that the phenyl group is weakly π-stacked over one of the pyridyl rings (Figure 5). Each complex gave the expected resonances in the ^{1}H NMR spectra. For example, complex **8** gave a $PtCH_2$ resonance at δ 2.29, $^2J_{PtH}$ = 87 Hz, and a singlet CMe_2 resonance at δ 1.36, as well as resonances for the phenyl group and the two nonequivalent 4-*t*-butylpyridine rings.

Complex **3** was not soluble enough to carry out low-temperature NMR spectroscopic experiments, but complex **4** gave useful data via monitoring the reaction with HCl. The HCl was added at −60 °C to a solution of **4** in acetone-d_6, and spectra were recorded as the sample was warmed to room

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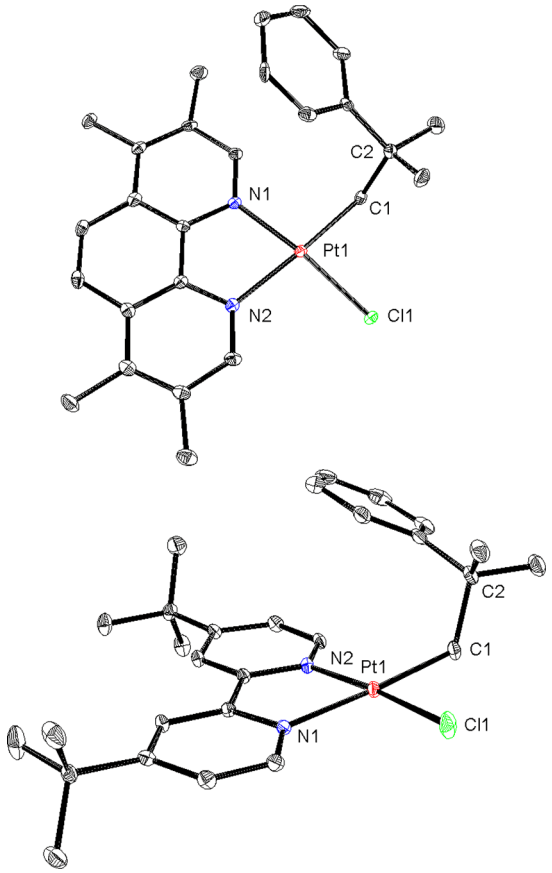
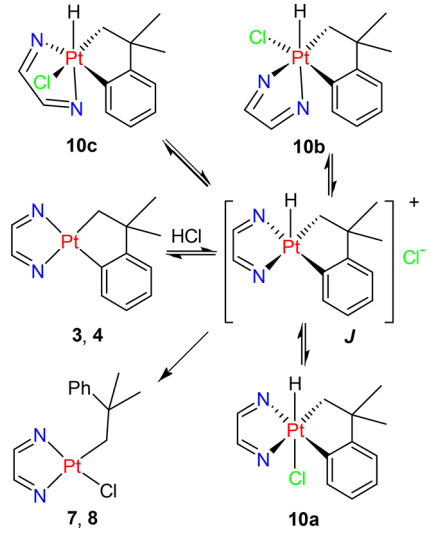


Figure 5. Structures of neophylplatinum(II) complexes **7** and **8**. Selected bond parameters: **7**, Pt(1)C(1) 2.064(4), Pt(1)N(1) 2.023(3), Pt(1)N(2) 2.121(3), Pt(1)Cl(1) 2.3069(14) Å; N(1)-Pt(1)N(2) 79.70(14), C(1)Pt(1)Cl(1) 89.49(13)°; **8**, Pt(1)C(1) 2.057(4), Pt(1)N(1) 2.105(4), Pt(1)N(2) 2.020(4), Pt(1)Cl(1) 2.292(4) Å; N(1)Pt(1)N(2) 78.90(11), C(1)Pt(1)Cl(1) 87.85(11)°.

temperature.[16−18] At −60 °C, a hydride resonance was observed at δ −19.14, $^1J_{PtH}$ = 1512 Hz, assigned to a platinum(IV) complex [$PtHCl(CH_2CMe_2C_6H_4)$(bubipy)], **10**, and this was unchanged at −40 °C. At −25 °C, a second hydride resonance was observed at δ −18.98, $^1J_{PtH}$ = 1474 Hz as the first one began to decay, and is attributed to an isomer of **10** (Scheme 9, Figure 6). The magnitudes of $^1J_{PtH}$ = 1512 and 1474 Hz are consistent with hydride *trans* to chloride and nitrogen respectively, by comparison to related complexes with diimine ligands.[16] Decomposition of the hydride to give neophylplatinum(II) complex **8** began at about 0 °C and was largely complete at 25 °C. Once formed, complexes **7** and **8** are stable in solution and do not isomerize to the corresponding 2-*t*-butylphenyl derivatives at room temperature or on heating to 55 °C in chloroform solution. With excess HCl, they react further to give *t*-butylbenzene and [$PtCl_2$(phen*)], **11** (Scheme 10), or [$PtCl_2$(bubipy)]. Complex **11** was then prepared independently via the reaction of [$PtCl_2(SMe_2)_2$] with phen* in dichloromethane (Scheme 10).

