Synthesis of Trimethylplatinum(IV) Complexes with *N,N*- and *N,O*-Heterocyclic Carbene Ligands and Their Reductive C−C Elimination Reactions

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Abstract: Reactions of the platinum(IV) complexes [PtMe$_3$(OCMe$_2$)$_3$](BF$_4$) (**1**(BF$_4$)), [(PtMe$_3$I)$_4$] (**2**), and [PtMe$_3$I(py)$_2$] (**3**) with the *N,N*-heterocyclic carbene 1,3-dimethylimidazol-2-ylidene (*N,N*-hc, **4**) resulted in a rapid reductive elimination of ethane, yielding platinum(II) complexes [PtMe(*N,N*-hc)$_3$]$^+$ (**7**), *trans*-[PtMeI(*N,N*-hc)$_2$] (**8**), and *cis*-[PtMe(py)(*N,N*-hc)$_2$]$^+$ (**10**), respectively. Subsequent substitution of the iodo ligand in **8** by pyridine resulted in the formation of *trans*-[PtMe(py)(*N,N*-hc)$_2$](CF$_3$COO) (**9**(CF$_3$COO)). **9** and **10** are stereoisomers. In contrast to this, the analogous reaction of [PtMe$_3$(OCMe$_2$)$_3$](BF$_4$) (**1**(BF$_4$)) with the *N,O*-heterocyclic carbene 3-methyloxazol-2-ylidene (*N,O*-hc, **5**) was found to yield the tris(carbene)trimethylplatinum(IV) compound [PtMe$_3$(*N,O*-hc)$_3$](BF$_4$) (**12**(BF$_4$)), which is thermally stable up to 218 °C in the solid state. Furthermore, reactions of [{PtMe$_3$(acac)}$_2$] (**15**) with the *N,X*-heterocyclic carbenes (X = N, O, S; *N,S*-hc = 3-methylthiazol-2-ylidene, **6**) resulted in the formation of monocarbenetrimethylplatinum(IV) complexes [PtMe$_3$(acac)(*N,X*-hc)] (X = N, **16**; X = O, **17**; X = S, **18**), which were found to be stable against reductive C−C elimination at ambient temperature. Reactions of **16** and **17** with 2,2′-bipyridine (bpy) in the presence of stoichiometric amounts of H(BF$_4$) yielded cationic monocarbeneplatinum(IV) complexes, which were isolated as tetrafluoroborate salts [PtMe$_3$(bpy)(*N,X*-hc)](BF$_4$) (X = N, **19**(BF$_4$); X = O, **20**(BF$_4$)). The compounds have been fully characterized analytically and NMR spectroscopically, and for the bis(carbene)platinum(II) compound **9**(CF$_3$COO) as well as the monocarbeneplatinum(IV) compounds **16** and **20**(BF$_4$) by single-crystal X-ray diffraction analyses. DFT calculations of mono-, bis-, and tris(carbene)trimethylplatinum(IV) complexes and their propensity to reductive eliminate ethane were performed. In accordance with the experimental findings, a much higher stability of the tris(*N,O*-hc)- compared with the tris(*N,N*-hc)trimethylplatinum(IV) complexes against reductive ethane elimination was found, which could be ascribed mainly to a higher steric demand of the *N,N*-hc ligand.

1. Introduction

The elementary steps both in organometallic chemistry and in homogeneous catalysis can be severely influenced and directed by electronic and steric properties of "innocent" coligands. In this respect five-membered *N*-heterocyclic carbenes (NHCs) with saturated as well as unsaturated rings have attracted more and more attention over the years.[1] They have proved to be strong σ-donor ligands and, in general, (if any) only weak π acceptors (compared to conventional phosphine ligands).[2,3] Furthermore, the electronic properties as well as the steric demand of these ligands can effectively be modified by variation of the N−R groups (**I** in Scheme 1).[3] Further variation can be achieved, for instance, by changing the heteroatom resulting in

N,X-heterocyclic ligands (X = O, S) and by making use of multidentate carbene ligands (**II** in Scheme 1).[4]

In contrast to the huge amount of complexes of NHCs with transition metals in lower oxidation states, only a limited number of these complexes are known with transition metals in higher oxidation states, and they are mainly complexes of "early" transition metals like Ti(IV), Zr(IV), V(V), and Re(V)/Re(VII).[1d,5] The most remarkable examples for the late transition metals are the ruthena(IV)−cyclobutane complexes containing NHC ligands, observed NMR spectroscopically at low temperatures, which gave insight into the olefin metathesis reaction,[6] as well as stable Ir(III) complexes with NHC ligands like [IrCl$_2$cp*(*N,N*-hc)] and [Ircp*(*N,N*-hc)(MeCN)$_2$]$^{2+}$, which were investigated for their activity in C−H activation as well as transfer

(1) (a) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2162. (b) Fürstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012. (c) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18. (d) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (e) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815. (f) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122.

(2) Tonner, R.; Heydenrych, G.; Frenking, G. *Chem.−Asian J.* **2007**, *2*, 1555.

(3) Cavallo, L.; Correa, A.; Costabile, C.; Jacobsen, H. *J. Organomet. Chem.* **2005**, *690*, 5407.

(4) (a) Quezada, C. A.; Garrison, J. C.; Tessier, C. A.; Youngs, W. J. *J. Organomet. Chem.* **2003**, *671*, 183. (b) Hahn, F. E. *Angew. Chem., Int. Ed. Engl.* **2006**, *45*, 1348.

(5) (a) Herrmann, W. A.; Öfele, K.; Elison, M.; Kühn, F. E.; Roesky, P. W. *J. Organomet. Chem.* **1994**, *480*, C7. (b) Abernethy, C. D.; Codd, G. M.; Spicer, M. D.; Taylor, M. K. *J. Am. Chem. Soc.* **2003**, *125*, 1128.

(6) (a) Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2005**, *127*, 5032. (b) Wenzel, A. G.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 16048.

Scheme 1
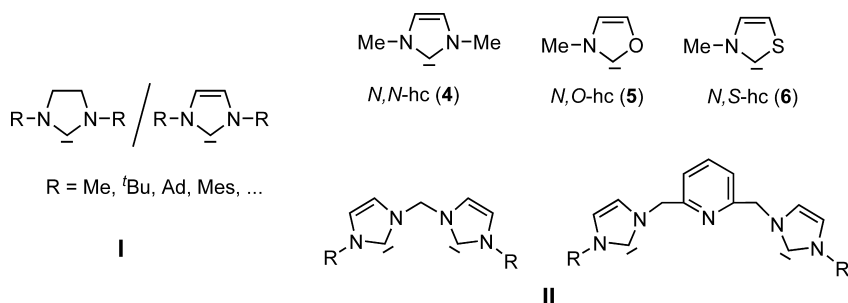
Scheme 2
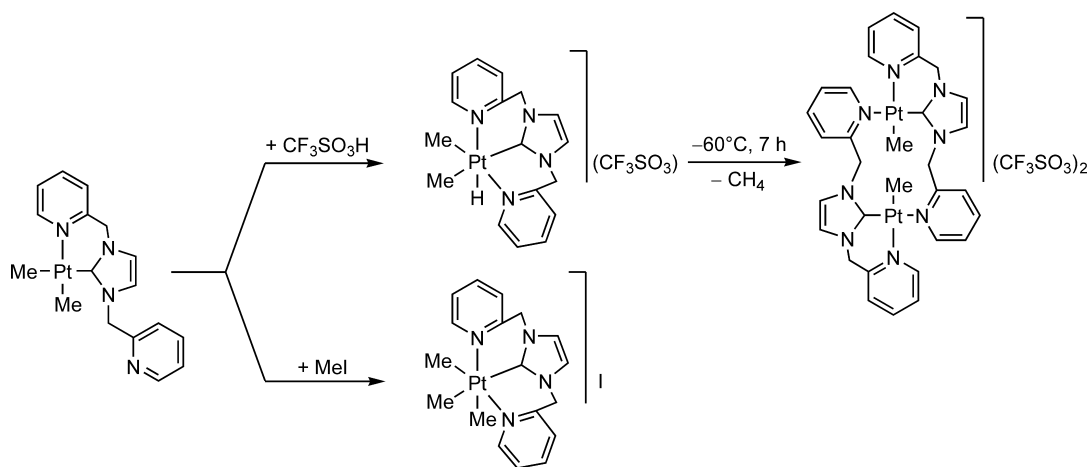
hydrogenation reactions.[7] In the case of Pt(IV), some bis(NHC) complexes of the type *trans*-[PtX$_4$(NHC)$_2$] (NHC = 1,3-dimethylbenzimidazol-2-ylidene, 4,4-dimethyloxazolidin-2-ylidene; X = Cl, CN, ...) have been prepared starting from Pt(IV) complexes mainly via ligand substitution reactions.[8] Furthermore, Pt(IV) complexes bearing NHC ligands can be assumed to be intermediates in an oxidative addition/reductive elimination reaction sequence starting from Pt(II) complexes.[9] A dimethylhydridoplatinum(IV) complex bearing a NHC ligand with two additional pyridine donor sites was identified to be an intermediate in such a reaction. In accordance with the reactivity of other platinum(IV) hydrides,[10] it undergoes a reductive C–H elimination even at −60 °C, resulting in a dinuclear platinum(II)–NHC complex (Scheme 2). A requisite trimethylplatinum(IV) complex was found to be stable at room temperature (Scheme 2).[11] Herein we report the synthesis and characterization of trimethylplatinum(IV) complexes with monodentate *N,N*-, *N,O*-, and *N,S*-heterocyclic carbene ligands (4−6, Scheme 1) and their reductive C−C elimination reactions.