A likely mechanism of reaction is shown in Scheme 9. For most platinum(II) complexes HCl oxidative addition occurs with *trans* stereochemistry via an ionic intermediate. In this case, protonation would give the 5-coordinate hydride intermediate **J** and chloride addition would then give **10a**. However, the 5-coordinate intermediate will easily undergo

Scheme 9. Proposed Mechanism for Formation of Neophylplatinum(II) Complexes 7 and 8 and Possible Isomers of Hydridoplatinum(IV) Complex 10[a]



[a]For **3** and **7**, NN = phen*; **4**, **8**, and **10**, NN = bubipy.

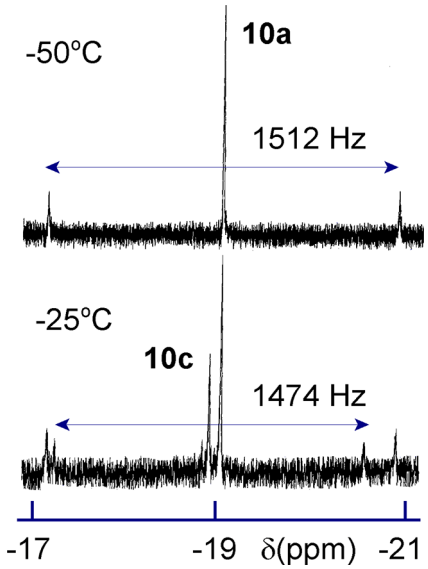
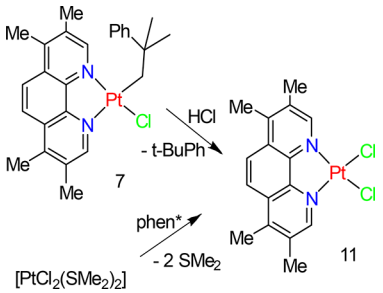


Figure 6. ^{1}H NMR spectra (400 MHz) of complex **10** in the hydride region: at −50 °C, top, and at −25 °C, bottom.

Scheme 10. Formation of [$PtCl_2$(phen*)], 11



rearrangement and might then give isomers **10b** or **10c**. The isomers have no symmetry, so they are not readily distinguished by the ^{1}H NMR spectra. The assignment of

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the second isomer to **10c** is based on theory (see below). The isomers equilibrate somewhat faster than the rate of C−H reductive elimination to give **8** (Scheme 9, NN = bubipy). Since **8** has no easily dissociated ligand, no subsequent isomerization to the *t*-butylphenylplatinum(II) complex is observed, in contrast to the dimethyl sulfide derivative (Schemes 6 and 7).

In the solid state structures of the phen* complexes **3**, **7**, and **11**, there are intermolecular π-stacking interactions between phen* groups. In the structure of **7**, one face is blocked by the neophyl group and the π-stacking leads to dimer formation with individual molecules related by an inversion center (Figure 7). The phen* ligands are therefore parallel but

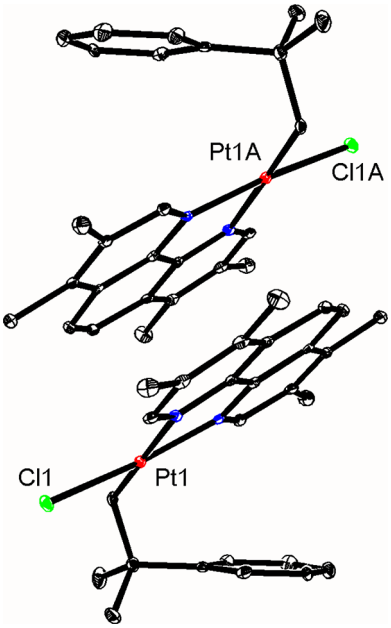

Figure 7. Supramolecular structure of complex **7**, formed by π-stacking between phen* groups. Symmetry equivalent atoms: *x*, *y*, *z*; 1 − *x*, 1 − *y*, 1 − *z*.

oriented in opposite directions. In all three complexes, **3**, **7**, and **11**, the phen* planes are separated by about 3.4 Å. Complexes **3** and **11** have supramolecular polymeric structures formed by π-stacking (Figure 8). In complex **3**, the neighboring molecules are again related by inversion symmetry, so the relative orientation is similar to that in complex **7** forming an AA′AA′ sequence along the polymer chain. However, complex **11** contains two independent molecules (A and B) that are oriented with their phen* ligands parallel but roughly orthogonal to one another (Figure 8). In this case, propagation of the structure is by operation of a 2-fold screw axis, so that the sequence along the polymer chain is ABA′B′ABA′B′. The dramatic difference in the orientation of the neighboring molecules is apparent in Figure 8.

DFT CALCULATIONS

To gain insight into the reactions, some DFT calculations were carried out (see the Experimental Section for details). The phen* and bupipy complexes were modeled using the parent 1,10-phenanthroline without substituents. Figure 9 shows the calculated structure of platinum(II) reagent **3*** (the * indicates phen in place of phen* or bubipy), along with two frontier

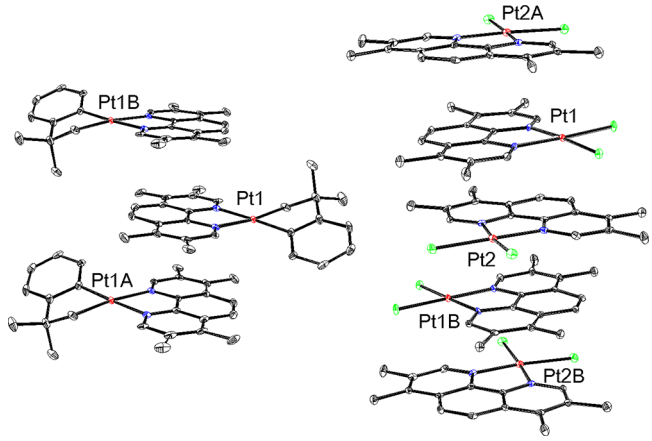

Figure 8. Supramolecular polymeric structures of (left) complex **3** and (right) complex **11**. Symmetry equivalent atoms: **3**, *x*, *y*, *z*; 1 − *x*, 1 − *y*, 1 − *z*; −*x*, 1 − *y*, 1 − *z*; **11**, *x*, *y*, *z*; 1 − *x*, 1/2 + *y*, 3/2 − *z*; 1 − *x*, −1/2 + *y*, 3/2 − *z*.

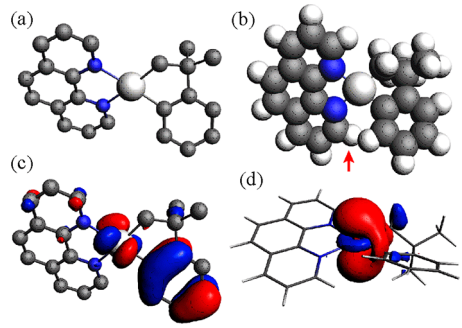

Figure 9. (a) Calculated structure of **3*** or **4***; (b) calculated structure including H atoms, with the red arrow indicating the steric interaction between *ortho* hydrogen atoms of the phen and C_6H_4 groups; (c) the HOMO and (d) the HOMO−1.

MO's. The puckering of the phen and cycloneophyl groups to minimize unfavorable steric effects arising from in-plane HH contact is reproduced well (Figure 9b, compared to Figure 2). The HOMO has mostly 2pπ character of the C_6H_4 group (Figure 9c) and the HOMO−1 has mostly platinum 5d_z2 character (Figure 9d). Addition of a proton to the HOMO would lead to S_E2 reactivity while addition to the HOMO−1 would lead to S_Eox reactivity by forming a platinum(IV) hydride intermediate.

The calculated structures and relative energies of HCl adducts **10*** and protonolysis product **8*** derived from **4*** (Scheme 9) are shown in Figure 10. The oxidative addition step to form **10*** and subsequent reductive elimination step to form **8*** are both favorable. The expected kinetic product of *trans* HCl addition **10a** is calculated to be less stable than corresponding *cis* adducts **10b** or **10c**, probably because the unfavorable H···H steric interaction (Figure 9b) is not present in the *cis* isomers. Isomer **10c** is calculated to be most stable, perhaps because it has a favorable (C_6H_4)H···Cl hydrogen bonding interaction between the aryl and chloride ligands, and this is the basis for its assignment as the second observed hydride (Figure 6).

Figure 11 shows the calculated structures and relative energies for the dimethyl sulfide complexes and proposed intermediates of Scheme 7. As for the phen* complex (Figure 10), the HOMO for platinum(II) complex **2** is calculated to

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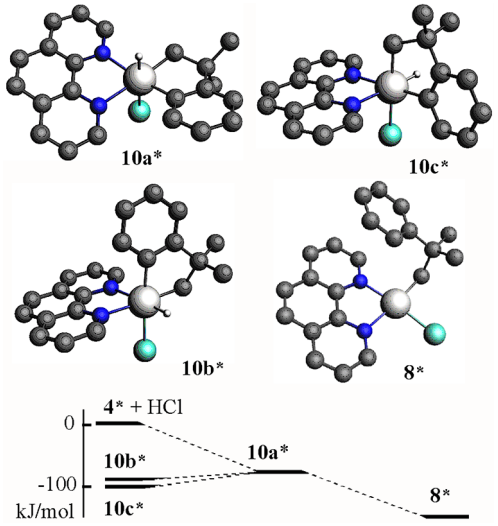

Figure 10. Calculated structures and relative energies of model compounds of Scheme 9. Relative energies (kJ mol^{-1}): **4*** + HCl = 0, **10a** = −74, **10b** = −94, **10c** = −99, **8*** = −138.