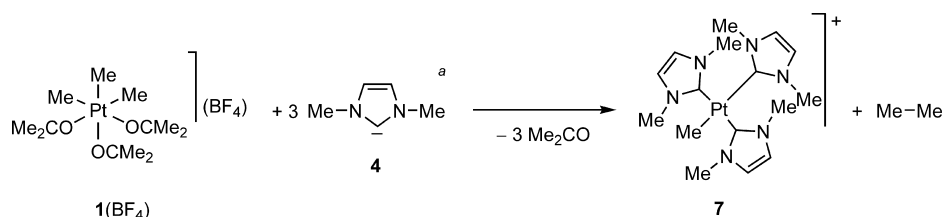The formation of heterocyclic carbeneplatinum(IV) complexes via ligand substitution reactions may be hampered by the kinetic inertness of Pt(IV) complexes due to the low-spin d^6 electron configuration of Pt(IV).[12] The cationic tris(acetone) complex in [PtMe$_3$(OCMe$_2$)$_3$](BF$_4$)[13] (**1**(BF$_4$)) was found to readily undergo ligand substitution reactions as acetone is only a weakly bound ligand which has, additionally, a methyl ligand in the *trans* position exerting a large *trans* effect. Therefore, this complex was used as a starting compound for the formation of the carbene complexes.

Trimethylplatinum(IV) complexes are known to undergo reductive elimination of ethane, especially in the presence of "soft" coligands like phosphines, whereas harder coligands like *N*-donors of the bipyridine type better stabilize the Pt(IV) oxidation state.[14] This tendency is much more pronounced in the stability of organopalladium complexes (Pd(II) versus Pd(IV)).[15] Furthermore, ligands that are strong donors should be able to stabilize higher oxidation states thermodynamically. Thus, it is of interest to investigate organoplatinum(IV) complexes having NHC coligands (strong σ-donors but hard ligands) with respect to reductive C−C eliminations, a fundamental step in organometallic chemistry and homogeneous catalysis.[16]

(7) (a) Corberan, R.; Peris, E. *Organometallics* **2008**, *27*, 1954. (b) Hanasaka, F.; Fujita, K.; Yamaguchi, R. *Organometallics* **2005**, *24*, 3422. (c) Hanasaka, F.; Tanabe, Y.; Fujita, K.; Yamaguchi, R. *Organometallics* **2006**, *25*, 826.

(8) (a) Demidov, V. N.; Kukushkin, Y. N.; Vedeneeva, L. N.; Belyaev, A. N. *Zh. Obsh. Khim.* **1988**, *58*, 738. (b) Weigand, W.; Nagel, U.; Beck, W. *Z. Naturforsch., B: Chem. Sci.* **1988**, *43*, 328.

(9) (a) Cetinkaya, B.; Cetinkaya, E.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 906. (b) Rourke, J. P. In *Comprehensive Organometallic Chemistry III*; Mingos, D. M. P., Crabtree, R. H., Eds.; Elsevier: Oxford, 2007; Vol. 8, p 405.

(10) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *219−221*, 157.

(11) Prokopchuk, E. M.; Puddephatt, R. J. *Organometallics* **2003**, *22*, 563.

(12) (a) Atwood, J. D. In *Inorganic and organometallic reaction mechanisms*; VCH: New-York, 1997. (b) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 846.

(13) Junicke, H.; Bruhn, C.; Ströhl, D.; Kluge, R.; Steinborn, D. *Inorg. Chem.* **1998**, *37*, 4603.

(14) Goldberg, K. I.; Yan, J. Y.; Breitung, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 6889.

(15) (a) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182. (b) van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706. (c) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1722.

Scheme 3

^{a} Prepared from (*N,N*-hcH)(BF$_4$)/KOAc.

Scheme 4
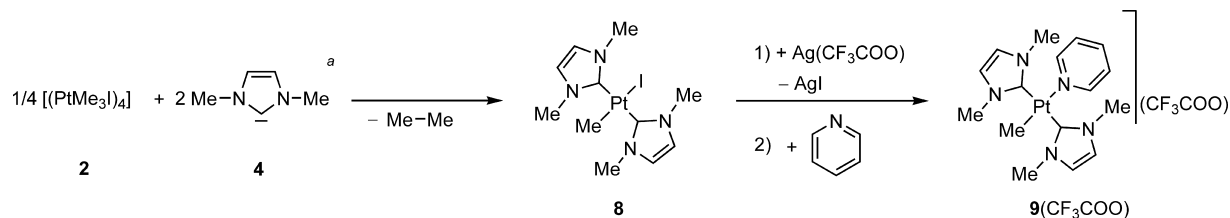
^{a} Prepared from (*N,N*-hcH)(BF$_4$)/KOAc.

2. Results and Discussion

2.1. Syntheses and Reactivity of *N,N*-Heterocyclic Carbene Platinum(II) Complexes. The syntheses of *N,X*-heterocyclic platinum complexes (X = N, O, S) was accomplished by substitution reactions. In general, such substitutions with *N,X*-heterocyclic carbenes might be performed by two different methods: (i) by synthesis and isolation of stable carbenes, which can be used as reactants, or (ii) by in situ synthesis of carbenes from a precursor compound. For all reactions reported in this article method (ii) was chosen, due to the reported low stability of *N,O*- and *N,S*-heterocyclic carbenes.[17]

The reaction of [PtMe$_3$(OCMe$_2$)$_3$](BF$_4$) (**1**(BF$_4$)) with an excess of (*N,N*-hcH)(BF$_4$) in the presence of KOAc in acetone led to the formation of the cationic tris(carbene)platinum(II) complex [PtMe(*N,N*-hc)$_3$]$^+$ (**7**) with reductive elimination of ethane (Scheme 3), whereas the ^{1}H NMR spectra indicated an almost quantitative conversion >90%. The subsequent workup procedure (see Experimental Section) resulted in the formation of an oil which could not be purified further. The oily substance was characterized by NMR spectroscopy (^{1}H, ^{13}C), thereby verifying the constitution of the cationic complex **7** and indicating the presence of residual amounts of the imidazolium salt (*N,N*-hcH)(BF$_4$). Even the use of platinum(IV) starting complexes with stronger coordinating coligands could not prevent the unwanted reductive elimination of ethane. Thus, the reaction of [(PtMe$_3$I)$_4$] (**2**) with (*N,N*-hcH)(BF$_4$) in the presence of KOAc proceeded with reductive elimination of ethane, yielding the platinum(II) complex *trans*-[PtMeI(*N,N*-hc)$_2$] (**8**) (Scheme 4). The reaction of **8** with Ag(CF$_3$COO) and pyridine led to the substitution of the iodo ligand by pyridine, yielding *trans*-[PtMe(py)(*N,N*-hc)$_2$](CF$_3$COO) (**9**(CF$_3$COO)) (Scheme 4). The two compounds **8** and **9**(CF$_3$COO) were isolated respectively as pale yellow and colorless, air-stable crystals in high yields (90%/80%) and were unambiguously characterized analytically, NMR spectroscopically, and by X-ray diffraction analysis (**9**(CF$_3$COO)).
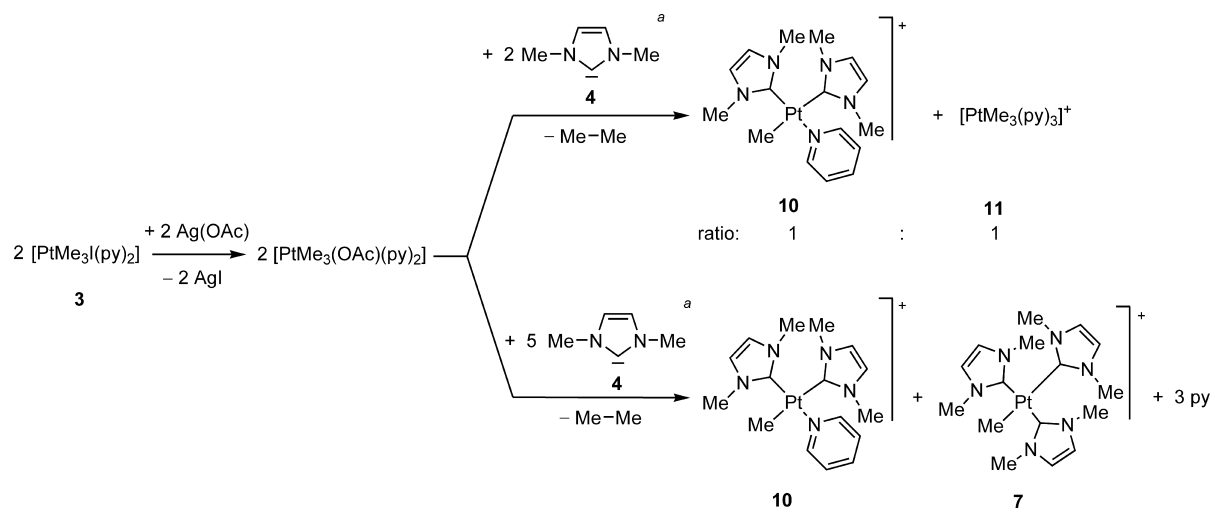
Furthermore, the reaction of the platinum(IV) complex [PtMe$_3$(OAc)(py)$_2$] (obtained from **3** and AgOAc) with a stoichiometric amount of (*N,N*-hcH)(BF$_4$)/KOAc in acetone resulted in reductive elimination of ethane and the formation of *cis*-[PtMe(py)(*N,N*-hc)$_2$]$^+$ (**10**) and [PtMe$_3$(py)$_3$]$^+$ (**11**) (Scheme 5). The use of an excess of the carbene ligand resulted in a mixture of bis- and tris(carbene)platinum(II) complexes *cis*-[PtMe(py)(*N,N*-hc)$_2$]$^+$ (**10**) and [PtMe(*N,N*-hc)$_3$]$^+$ (**7**) (Scheme 5). If a large excess (>10 equiv) of the carbene was used, a complete conversion yielding the tris(carbene)complex **7** was observed. Although these complexes were not isolated as pure substances, their identities could be determined unambiguously by NMR spectroscopy (^{1}H, ^{13}C) and ESI mass spectrometry.