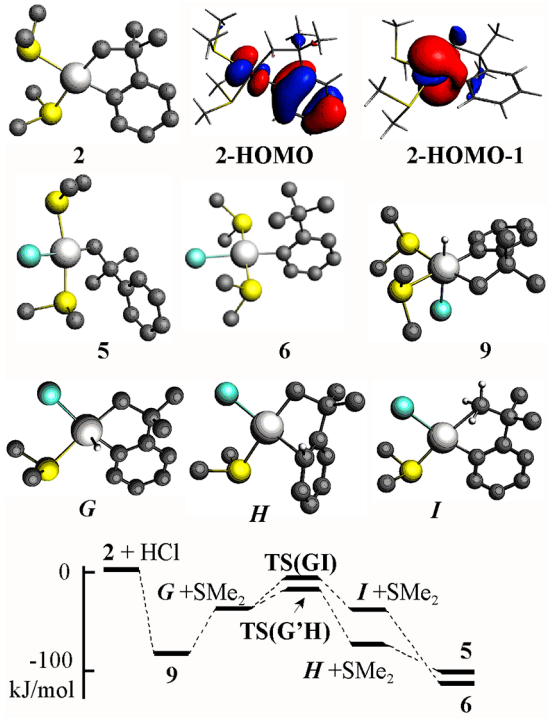

Figure 11. Calculated structures and relative energies of compounds of Scheme 7. Relative energies (kJ mol^{-1}): **2** + HCl = 0, **9** = −96, **G** + SMe_2 = −43, **TS(GI)** = 0, **TS(G′H)** = −27, **H** + SMe_2 = −82, **I** + SMe_2 = −42, **5** = −134, **6** = −139.

have mostly π-character of the C_6H_4 group, with the platinum $5d_{z^2}$ orbital at slightly lower energy as the HOMO−1. Nevertheless, the proton attacks at platinum to give hydridoplatinum(IV) intermediate **9**. Dissociation of dimethyl sulfide from **9** gives [$PtHCl(CH_2CMe_2C_6H_4)(SMe_2)$], for which the most stable isomer is calculated to be **G**, with **G′** being only 2 kJ mol^{-1} higher in energy (Scheme 7). Reductive elimination, with C−H bond formation, can then give either **H** or **I** by coupling of the hydride with the C_6H_4 or CH_2 group of **G′** or **G**, respectively, with **H** at lower energy. Formation of **H** over **I** is also kinetically favored, with a difference in calculated activation energies of 27 kJ mol^{-1} (Figure 11). Kinetically, the preference for **H** over **I** is attributed to the better alignment of frontier orbitals involved in aryl C−H bond formation and thermodynamically because the Pt−arene interaction in **H** is stronger than the agostic PtHC interaction in **I**.[6] The kinetic preference for **5** over **6** is then readily rationalized by the facile addition of dimethyl sulfide to **H** (Figure 11). The subsequent isomerization of **5** to **6** is calculated to be favored by 5 kJ mol^{-1} and involves reversible back reaction from **5** to **G**, involving arene C−H bond activation and eventual formation of **I** and then **6**, with the final equilibrium favoring **6** over **5**, consistent with the experimental observations (Schemes 6 and 7).

CONCLUSIONS

The use of the dimethyl sulfide ligand for the synthesis of cycloneophyl derivatives of platinum(II) has two advantages over the originally used 1,5-cyclooctadiene.[1−4] First, the cycloneophyl group forms spontaneously on reaction of [$PtCl_2(SMe_2)_2$] with neophylmagnesium chloride (compare Schemes 3 and 4), and second, the dimethyl sulfide ligands in **1** are more easily displaced to give other cycloneophylplatinum(II) complexes (Scheme 5). The reactions of the cycloneophylplatinum(II) complexes with HCl are shown to occur by the oxidative addition/reductive elimination mechanism ($S_E$ox) by detection of the platinum(IV) hydride intermediates (Schemes 7 and 9). In contrast the protonolysis of the Pd−C bond of related cycloneophylpalladium(II) complexes is now thought to occur by the concerted S_E2 mechanism.[13] However, both mechanisms lead to selective cleavage of the metal-aryl bond in the first instance to give a neophylplatinum(II) or neophylpalladium(II) complex.[13] More generally, for methyl(aryl) complexes it has been suggested that the S_E2 mechanism should give selective protonolysis of the aryl−metal bond, whereas the $S_E$ox mechanism should give selective cleavage of the alkyl−metal bond.[25] However, this rule does not apply for cyclometalated complexes such as **2**−**4** in which the fixed orientation of the aryl group favors reductive elimination at the aryl−platinum center.[26−28] In the case of dimethyl sulfide complex **5**, the neophyl group can undergo reversible isomerization to give 2-*t*-butylphenyl complex **6**, and the reaction is again enabled by the easy dissociation of a dimethyl sulfide ligand (Schemes 6 and 7). The reactions of the diimine complexes (Schemes 8 and 9) clearly follow the $S_E$ox mechanism, but the hydride intermediate is transient in the protonolysis reactions with dimethyl sulfide complex **2**. This system appears to lie close to the borderline where the $S_E$ox and S_E2 mechanisms are competitive.[29−36]

Because the dimethyl sulfide complexes undergo both protonolysis and reversible C−H bond activation, this work gives particularly clear insight into the important reactions of C−H bond activation and of protonolysis of Pt−C bonds by the oxidative addition/reductive elimination mechanisms [mechanisms (ii) and (iv) in Scheme 1].[13,17,18,25,29−36] The easy access to cycloneophylplatinum(II) complexes by the dimethyl sulfide route described here will allow further studies of their organometallic chemistry and potential role in catalysis.

EXPERIMENTAL SECTION

NMR spectra were recorded using Bruker 400 NMR, Inova 400, and Inova 600 spectrometers; the labeling system is shown in Chart 1. Single-crystal X-ray diffraction measurements were made using a

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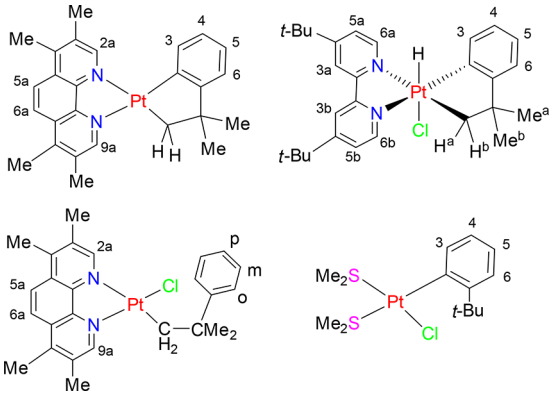
Chart 1. NMR Labelling Scheme



Bruker APEX-II CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Single crystals of the complexes were immersed in paraffin oil and mounted on MiteGen micromounts. The structures were solved using direct methods and refined by the full-matrix least-squares procedure of SHELXTL. Crystallographic data are given in the crystallographic information files (CCDC 1849221−1849227). DFT calculations were carried out by using the Amsterdam Density Functional (ADF) program based on the BLYP functional, with double-ζ basis set and first-order scalar relativistic corrections. Transition state energies were calculated using the NEB-ASE protocol in ADF.[37] The complex [$PtCl_2(SMe_2)_2$] was synthesized according to the literature procedure.[19]

[$Pt_2(CH_2CMe_2C_6H_4)_2(\mu$-$SMe_2)_2$], 1. To a suspension of finely powdered *cis/trans*-[$PtCl_2(SMe_2)_2$] (1.0 g, 2.56 mmol) in dry diethyl ether (100 mL) under nitrogen at 0 °C was added 2-methyl-2-phenylpropylmagnesium chloride solution in diethyl ether (15.4 mL, 0.5 M, 7.7 mmol). The solution was stirred for 30 min, then allowed to warm to room temperature and stirred for 4 h. To the resulting brownish suspension was added a solution of saturated aqueous NH_4Cl (10 mL) and distilled water (100 mL). The mixture was extracted with diethyl ether (3 × 50 mL). The pale-brown, organic extracts are combined and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure, and the solid product was washed with pentane (3 × 50 mL) and acetone (2 × 20 mL) and dried under vacuum. Yield: 0.65 g, 65%. NMR in $CDCl_3$: **1a**, δ(^{1}H) 6.90−7.05 (m, 8H, Ar), 3.11 (s, 12H, $^3J_{PtH}$ = 16 Hz, SMe_2), 2.32 (s, 4H, $^2J_{PtH}$ = 92 Hz, CH_2), 1.32 (s, 12H, CMe_2). δ(^{13}C) 166.9, 147.8, 133.2, 125.1, 124.3, 123.2, 48.1(CH_2), 39.5 (C−Ar), 33.7 (Me), 24.9 (SMe_2) ppm. **1b**, δ(^{1}H) 6.97−7.10 (m, 8H, Ar), 3.26 (s, 6H, $^3J_{PtH}$ = 16 Hz, SMe_2), 2.99 (s, 6H, $^3J_{PtH}$ = 18 Hz, SMe_2), 2.29 (s, 4H, $^2J_{PtH}$ = 98 Hz, CH_2), 1.32 (s, 12H, Me). δ (^{13}C) 166.8, 148.8, 133.1, 125.1, 124.2, 123.1, 48.2 (CH_2), 38.2 (C−Ar), 31.3 (Me), 25.1(SMe_2), 24.8 (SMe_2) ppm.