2.2. Syntheses and Reactivity of Heterocyclic Carbenetrimethylplatinum(IV) Complexes. Reactions of the *N,O*-heterocyclic carbene with trimethylplatinum(IV) complexes were also investigated. In contrast to the reaction of [(PtMe$_3$(OCMe$_2$)$_3$]-(BF$_4$) (**1**(BF$_4$)) with the *N,N*-heterocyclic carbene **4**, the analogous reaction with the *N,O*-heterocyclic carbene **5** proceeded without the reductive elimination of ethane. Thus, the reaction of [PtMe$_3$(OCMe$_2$)$_3$](BF$_4$) (**1**(BF$_4$)) with an excess of the *N,O*-heterocyclic azolium salt (*N,O*-hcH)(BF$_4$) and KOAc yielded a tris(carbene)trimethylplatinum(IV) complex salt, [PtMe$_3$(*N,O*-hc)$_3$](BF$_4$) (**12**(BF$_4$)) (Scheme 6), which was isolated as colorless, air-stable crystals in moderate yield (40%). To study this difference in reactivity, a half equivalent of either (*N,N*-hcH)(BF$_4$) or (*N,O*-hcH)(BF$_4$) and an excess of KOAc was added to [PtMe$_3$(OCMe$_2$)$_3$](BF$_4$) (**1**(BF$_4$)). Characterization of the reaction mixtures by ^{1}H NMR spectroscopy indicated the formation of *N,N*- and *N,O*-heterocyclic monocarbeneplatinum-(IV) complexes [PtMe$_3$Y$_2$(*N,X*-hc)]^z (X = N, **13**; X = O, **14**; Y = OCMe$_2$, OAc; z = 1, 0, −1) with a degree of conversion of 30% and 10%, respectively. The isolation of these complexes failed due to decomposition reactions, and therefore the nature of the ligand Y (acetone vs acetate) remains unclear. On the other hand, no defined carbene platinum complexes could be obtained in reactions of the other complexes ([(PtMe$_3$I)$_4$], **2**; [PtMe$_3$(py)$_2$], **3**) with (*N,O*-hcH)(BF$_4$) in the presence of KOAc, probably due to the low stability of the corresponding *N,O*-heterocyclic carbene **5** in solution.[17]

The dinuclear acetylacetonatoplatinum(IV) complex [{PtMe$_3$-(acac)}$_2$] (**15**) proved to be redox stable in reactions with all of
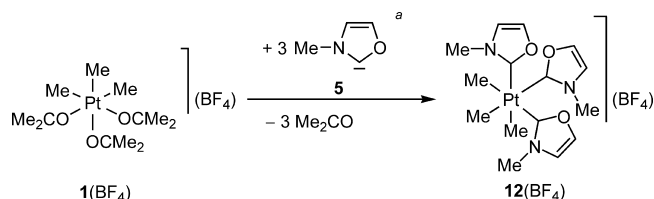
(16) (a) Öfele, K.; Herrmann, W. A.; Mihalios, D.; Elison, M.; Herdtweck, E.; Scherer, W.; Mink, J. *J. Organomet. Chem.* **1993**, *459*, 177. (b) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485. (c) Lee, M.-T.; Hu, C.-H. *Organometallics* **2004**, *23*, 976.
(17) Arduengo, A. J., III *Acc. Chem. Res.* **1999**, *32*, 913.

Scheme 5

2 [PtMe₃I(py)₂] **3**

+ 2 Ag(OAc) / − 2 AgI → 2 [PtMe₃(OAc)(py)₂]

+ 2 Me–N⌒N–Me **4**, − Me–Me →

10 + [PtMe₃(py)₃]⁺ **11**

ratio: 1   :   1

+ 5 Me–N⌒N–Me **4**, − Me–Me →

10 + **7** + 3 py

a Prepared from (*N,N*-hcH)(BF₄)/KOAc.

Scheme 6

1(BF₄) + 3 Me–N⌒O **5**, − 3 Me₂CO → **12**(BF₄)

a Prepared from (*N,O*-hcH)(BF₄)/KOAc.

the heterocyclic carbenes *N,X*-hc (X = N, **4**; X = O, **5**; X = S, **6**) under investigation. Thus, the reaction of **15** with (*N,X*-hcH)(BF₄) (X = N, O, S) in the presence of an excess of KOAc in acetone led to the formation of the neutral monocarbenetrimethylplatinum(IV) complexes [PtMe₃(acac)(*N,X*-hc)] (X = N, **16**; X = O, **17**; X = S, **18**) (Scheme 7). In the case of the *N,N*-heterocyclic carbene complex [PtMe₃(acac)(*N,N*-hc)] (**16**), a stoichiometric amount of the azolium salt (*N,N*-hcH)(BF₄) was used, whereas in the synthesis of **17/18** an excess of the azolium salts (*N,X*-hcH)(BF₄) (X = O, S) was required to compensate for the limited stability of the *N,O*- and *N,S*-heterocyclic carbenes.[17] All complexes were isolated as colorless, air-stable crystals in moderate yields (**16**, 70%; **17/18**, 60%) and unambiguously characterized analytically, NMR spectroscopically, and by X-ray diffraction analysis (**16**). Reactions of these monocarbenetrimethylplatinum(IV) complexes [PtMe₃(acac)-(*N,X*-hc)] (X = N, **16**; X = O, **17**) with bipyridine in the presence of stoichiometric amounts of H(BF₄) led to the substitution of the acetylacetonato ligand by the bipyridine ligand, yielding the compounds [PtMe₃(bpy)(*N,X*-hc)](BF₄) (X = N, **19**(BF₄); X = O, **20**(BF₄)) (Scheme 7). Both compounds were isolated as colorless, air-stable crystals in high yields (80%) and characterized analytically, NMR spectroscopically, and by X-ray diffraction analysis (**20**(BF₄)).

2.3. NMR Spectroscopy. All compounds were characterized by means of ¹H and ¹³C NMR spectroscopy with all signals in the expected range and having the correct intensities in the ¹H NMR spectra. In the case of the platinum(II) complexes, in accordance with the *trans* (**8**, **9**) and *cis* (**10**) configurations, one and two sets of signals, respectively, were found for the carbene ligands. The magnitude of the $^1J_{Pt,C}$ and $^2J_{Pt,H}$ coupling constants of the methyl ligands (Table 1) exhibited the expected order of the *trans* influence ($^1J_{Pt,C}/^2J_{Pt,H}$ in Hz): I⁻ (760.7/93.0)

< py (662.0/84.2) < *N,N*-hc (494.7−531.7/57.1−62.7). In Table 1, analogous complexes with Fischer-type carbene ligands are included for comparison. Inspection of the requisite coupling constants exhibited a lower *trans* influence of the *N,N*-heterocyclic carbenes compared with Fischer-type carbenes ($^1J_{Pt,C}/^2J_{Pt,H}$ in Hz): *N,N*-hc **7/10** (494.7−531.7/62.7−57.1) < =C(OR)R′ **21/22** (338−373/47.8−48.0).

In the case of the neutral platinum(IV) complexes [PtMe₃-(acac)(*N,X*-hc)] (X = N, **16**; X = O, **17**; X = S, **18**), the magnitude of the $^1J_{Pt,C}$ and $^2J_{Pt,H}$ coupling constants of the methyl ligands (Table 2) follows the order of the *trans* influence ($^1J_{Pt,C}/^2J_{Pt,H}$ in Hz): acac (725.5−731.3/75.5−76.4) ≪ *N,O*-hc (563.1/53.1) ≈ *N,S*-hc (562.0/53.5) < *N,N*-hc (547.0/52.3). A similar order was observed for the cationic complexes [PtMe₃(bpy)(*N,X*-hc)]⁺ (X = N, **19**; X = O, **20**) ($^1J_{Pt,C}/^2J_{Pt,H}$ in Hz): bpy (660.7−652.0/69.7−69.3) ≪ *N,O*-hc (514.0/54.2) < *N,N*-hc (503.8/53.3). These values indicate a significantly larger *trans* influence for the *N,N*- than for the *N,O*-heterocyclic carbene ligand, which might be attributed to the higher electronegativity of the O compared with the N atom (χ = 3.44 vs 3.04).[18]

2.4. Crystal Structures. Crystals suitable for X-ray diffraction analyses were obtained by crystallization of [PtMe₃(acac)(*N,N*-hc)] (**16**) from benzene/*n*-pentane and of *trans*-[PtMe(py)(*N,N*-hc)₂](CF₃COO) (**9**(CF₃COO)) and [PtMe₃(bpy)(*N,O*-hc)](BF₄) (**20**(BF₄)) from CH₂Cl₂/*n*-pentane. Complex **9**(CF₃COO) crystallized as isolated cations and anions without unusual intermolecular interactions. The structure of the cation *trans*-[PtMe(py)(*N,N*-hc)₂]⁺ (**9**) is presented in Figure 1, where selected bond lengths and angles are given in the caption. The platinum(II) atom exhibited a C₃N primary donor set in a square planar arrangement (sum of interior angles: 360.0(8)°). In accordance with NMR spectroscopic measurements, the carbene ligands are in mutual *trans* positions. Their heterocyclic rings are nearly perpendicular to the coordination plane (N2–C2–Pt–C1, 96.6(9)°; N4–C3–Pt–C1, −98(1)°), probably for steric reasons. As expected, the Pt–C$_{sp^2}$ bonds are shorter than the Pt–C$_{sp^3}$ bond (2.00(1)/2.02(1) Å vs 2.07(1) Å). Furthermore, the platinum–carbene bonds are within the range reported for

(18) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins: New York, 1993.