[$Pt(CH_2CMe_2C_6H_4)(SMe_2)_2$], 2. To a suspension of **1** (0.040 g, 0.051 mmol) in acetone-d_6 (1 mL) under a nitrogen atmosphere was added SMe_2 (3.8 μL, 0.052 mmol) to form a yellow solution. The ^{1}H NMR spectrum indicated formation of complex **2** (80%) in equilibrium with **1** and free SMe_2. NMR in acetone-d_6: δ(^{1}H) 9.36 (d, 1H, $^3J_{HH}$ = 8 Hz, $^3J_{PtH}$ = 64 Hz, H^3), 9.06 (t, 1H, $^3J_{HH}$ = 8 Hz, H^5), 7.80 (d, 1H, $^3J_{HH}$ = 8 Hz, H^6), 7.70 (t, 1H, $^3J_{PtH}$ = 8 Hz, H^4), 2.49 (s, 6H, $^2J_{PtH}$ = 25 Hz, SMe_2), 2.48 (s, 6H, $^2J_{PtH}$ = 20 Hz, SMe_2), 2.17 (s, 2H, $^2J_{PtH}$ = 96 Hz, CH_2), 1.25 (s, 6H, CMe_2). δ(^{13}C) 157.9, 139.8, 124.1, 114.4, 113.9, 112.6, 38.3, 29.5 (CH_2), 24.7 (CMe_2), 11.8 (SMe_2), 11.1 (SMe_2).

[$Pt(CH_2CMe_2C_6H_4)$(phen*)], 3. To a suspension of **1** (0.080 g, 0.103 mmol) in acetone (2 mL) was added a solution of phen* (0.048 g, 0.205 mmol) in acetone (2 mL) under inert atmosphere, and the mixture was stirred for 1 h. to give complex **3** as an orange precipitate, which was separated, washed with acetone and pentane (2 × 5 mL), and dried in vacuo. Yield: 0.090 g, 78%. Anal. Calcd for $C_{26}H_{28}N_2Pt$: C, 55.41; H, 5.01; N, 4.97. Found: C, 55.47; H, 5.18; N, 4.76%. NMR in dichloromethane-d_2: δ(^{1}H) 9.51 (s, 1H, H^{2a}), 9.17 (s, 1H, H^{9a}), 8.11 (s, 2H, H^{5a} and H^{6a}), 7.64 (d, 1H, $^3J_{HH}$ = 7 Hz, $^3J_{PtH}$ = 52 Hz, H^3), 7.00 (dd, 1H, $^3J_{HH}$ = 7 Hz, 9 Hz, H^4), 6.95 (dd, 1H, $^3J_{HH}$ = 7 Hz, 9 Hz, H^5), 6.90 (d, 1H, $^3J_{HH}$ = 7 Hz, H^6), 2.77 (s, 2H, $^2J_{PtH}$ = 93 Hz, CH_2), 2.66 (s, 6H, CMe_2), 2.65 (s, 3H, Me), 2.61 (s, 3H, Me), 1.40 (s, 6H, 2 × Me).

[$Pt(CH_2CMe_2C_6H_4)$(bubipy)], 4. To a suspension of **1** (0.027 g, 0.035 mmol) in acetone-d_6 (1 mL) under a nitrogen atmosphere in an NMR tube was added a solution of bubipy (0.019 g, 0.070 mmol) in acetone-d_6 (1 mL) under inert atmosphere to form a dark red solution. The ^{1}H NMR spectrum after 1 h indicated formation of complex **4**, and the spectrum after 1 week was unchanged. NMR in acetone-d_6: δ(^{1}H) 9.36 (d, 1H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 16 Hz, H^{6a}), 9.06 (d, 1H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 20 Hz, H^{6b}), 8.53 (s, 2H, H^{3a} and H^{3b}), 7.80 (d, 1H, $^3J_{HH}$ = 6 Hz, H^{5a}), 7.70 (d, 1H, $^3J_{HH}$ = 6 Hz, H^{5b}), 7.44 (d, 1H, $^3J_{HH}$ = 7 Hz, $^3J_{PtH}$ = 48 Hz, H^3), 6.82 (dd, 1H, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 10 Hz, H^5), 6.79 (d, 1H, $^3J_{HH}$ = 10 Hz, H^6), 6.78 (t, 1H, $^3J_{HH}$ = 10 Hz, H^4), 2.48 (s, 2H, $^2J_{PtH}$ = 94 Hz, CH_2), 1.46 (s, 9H, *t*Bu), 1.45 (s, 9H, *t*Bu), 1.34 (s, 6H, CMe_2). δ(^{13}C) 173.3, 169.2, 162.4, 162.3, 157.5, 156.9, 149.4, 147.0, 134.8, 124.7, 124.6, 124.0, 122.6, 121.9, 121.2, 121.0, 48.2 (CMe_2), 36.3 (2xCMe_3), 34.5 (2 × Me), 32.0 (CH_2), 30.3 (*t*-Bu), 30.2 (*t*-Bu).