Scheme 7

X = N−Me (**4**),
O   (**5**),
S   (**6**)

X = N−Me (**16**),
O   (**17**),
S   (**18**)

X = N−Me (**19**(BF₄)),
O   (**20**(BF₄))
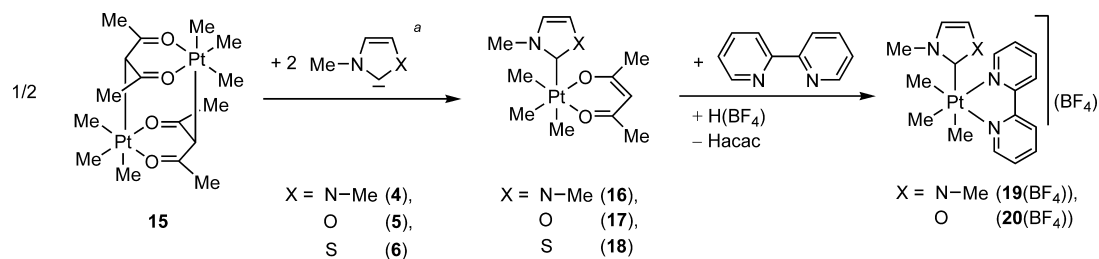
a Prepared from the requisite azolium salt and KOAc.

Table 1. Selected Coupling Constants (in Hz) for Carbene Platinum(II) Complexes [PtMe(N,N-hc)₃]⁺ (**7**), *trans*-[PtMeI(N,N-hc)₂] (**8**), *trans*-[PtMe(py)(N,N-hc)₂](CF₃COO) (**9**(CF₃COO)), and *cis*-[PtMe(py)(N,N-hc)₂]⁺ (**10**)

			7	**8**	**9**(CF₃COO)	**10**	**21**(OTf)[d]	**22**(PF₆)[d]
$^1J_{Pt,C}$	PtCH₃	*trans* to I/N		760.7[b]	662.0[a]			
		trans to C	494.7[a]			531.7[a]	388	373.4
$^2J_{Pt,H}$	PtCH₃	*trans* to I/N		93.0[b]	84.2[a]			
		trans to C	62.7[c]			57.1[a]	47.8	48.0

a Recorded in acetone-d_6. *b* Recorded in chloroform-d. *c* Recorded in methanol-d_4. *d* The values of *trans*-[Pt(Me){=C(CH₂)₃O}(PPh₃)₂](OTf) (**21**(OTf))[41] and *trans*-[PtMe(PMe₂Ph)₂{=C(OMe)Me}](PF₆) (**22**(PF₆))[42] are given for comparison.

Table 2. Selected NMR Data (δ in ppm, J in Hz)[a] for Platinum(IV) Complexes [PtMe₃(acac)(N,X-hc)] (X = N, **16**; X = O, **17**, X = S, **18**), [PtMe₃(bpy)(N,X-hc)](BF₄) (X = N, **19**(BF₄); X = O, **20**(BF₄)), [PtMe₃(N,O-hc)₃](BF₄) (**12**(BF₄)), and [PtMe₃Y₂(N,X-hc)]^z (X = N, **13**; X = O, **14**)[b]

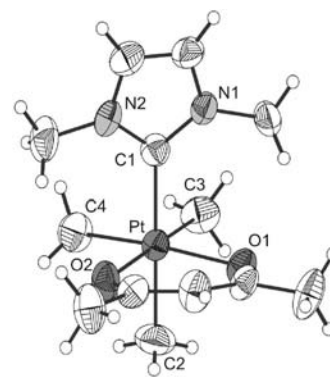|			**16**	**17**	**18**	**19**(BF₄)	**20**(BF₄)	**12**(BF₄)	**13**	**14**
δ_C	$C_{carbene}$		175.7	201.5	215.4	169.5	192.8	184.5		
$^1J_{Pt,C}$	PtCH₃	*trans* to C	547.0	563.1	562.0	503.8	514.0	494.7		
		trans to O/N	731.3	725.5	729.0	660.7	652.0			
	PtC$_{carbene}$		658.3	699.0	581.6	652.6	688.9	662.9		
$^2J_{Pt,H}$	PtCH₃	*trans* to C	52.3[c]	53.1[c]	53.5[c]	53.3	54.2	55.6[d]	45.9[c]	51.9[c]
		trans to O/N	76.4[c]	75.5[c]	75.5[c]	69.3	69.7		79.5[c]	80.1[c]

a If not otherwise stated, recorded in chloroform-d. *b* Y₂ = (OCMe₂)₂, $z = +1$; Y₂ = (OAc)₂, $z = -1$; Y₂ = (OAc)(OCMe₂), $z = 0$. *c* Recorded in acetone-d_6. *d* Recorded in methanol-d_4.
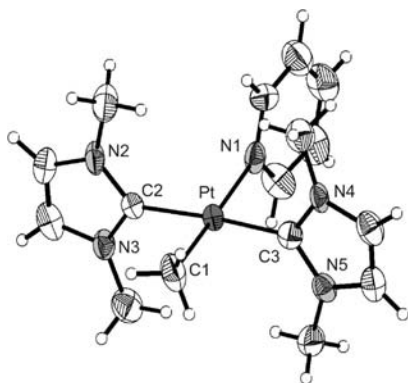
Figure 1. Molecular structure of the cation in crystals of *trans*-[PtMe-(py)(N,N-hc)₂](CF₃COO) (**9**(CF₃COO)), showing 50% thermal ellipsoids. Selected bond distances (Å) and angles (°): Pt−C1, 2.07(1); Pt−C2, 2.00(1); Pt−C3, 2.02(1); Pt−N1 2.152(9); C1−Pt−N1, 177.4(5); C2−Pt−C3, 175.4(4); C1−Pt−C2, 87.5(4); C1−Pt−C3, 88.0(5); N2−C2−Pt−C1, 96.6(9); N4−C3−Pt−C1, −98(1).
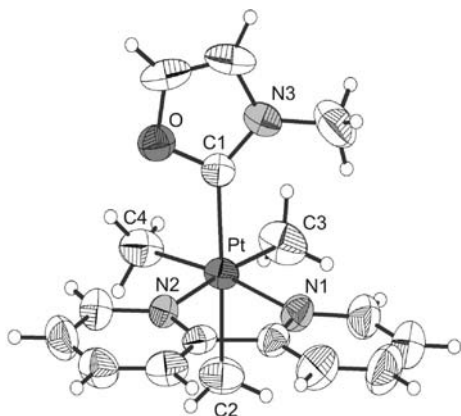
Figure 2. Molecular structure of [PtMe₃(acac)(N,N-hc)] (**16**), showing 50% thermal ellipsoids. Selected bond distances (Å) and angles (°): Pt−C1, 2.11(1); Pt−C2, 2.03(1); Pt−C3, 2.07(1); Pt−C4, 2.05(1); Pt−O1, 2.165(7); Pt−O2, 2.165(7); C1−Pt−C2, 175.1(5); C1−Pt−C3, 94.7(5); C1−Pt−C4, 95.6(5); C1−Pt−O1, 89.3(3); C1−Pt−O2, 88.1(4).

other Pt(II)−C$_{N,N\text{-hc}}$ bonds (median 1.989 Å, lower/upper quartile 1.967/2.023 Å, number of observations $n = 26$).[19]

Compounds **16** and **20**(BF₄) crystallized as isolated molecules and isolated cations and anions, respectively, without unusual interactions. The molecular structures of [PtMe₃(acac)(N,N-hc)] and [PtMe₃(bpy)(N,O-hc)]⁺ are given in Figures 2 and 3. Both

structures exhibited a slightly distorted octahedral coordination sphere of the platinum(IV) atom (*trans* angles: 175.0(4)−176.6(4)°, **16**; 172.9(3)−178.4(4)°, **20**), showing the three methyl ligands in facial arrangement. Unexpectedly, the Pt−C$_{N,N\text{-hc}}$ bond in **16** (2.11(1) Å) is significantly longer than analogous Pt(II)−C$_{N,N\text{-hc}}$ bonds (see preceding discussion). This might be caused by a steric repulsion between the *N*-methyl groups of the carbene ligand and the *cis*-standing methyl and acetylacetonato ligands.

In both complexes **16** and **20**, the planes of the carbene ligands lie between the methyl ligands and the coligands (acac/

(19) *Cambridge Structural Database (CSD)*, Version 5.29; Cambridge University Chemical Laboratory: Cambridge, 2007.

Figure 3. Molecular structure of the cation in crystals of [PtMe$_3$(bpy)(*N,O*-hc)](BF$_4$) (**20**(BF$_4$)), showing 50% thermal ellipsoids. Selected bond distances (Å) and angles (°): Pt−C1, 2.090(7); Pt−C2, 2.104(8); Pt−C3, 2.040(8); Pt−C4, 2.065(8); Pt−N1, 2.157(7); Pt−N2, 2.153(7); C1−Pt−C2, 178.4(4); C1−Pt−C3, 93.4(3); C1−Pt−C4, 88.6(3); C1−Pt−N1, 96.1(3); C1−Pt−N2, 89.2(2).

bpy), thus bisecting the C−Pt−O and C−Pt−N angles, respectively. Quantum chemical calculations at the DFT level of theory demonstrated that this conformation is the most stable one in the gas phase (see Supporting Information).