[$PtCl(CH_2CMe_2Ph)(SMe_2)_2$], 5, [$PtCl(C_6H_4$-2-*t*-Bu))($SMe_2)_2$], 6, and [$PtHCl(CH_2CMe_2C_6H_4)(SMe_2)_2$], 9. To a solution of complex **1** (0.030 g, 0.038 mmol) in acetone-d_6 (1 mL) in an NMR tube at −60 °C was added 2 mL of solution of cold HCl (0.077 mmol), generated by reaction of Me_3SiCl (24.4 μL, 0.192 mmol) with H_2O (3.5 μL, 0.192 mmol) in 5 mL of acetone-d_6. The reaction was monitored by ^{1}H NMR as the solution was allowed to warm slowly to room temperature. NMR in acetone-d_6 at −60 °C: **9**, δ(^{1}H) = −18.80 (s, $^1J_{PtH}$ = 1473 Hz, PtH). NMR in acetone-d_6 at 25 °C: **5**, δ(^{1}H) 7.49 (d, 2H, $^3J_{HH}$ = 8 Hz, H°), 7.24 (t, 2H, $^3J_{HH}$ = 8 Hz, H^m), 7.12 (t, 1H, $^3J_{HH}$ = 8 Hz, H^p), 2.39 (s, 12H, $^3J_{PtH}$ = 52 Hz, SMe_2), 1.98 (s, 2H, $^2J_{PtH}$ = 90 Hz, $PtCH_2$), 1.41 (s, 6H, CMe_2). **6**, δ(^{1}H) 7.82 (d, 1H, $^3J_{HH}$ = 8 Hz, $^3J_{PtH}$ = 38 Hz, H^3), 7.19 (d, $^3J_{HH}$ = 8 Hz, H^6) 6.80−6.85 (m, 2H, H^4,H^5), 2.84 (br s, 12H, SMe_2), 1.62 (s, 9H, *t*-Bu).

A similar reaction of **1** with DCl in CH_2Cl_2, gave **9**-d_1 at −50 °C and **5**-d_1 at 25 °C (Figure 4). In one attempt to crystallize complex **5**, a new polymorph of *cis*-[$PtCl_2(SMe_2)_2$] was obtained (Figure S12).

[$PtCl(CH_2CMe_2Ph)$(phen*)], 7. To a solution of complex **1** (0.101 g, 0.128 mmol) in acetone (5 mL) was added ligand phen* (0.060 g, 0.257 mmol) to generate a solution of complex **3**. To this mixture was added a solution of HCl, generated by reaction of Me_3SiCl (33 μL, 0.259 mmol) with H_2O (4.6 μL, 0.259 mmol) in acetone. The solution was stirred for 1h to give a cream precipitate, which was separated by filtration, washed with acetone (2 × 10 mL) and pentane (2 × 10 mL) and dried under vacuum, then recrystallized from CH_2Cl_2 by slow evaporation. Yield: 0.092 g, 59%. Anal. Calcd for $C_{26}H_{29}ClN_2Pt$: C, 52.04; H, 4.87; N, 4.67. Found: C, 52.32; H, 4.97; N, 4.62%. NMR in CD_2Cl_2: δ(^{1}H) 9.43 (s, 1H, $^3J_{PtH}$ = 12 Hz, H^{2a}), 8.21 (s, 1H, $^3J_{PtH}$ = 61 Hz, H^{9a}), 8.00 (d, 1H, $^3J_{HH}$ = 9 Hz, H^{6a}), 7.96 (d, 1H, $^3J_{HH}$ = 9 Hz, H^{5a}), 7.70 (d, 2H, $^3J_{HH}$ = 8 Hz, H°), 6.95 (dd, 2H, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 8 Hz, H^m), 6.84 (t, 1H, $^3J_{HH}$ = 7 Hz, H^p), 2.65 (s, 3H, Me), 2.61 (s, 3H, Me), 2.48 (s, 3H, Me), 2.36 (s, 2H, $^2J_{PtH}$ = 89 Hz, CH_2), 2.28 (s, 3H, Me), 1.56 (s, 6H, 2 × Me). δ(^{13}C) 153.9, 150.3, 149.0, 147.4, 144.9, 144.6, 143.8, 134.4, 133.9, 129.3, 128.8, 127.6, 127.4, 124.7, 123.5, 123.3, 42.0, 32.4 (Me), 23.2 (CH_2), 18.5 (Me), 18.3 (Me), 15.5 (Me), 15.4 (Me).