2.5. Quantum Chemical Calculation. The synthetic work exhibited that the cationic tris(acetone)trimethylplatinum(IV) complex **1** reacted with an excess of the *N,O*-heterocyclic carbene yielding a cationic tris(carbene)trimethylplatinum(IV) complex [PtMe$_3$(*N,O*-hc)$_3$]$^+$ (**12**), whereas the requisite reaction with an excess of *N,N*-heterocyclic carbene resulted in reductive elimination of ethane and the formation of the cationic tris(carbene)monomethylplatinum(II) complex **7** (Scheme 8). To gain further insight into this fundamental difference in reactivity, comprehensive quantum chemical calculations were performed at the DFT level of theory. Because the ligand substitution reactions yielding the cationic tris(carbene)complexes **7** and **12** starting from the tris(acetone) complex **1** are stepwise processes, the monocarbenebis(acetone)-(**26c-1/33c-1**) and the bis(carbene)monoacetone−trimethylplatinum(IV) complexes (**39c-1/44c-1**) were included in the calculations and had − along with the tris(carbene)trimethylplatinum(IV) complexes **47c-1/12c-1** − also to be considered as starting complexes for the ethane elimination. Furthermore, a coordination of the acetate anion (instead of acetone) to platinum was taken into account whereby the acetato ligand can be either η^1 or η^2 bound.

[Numbering scheme of calculated compounds: The number is followed by the letter "c". In general, when calculations revealed the existence of different isomers, they are numbered like **26c-1**, **26c-2**, ..., where "-1" refers to the energetically most stable isomer.]

To establish whether the mono- and bis(carbene) complexes with acetone or acetato ligands are thermodynamically more stable, the Gibbs free energies of all relevant ligand substitution reactions (acetone vs acetate) were calculated (Table 3). In all these calculations the effect of the solvent (acetone) was modeled according to Tomasi's polarized continuum model.[20] The values in the gas phase showed, in general, the same trend and are given in the Supporting Information. The most stable

monocarbenetrimethylplatinum(IV) complex has an η^2-acetato ligand bound, whereas all other relevant monocarbenetrimethylplatinum(IV) complexes were found to have significantly higher energies (>11 kcal/mol, entries 2−6). In the case of the *N,N*-heterocyclic bis(carbene)trimethylplatinum(IV) complexes, unexpectedly, the most stable compound proved to be a five-fold coordinated platinum complex **37c-1** (entry 7), whereas in the case of the *N,O*-heterocyclic bis(carbene)trimethylplatinum(IV) complexes the highest stability was observed for the six-fold coordinated acetato complex **43c-1** (entry 8).

The structures of selected *N,N*- and *N,O*-heterocyclic carbenetrimethylplatinum(IV) complexes are presented in Figure 4. Selected structural parameters are given in Table 4. A complete summary including the structures and energies of all complexes calculated within this work is given in the Supporting Information. Comparison of the calculated monocarbene complex [PtMe$_3$(η^2-OAc)(*N,N*-hc)] (**23c-1**) with the structurally similar synthesized complex [PtMe$_3$(η^2-acac)(*N,N*-hc)] (**16**) revealed that the Pt−C bond lengths are in the same range in both complexes (Pt−C$_{methyl}$, 2.057−2.082 Å in **23c-1** versus 2.03(1)−2.07(1) Å in **16**; Pt−C$_{carbene}$, 2.128 Å in **23c-1** versus 2.11(1) Å in **16**). In both the *N,N*- and the *N,O*-heterocyclic complexes, the Pt−C$_{carbene}$ bond lengths demonstrated the order mono- < bis- < tris(carbene) complexes, which parallels the electron density on the platinum(IV) atoms. Furthermore, in the *N,O*-heterocyclic carbene complexes the Pt−C$_{carbene}$ bonds were found to be significantly shorter (up to 0.06 Å) than those in the requisite *N,N*-heterocyclic carbene complexes (Table 4). This might be explained in terms of the higher electronegativity of O (compared with N) resulting − according to Bent's rules[21] − in a higher s-electron density of the carbene donor orbital and/or increasing steric repulsion between the *N*-methyl groups of the *N,N*-heterocyclic carbene ligands and the ligands in the *cis* position.

To gain further insight into the reactivity, the stepwise ligand substitution reactions yielding the tris(carbene) starting from the monocarbene complexes (based on the thermodynamically most stable complexes of each type) are examined (Figure 5). In the case of the *N,N*-heterocyclic carbene complexes, the formation of the bis- (**38c-1/37c-1**) and tris(carbene) complexes (**47c-1**) is nearly thermodynamically neutral. On the other hand, the formation of the requisite *N,O*-heterocyclic bis(carbene) complexes (**43c-1/42c-1**) is also roughly thermodynamically neutral, but the subsequent formation of the tris(carbene)complex (**12c-1**) is highly exergonic ($\Delta G = -11.6/-16.3$ kcal/mol).

Ligand substitution reactions on octahedral platinum(IV) complexes are found, in general, to proceed via dissociative pathways having a five-fold coordinated platinum complex as an intermediate, whereas associative reaction pathways are observed only for platinum(IV) complexes with strongly electron-withdrawing groups.[22] It is known that the transition states of dissociative reactions cannot be calculated.[23] But it can be expected that reactions of the type

$$L_5Pt(IV) - L' \rightleftharpoons L_5Pt(IV) + L'$$
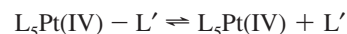
proceed in the exergonic direction without remarkable activation barriers, especially compared to the activation barrier for

(20) (a) Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032. (b) Cossi, M.; Barone, V.; Mennucci, B.; Tomasi, J. *Chem. Phys. Lett.* **1998**, *286*, 253. (c) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151.

(21) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.
(22) (a) Gallego, C.; Gonzales, G.; Martinez, M.; Merbach, A. E. *Organometallics* **2004**, *23*, 2434. (b) Bernhardt, P. V.; Gallego, C.; Martinez, M.; Parella, T. *Inorg. Chem.* **2002**, *41*, 1747.
(23) Lorant, F.; Behar, F.; Goddard, W. A., III; Tang, Y. *J. Phys. Chem. A* **2001**, *105*, 7896.

Scheme 8
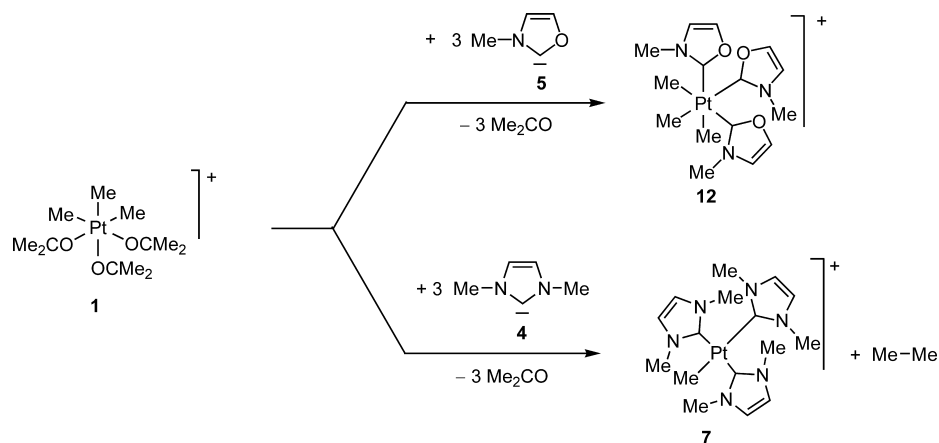
Table 3. Gibbs Free Energies[a] of Substitution Reactions (Acetone versus Acetate) in Mono- and Bis(carbene)trimethylplatinum(IV) Complexes Relative to the Lowest Energetic Conformer in Entries 1 and 7, Respectively, and Number of Conformers (n) of These Complexes[b]

entry	complex	C.N.[d]	X = N		X = O	
			ΔG	n	ΔG	n
	Monocarbene Complexes					
1	[PtMe$_3$(η^2-OAc)(*N,X*-hc)] (**23c/30c**)[c] + OAc$^-$ + 2OCMe$_2$	6	0	2 (4.5)	0	2 (3.1)
2	[PtMe$_3$(η^1-OAc)(*N,X*-hc)] (**23c/30c**) + OAc$^-$ + 2OCMe$_2$	5	11.8	4 (16.8)	11.2	6 (15.6)
3	[PtMe$_3$(OAc)$_2$(*N,X*-hc)]$^-$ (**24c/31c**) + 2OCMe$_2$	6	20.8	3 (23.7)	18.1	2 (23.4)
4	[PtMe$_3$(OAc)(OCMe$_2$)(*N,X*-hc)] (**25c/32c**) + 2OAc$^-$ + OCMe$_2$	6	22.4	1	22.2	1
5	[PtMe$_3$(OCMe$_2$)$_2$(*N,X*-hc)]$^+$ (**26c/33c**) + 2OAc$^-$	6	36.8	1	37.0	1
6	[PtMe$_3$(OCMe$_2$)$_2$(*N,X*-hc)]$^+$ (**27c/34c**) + 2OAc$^-$ + OCMe$_2$	5	34.0	1	34.0	1
	Bis(carbene) Complexes					
7	[PtMe$_3$(*N,X*-hc)$_2$]$^+$ (**37c/42c**) + OAc$^-$ + OCMe$_2$	5	0	1	0	3 (1.7)
8	[PtMe$_3$(OAc)(*N,X*-hc)$_2$] (**38c/43c**) + OCMe$_2$	6	1.6	4 (6.0)	−4.7	9 (3.3)
9	[PtMe$_3$(OCMe$_2$)(*N,X*-hc)$_2$] (**39c/44c**) + OAc$^-$	6	8.4	1	7.3	1

[a] ΔG values are BSSE corrected. [b] The energies of all equilibrium structures are given in the Supporting Information. The free energy of the highest energetic conformer (relative to the most stable one) is given in parentheses. [c] Here and in the following entries the first figure refers to the *N,N*-hc and the second one to the *N,O*-hc complex. [d] Coordination number of Pt.

reductive elimination of ethane, as will be discussed below. From this follows, of course, that in the endergonic direction the activation barriers are only slightly higher than the free reaction energy. Taking this into account, inspection of the energies of the six-fold coordinated carbene complexes together with those of the five-fold coordinated intermediate complexes (Figure 5) shows that an equilibrium between the *N,N*-heterocyclic mono-, bis-, and tris(carbene) complexes (**23c-1** ⇌ **38c-1/37c-1** ⇌ **47c-1**) can be expected, whereas in the case of the *N,O*-heterocyclic carbene complexes the formation of the tris(carbene) complex (**43c-1/42c-1** → **12c-1**) should be irreversible.

The energy profiles of the reductive elimination of ethane in *N,N*- and *N,O*-heterocyclic monocarbeneplatinum(IV) complexes are presented in Figure 6. The transition-state structures of both reactions highlight that an approach of the C-atoms of two methyl ligands and the cleavage of one Pt—O bond of the η^2-OAc ligand take place simultaneously. The activation barriers for the two reactions are very close (25.4 and 27.4 kcal/mol, respectively). According to the Eyring equation based on first-order kinetics, these values lead to half-times of several days at room temperature. Thus, the two monocarbene complexes (**23c-1/30c-1**) should be stable toward a reductive elimination of ethane, in accordance with the experimental findings.

The energy profiles of the reductive eliminations of ethane starting from the six-fold coordinated monoacetatobis(carbene)-platinum(IV) complexes (**38c-1/43c-1**) are shown in Figure 7.

In accordance with other elimination reactions from platinum(IV) complexes, these reactions include two steps, namely the cleavage of one Pt—O bond of the η^2-bound acetato ligand (resulting in the formation of five-fold coordinated complexes) followed by the reductive ethane elimination.[14,24] In the case of the *N,N*-heterocyclic complex (**38c-1**) the first reaction is approximately thermodynamically neutral ($\Delta G = -1.6$ kcal/mol), whereas the same process is significantly endergonic ($\Delta G = 4.7$ kcal/mol) in the case of the *N,O*-heterocyclic carbene complex (**43c-1**). Thus, the overall activation energy barrier for reductive ethane elimination (based on the thermodynamically most stable complexes **37c-1** and **43c-1**) has values of 8.8 and 17.5 kcal/mol, respectively. Although the transition states of the first reactions could not be localized, the activation barriers should be significantly smaller than those for the second reactions (see discussion vide supra). According to the Eyring equation based on first-order kinetics, the overall barriers lead us to expect half-times in the range of microseconds (**37c-1**) and milliseconds (**43c-1**), respectively. Thus, bis(carbene)platinum(IV) complexes are considered to be unstable intermediates.

(24) (a) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 1456. (b) Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *Organometallics* **2001**, *20*, 2669. (c) Crumpton-Bregel, D. M.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 9442. (d) Procelewska, J.; Zahl, A.; Liehr, G.; van Eldik, R.; Smythe, N. A.; Williams, B. S.; Goldberg, K. I. *Inorg. Chem.* **2005**, *44*, 7732. (e) Luedtke, A. T.; Goldberg, K. I. *Inorg. Chem.* **2007**, *46*, 8496.
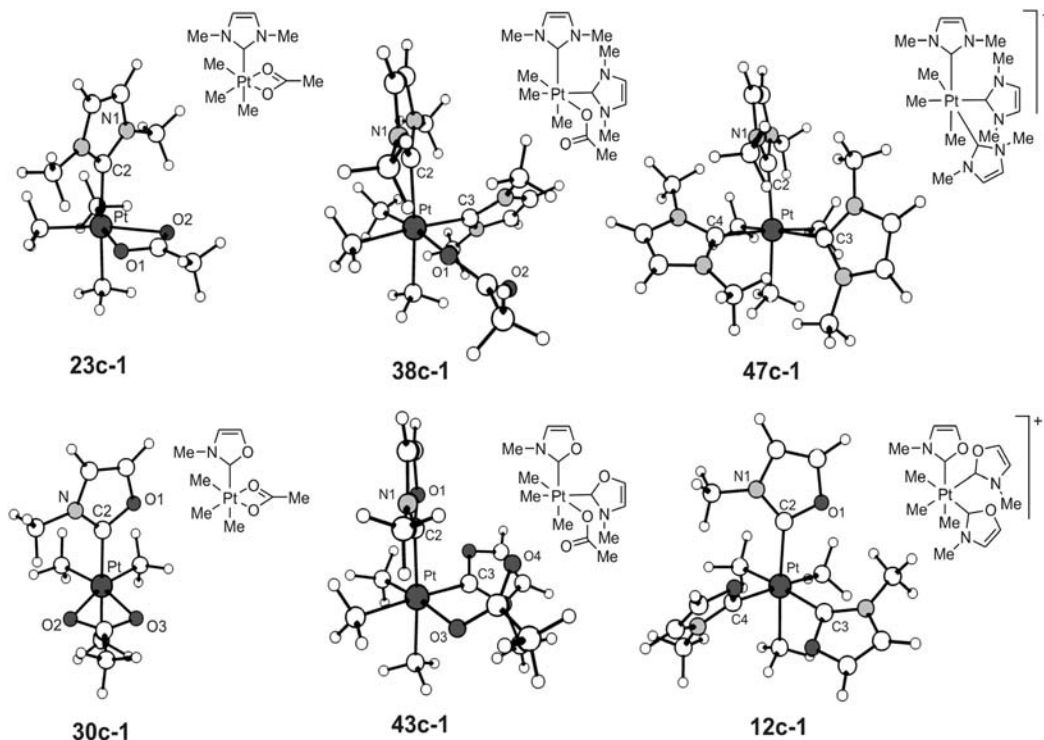
Figure 4. Calculated molecular structures of selected mono-, bis-, and tris(carbene)trimethylplatinum(IV) complexes.

Table 4. Selected Bond Lengths (in Å) in Mono-, Bis-, and Tris(carbene)trimethylplatinum(IV) Complexes

		23c-1	38c-1	47c-1	30c-1	43c-1	12c-1
Pt−C$_{Me}$	*trans* to C	2.082	2.109/2.104	2.118−2.125	2.081	2.110/2.110	2.127−2.128
	trans to O	2.057/2.057	2.084		2.058/2.063	2.085	
Pt−C$_{carbene}$		2.128	2.141/2.151	2.155−2.249	2.090	2.088/2.088	2.114−2.120
Pt−O$_{OAc}$		2.281/2.280	2.207		2.271/2.302	2.219	

DFT calculations by Puddephatt et al.[25] showed that the activation barriers for the ethane elimination starting from five-fold coordinated cationic bis(phosphino)- and bis(amino)tri-methylplatinum(IV) complexes [PtMe$_3$(PH$_3$)$_2$]$^+$/[PtMe$_3$(NH$_3$)$_2$]$^+$ are much higher (25/26 kcal/mol) than those of the bis(carbene) complexes shown in Figure 7. In accordance with that, the six-

fold coordinated complex [PtMe$_3$(OAc)(dppe)] was found to have a half-time of reductive ethane elimination in the order of 10 min to several days (depending on the solvent) at 100 °C.[26] The reason for this difference might be the stronger *trans* influence of the *N,X*-heterocyclic carbenes, which gives rise to a weakening of the Pt−Me bonds in the *trans* position in the
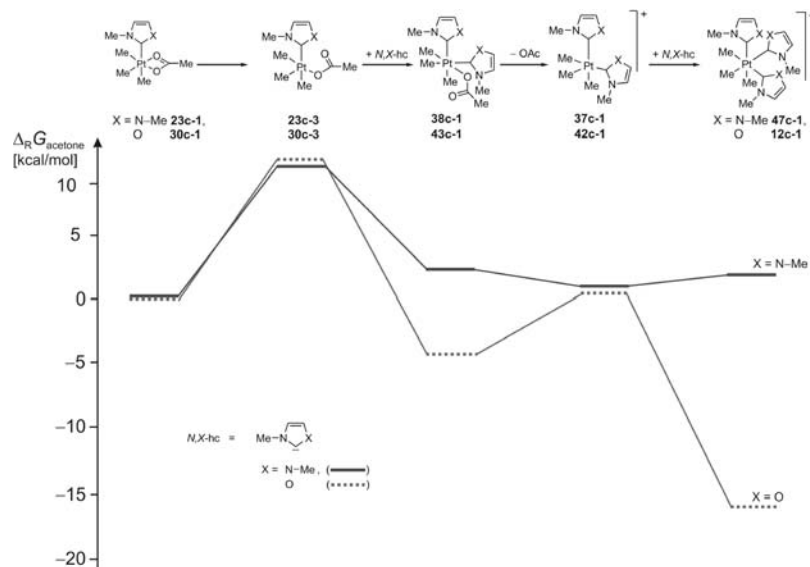
Figure 5. Gibbs free energy profile in acetone of the substitution reactions including mono-, bis-, and tris(carbene)platinum(IV) complexes: *N,N*-, solid; *N,O*-, dashed.
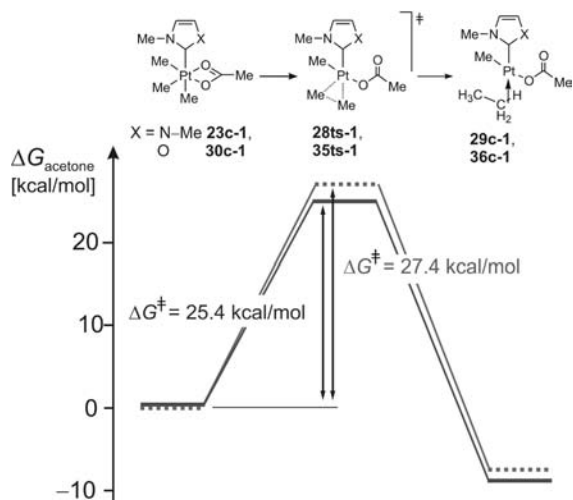
Figure 6. Gibbs free energy profile in acetone of reductive ethane elimination in *N,N*- and *N,O*-heterocyclic monocarbeneplatinum(IV) complexes: *N,N*-, solid; *N,O*-, dashed.

five-fold coordinated educts, destabilizing them with respect to the transition states. Due to a relatively late transition state with partially cleaved Pt—Me bonds, the former influence should be the dominant one, which results in a lower activation barrier in the carbene over phosphine platinum(IV) complexes.