[$PtCl(CH_2CMe_2Ph)$(bubipy)], 8. This was prepared similarly but using the ligand bubipy. Product **8** was recrystallized from acetone/pentane by slow diffusion. Yield: 64%. Anal. Calcd for $C_{28}H_{37}ClN_2Pt$: C, 53.20; H, 5.90; N, 4.43. Found: C, 53.36; H, 6.01; N, 4.47%. NMR in dichloromethane-d_2: δ(^{1}H) 9.44 (d, 1H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 14 Hz, H^{6a}), 8.26 (d, 1H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 57 Hz, H^{6b}), 7.79, 7.92 (each s, 1H, H^{3a},H^{3b}), 7.63 (d, 2H, $^3J_{HH}$ = 6 Hz, H^{5b}), 7.62 (d, 2H, $^3J_{HH}$ = 6 Hz, H°), 7.00 (dd, 2H, $^3J_{HH}$ = 7 Hz, ^{3}JHH = 8 Hz, H^m), 6.93 (d, 1H, $^3J_{HH}$ = 6 Hz, H^{5a}), 6.88 (t, 1H, $^3J_{HH}$ = 8 Hz, H^p), 2.29 (s, 2H, $^2J_{PtH}$ = 87 Hz, $PtCH_2$), 1.53 (s, 9H, *t*Bu), 1.42 (s, 9H, *t*Bu), 1.36 (s, 6H, CMe_2). δ(^{13}C) 163.2, 161.3,157.3, 155.1, 153.8, 149.2, 147.8,

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127.6, 127.5, 125.0, 124.6, 123.9, 119.5, 118.8, 42.0, 36.1, 35.9, 32.4 (Me), 30.6 (Me of *t*Bu), 30.2 (Me of *t*Bu), 23.8 (CH_2).

[PtHCl($CH_2CMe_2C_6H_4$)(bubipy)], 10. To a solution of complex **4** (0.018 g, 0.031 mmol) in acetone-d_6 (1 mL) in a NMR tube at −50 °C was added 1 mL of solution of cold HCl, generated by reaction of Me_3SiCl (19.6 μL, 0.154 mmol) with H_2O (2.8 μL, 0.154 mmol) in 5 mL acetone-d_6. The formation of complex **10** was monitored by ^1H NMR. NMR in acetone-d_6 at −50 °C: $\delta(^1H)$ = 9.27 (d, 1H, $^3J_{HH}$ = 6 Hz, H^{6a}), 8.96 (d, 1H, $^3J_{HH}$ = 6 Hz, H^{6b}), 8.86, 8.91 (s, each 1H, H^{3a}, H^{3b}), 7.98 (d, 1H, $^3J_{HH}$ = 6 Hz, $^3J_{PtH}$ = 39 Hz, H^3), 7.84, 7.86 (d, each 1H, $^3J_{HH}$ = 6 Hz, H^{5a}, H^{5b}), 7.52 (d, 1H, $^3J_{HH}$ = 7 Hz, H^6), 6.92 (dd, 1H, $^3J_{HH}$ = 7 Hz, 6 Hz, H^5), 6.79 (t, 1H, $^3J_{HH}$ = 6 Hz, H^5), 2.56, 2.24 (d, each 1H, $^2J_{HH}$ = 15 Hz, $PtCH^aH^b$), 1.44, 1.45 (s, each 3H, CMe^aMe^b), 1.39 (s, 18H, *t*Bu), −19.14 (s, $^1J_{PtH}$ = 1512 Hz, PtH).

[$PtCl_2$(phen*)], 11. To a solution of [$PtCl_2(SMe_2)_2$] (0.121 g, 0.310 mmol) in CH_2Cl_2 (5 mL) was added phen* (0.0.073 g, 0.310 mmol). The product formed as an insoluble yellow solid, which was separated, washed with CH_2Cl_2 (2 × 10 mL) and pentane (2 × 10 mL) and dried under vacuum. Yield: 0.114 g, 73%. Anal. Calcd for $C_{16}H_{16}Cl_2N_2Pt$: C, 38.26; H, 3.21; N, 5.58. Found: C, 38.09; H, 3.27; N, 5.39%.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00650.

Selected NMR spectra, structure of *cis*-[$PtCl_2(SMe_2)_2$], summary of crystallographic data (PDF)

Calculated atomic coordinates for the complexes calculated by DFT (XYZ)

Accession Codes

CCDC 1849221−1849227 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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