Structures of selected transition states of the ethane elimination from bis(carbene)trimethylplatinum(IV) complexes as well as the resulting platinum(II) complexes are shown in Figure 8. Selected structural parameters are given in Table 5. Analogous structural parameters were found for the transition states of the ethane elimination starting from monocarbenetrimethylplatinum(IV) complexes (see Supporting Information). In both of these transition states (**40ts-1/45ts-1**), relatively short C···C distances of the evolving ethane molecules (2.016/2.042 Å) as well as square planar coordination spheres of the platinum atoms indicate "late" (product-like) transition states. The reductive eliminations of ethane result, primarily, in the formation of complexes **41c-1/46c-1**, which can be described as platinum-(II) complexes having *σ*-C—H-bound ethane ligands. Thus, these complexes show no elongation of the C—C bond for the coordinated ethane molecules (C4—C5 1.529/1.529 Å, **41c-1/46c-1**; for comparison, C—C in non-coordinated ethane, 1.532 Å) but slight elongations of the C—H bond coordinated to Pt (C4—H1 1.141/1.145 Å, **41c-1/46c-1**; C—H in non-coordinated ethane, 1.100 Å). Analogous transition-state structures were found by Puddephatt et al. for reductive ethane elimination reactions from the bis(amino) and bis(phosphino) complexes mentioned above.[25]

The reductive elimination of ethane starting from the tris(carbene) complexes (**47c-1/12c-1**) requires cleavage of a carbene ligand, resulting in five-fold coordinated platinum(IV) complexes followed by the actual reductive elimination reactions. In the energy profile shown in Figure 9, significantly different overall activation barriers were calculated, namely 7.6 and 29.1 kcal/mol in the case of *N,N*- and *N,O*-heterocyclic tris(carbene) complexes **47c-1** and **12c-1**, respectively. It is apparent from inspection of the reaction profiles that this is mainly caused by the first reaction step being nearly thermodynamically neutral in the case of the *N,N*-heterocyclic complex **47c-1** but strongly endergonic in the case of the *N,O*-heterocyclic complex **12c-1**.

(25) Hill, G. S.; Puddephatt, R. J. *Organometallics* **1998**, *17*, 1478.
(26) Williams, B. S.; Goldberg, K. I. *J. Am. Chem. Soc.* **2001**, *123*, 2576.

Thus, this fundamental difference in the energy of the association/dissociation of a third carbene ligand proves to be the main reason for the different reactivity of the *N,N*- and *N,O*-heterocyclic carbene complexes. This difference might be reasoned by the additional steric effects of the second *N*-methyl group in the *N,N*-heterocyclic carbene ligands (compared to the *N,O*-heterocyclic ones) and/or by the higher electron density on the platinum atom in the *N,N*-heterocyclic bis(carbene) complex (**37c-1**). To evaluate the importance of these two factors, analogous five- and six-fold complexes having *N,N*-heterocyclic carbene ligands in which one N—Me group is replaced by an N—H group (abbreviated as *N,N**-hc) were studied. This substitution is not expected to alter the electronic properties much, but the steric demand should be about that of the *N,O*-hc ligand. As shown in Scheme 9, the free energies of association of the third *N,N*-, *N,O*-, and *N,N**-heterocyclic carbenes exhibited the order *N,O*-hc < *N,N**-hc ≪ *N,N*-hc, which parallels the steric demand of these carbene ligands, thus indicating the dominance of steric influences of the carbenes on these reactions.

2.6. Conclusions. From the experimental investigations and quantum chemical calculations performed in this work the following conclusions can be drawn:

1. Monocarbenetrimethylplatinum(IV) complexes are efficiently stabilized by bidentate coligands (acac and bpy), as was shown by the formation of complexes of the types [PtMe₃(acac)(*N,X*-hc)] (X = N, O, S) (**16–18**) and [PtMe₃(bpy)(*N,X*-hc)](BF₄) (X = N, O) (**19**(BF₄)/**20**(BF₄)).

2. Tris(carbene)trimethylplatinum(IV) complexes were found to be stable with the *N,O*-hc ligand, whereas the requisite reaction with the *N,N*-hc ligand resulted in rapid reductive elimination of ethane and subsequent formation of platinum(II) carbene complexes. Neither the tris(*N,N*-hc)- nor the bis(*N,X*-hc)trimethylplatinum(IV) complexes (X = N, O) could be detected NMR spectroscopically as intermediates.

3. In accordance with the experimental findings above, high-level DFT calculations of mono-, bis-, and tris(*N,X*-hc)trimethylplatinum(IV) complexes (X = N, O) and their propensity to reductively eliminate ethane exhibited in the case of mono- and bis(*N,X*-hc) complexes a high stability and instability, respectively, toward reductive ethane elimination almost irrespective of the heteroatom X. Herewith it has been taken into consideration that, in general, in octahedral platinum(IV) complexes prior to the actual reductive elimination reaction, a ligand dissociation proceeds forming a five-fold coordinated platinum-(IV) intermediate.[14,24]

4. In contrast, the tris(carbene) complex [PtMe₃(*N,N*-hc)₃]⁺ (**47c-1**) proved to be much more prone to dissociation of a carbene ligand, resulting in the formation of a five-fold coordinated complex [PtMe₃(*N,N*-hc)₂]⁺ (**37c-1**), than the complex [PtMe₃(*N,O*-hc)₃]⁺ (**12c-1**). On the other hand, the actual activation barriers of the reductive elimination reactions proved to be — as was found for other carbene complexes (see above) — in the same range both for X = N and X = O. Thus, the ease of the dissociation of a carbene ligand seems to be the deciding factor for the fundamentally different reactivity between the *N,N*-hc and *N,O*-hc platinum(IV) complexes.

5. As supported by comparative calculations of the *N,N*-hc (1,3-dimethylimidazol-2-ylidne) and the *N,N**-hc ligands (1-methylimidazole-2-ylidene), the ease of the carbene ligand dissociation in the complex [PtMe₃(*N,N*-hc)₃]⁺ (**47c-1**) can be attributed mainly to the steric hindrance of the three *N,N*-hc ligands in the facial position.
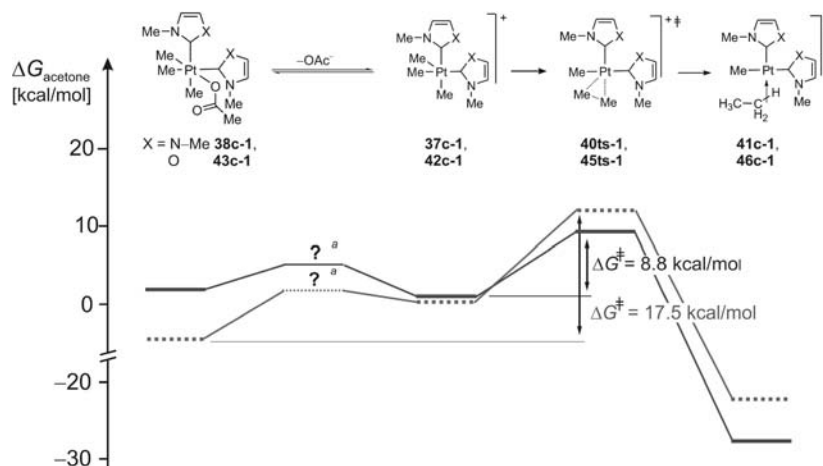
Figure 7. Gibbs free energy profile in acetone of reductive ethane elimination in *N,N*- and *N,O*-heterocyclic bis(carbene)platinum(IV) complexes: *N,N*-, solid; *N,O*-, dashed. [a]Due to the dissociative character of this process, a transition state could not be determined.
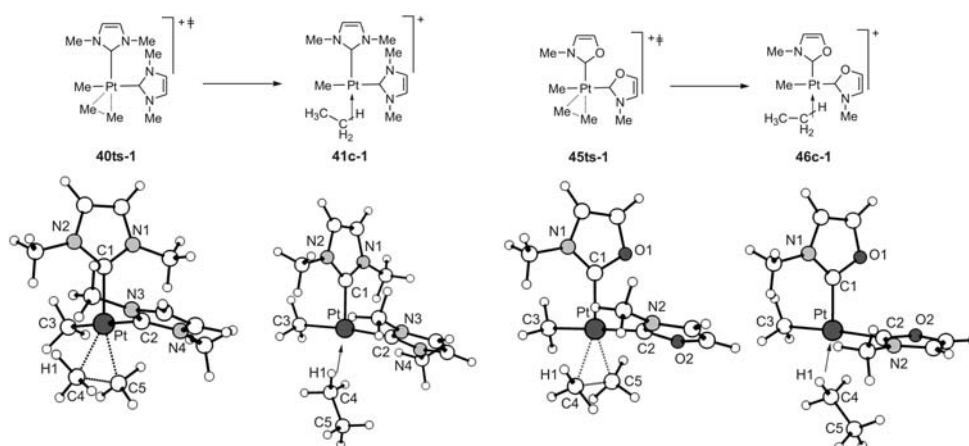
Figure 8. Molecular structures of calculated transition states of ethane elimination from bis(carbene)trimethylplatinum(IV) complexes (**40ts-1/45ts-1**) and equilibrium structures of calculated bis(carbene)platinum(II) complexes (**41c-1/46c-1**).

Table 5. Selected Bond Lengths (in Angström) of Calculated Transition States of Ethane Elimination from Bis(carbene)trimethylplatinum(IV) Complexes (**40ts-1/45ts-1**) and Equilibrium Structures of Calculated Bis(carbene)platinum(II) Complexes (**42c-1/46c-1**)

	40ts-1	45ts-1	42c-1	46c-1	C_2H_6
Pt−C4/C5	2.228/2.227	2.224/2.216	2.099/3.917	2.534/3.691	
Pt−C$_{carbene}$ *trans* to Me	2.227	2.091	2.108	2.083	
Pt−C$_{carbene}$ *trans* to C4/C5	2.031	2.008	1.950	1.930	
C4−C5	2.016	2.042	1.529	1.529	1.532
C4−H1	1.106	1.108	1.141	1.145	1.100

6. Despite the higher donor strength of the *N,X*-heterocyclic carbenes compared to phosphines, the activation barrier for reductive ethane elimination is significantly lower in the five-fold coordinated bis(*N,X*-hc)- (X = N, O) (**37c-1**, **42c-1**) than in bis(phosphino)trimethylplatinum(IV) complexes.[25] This might be reasoned by a stronger *trans* influence of the *N,X*-heterocyclic carbenes resulting, in the five-fold coordinated platinum(IV) complexes, in a weakening of the Pt−Me bonds in the *trans* position, thus lowering the activation barriers. Because the transition state is relatively late on the reaction coordinate, the former influence should be the dominant one, giving rise to a lower stability of the carbene over phosphine−platinum(IV) complexes.

Thus, the present experimental and theoretical investigations both give insight into the course of the reductive C−C elimination reaction, being an elementary step of fundamental importance both in organometallic chemistry and in homogeneous catalysis. Furthermore, a deeper understanding of the influence of different kinds of NHC ligands on the redox chemistry of transition metal complexes was obtained.

3. Experimental Section

3.1. General Comments. All reactions and manipulations were carried out under argon using standard Schlenk techniques. Solvents were dried prior to use: CH_2Cl_2 over CaH_2, Me_2CO over molecular sieve 3 Å, *n*-pentane, benzene, and Et_2O over sodium benzophenone. Microanalyses (C, H, N) were performed by staff at the microanalytical laboratory of the University of Halle using CHNS-932 (LECO) and Vario EL elemental analyzers (Elementaranalysensysteme). ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini 200, VXR 400, and Unity 500 NMR spectrometers. The notation "s+d" points out that the main singlet signal is superimposed on [195]Pt satellites. Solvent signals and residual protons of solvent signals were used as internal standards. ESI spectra were recorded on a Finningan Mat spectrometer LCQ using the following conditions: carrier gas, N_2; flow rate, 8 μL/min; spray voltage, 4.1 kV; temperature of the capillary, 150 °C; voltage of the capillary, 34 kV. The starting compounds [(PtMe$_3$I)$_4$] (**2**), [PtMe$_3$-(OCMe$_2$)$_3$](BF$_4$) (**1**(BF$_4$)), [PtMe$_3$I(py)$_2$] (**3**), and (*N,X*-hcH)I (X =
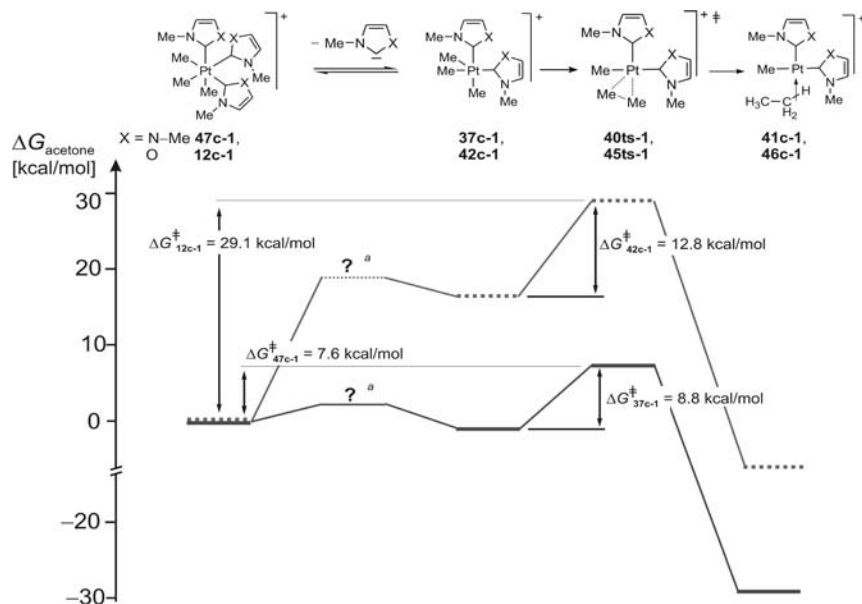
Figure 9. Gibbs free energy profile in acetone of reductive ethane elimination in *N,N*- and *N,O*-heterocyclic tris(carbene)platinum(IV) complexes: *N,N*-, solid; *N,O*-, dashed. [a]Due to the dissociative character of this process, a transition state could not be determined.

Scheme 9

X =	N-Me	**37c-1**	1.2	**47c-1**
	N-H	**48c-1**	−14.4	**49c-1**
	O	**42c-1**	−16.3	**12c-1**
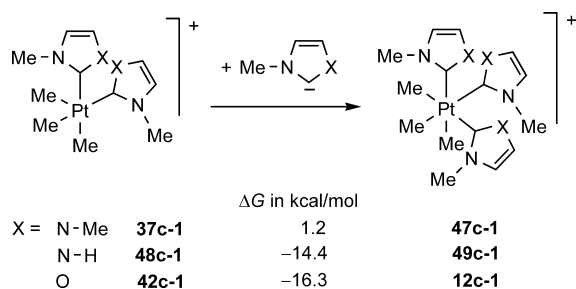
N, O, S) were obtained according to the published literature procedures.[13,27−29]

3.2. Reactivity of Platinum(IV) Complexes toward *N,X*-Heterocyclic Carbene Ligands. Preparation of (*N,X*-hc)(BF₄) (X = N, O, S). Ag(BF₄) (195 mg, 1.00 mmol) was added to a solution of the corresponding azolium iodide (*N,X*-hcH)I (X = N, O, S) (1.00 mmol) in acetone (10 mL). After stirring for 2 h at ambient temperature, the suspension was filtered, and the resulting solution was used for further reactions.

(*N,N*-hcH)(BF₄): ¹H NMR (400 MHz, (CD₃)₂CO) δ 4.02 (s, 6H, NC*H*₃), 7.69 (s, 2H, N(C*H*)₂N), 9.49 (s, 1H, C*H*).

(*N,O*-hcH)(BF₄): ¹H NMR (400 MHz, (CD₃)₂CO) δ 4.17 (d, ⁴*J*ₚₜ,ₕ = 0.8 Hz, 3H, NC*H*₃), 8.17 (s, 1H, N(C*H*)₂O), 8.62 (s, 1H, N(C*H*)₂O) 9.89 (s, 1H, C*H*).

(*N,S*-hcH)(BF₄): ¹H NMR (400 MHz, (CD₃)₂CO) δ 4.52 (s, 3H, NC*H*₃), 8.48 (s, 2H, N(C*H*)₂S), 8.64 (s, 1H, N(C*H*)₂S), 10.47 (s, 1H, C*H*).

Preparation of [{PtMe₃(acac)}₂] (15). This complex was synthesized by a modification of the procedure described in ref 30. To a solution of [PtMe₃(OCMe₂)₃](BF₄) (1(BF₄)) (0.100 mmol) in acetone (5 mL) were added KOAc (19.6 mg, 0.200 mmol) and Hacac (10.0 mg, 0.100 mmol) with stirring. After 3 h at ambient temperature all solvents were removed under reduced pressure,

K₂CO₃ (138 mg, 1.00 mmol) was added, and the mixture was extracted with benzene (10 mL). The volume of the solution was reduced to 2 mL. Layering with *n*-pentane (2 mL) resulted, within 12 h, in the formation of colorless, air-stable crystals which were filtered, washed with *n*-pentane (3 × 1 mL), and dried in a vacuum: yield 65 mg (95%); *T*dec = 145 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.04 (s+d, ²*J*ₚₜ,ₕ = 72.3 Hz, 18H, PtC*H*₃), 1.98 (s, 12H, C(O)C*H*₃), 4.61 (s+d, ²*J*ₚₜ,ₕ = 33.8 Hz, 2H, C*H*); ¹³C NMR (126 MHz, CDCl₃) δ −12.1 (s+d, ¹*J*ₚₜ,c = 754.1 Hz, Pt*C*H₃ *trans* to O), 3.7 (s+d, ¹*J*ₚₜ,c = 740.4 Hz, Pt*C*H₃ *trans* to C), 31.1 (s+d, ³*J*ₚₜ,c = 8.4 Hz, *C*H₃), 79.7 (ν₁/₂ = 37 Hz, *C*H), 195.3 (ν₁/₂ = 17 Hz, *C*O).

Reaction of [PtMe₃(OCMe₂)₃](BF₄) (1(BF₄)) with (*N,N*-hcH)(BF₄)/KOAc. To a solution of [PtMe₃(OCMe₂)₃](BF₄) (1(BF₄)) (0.100 mmol) in acetone (5 mL) were added KOAc (78.5 mg, 0.800 mmol) and a solution of (*N,N*-hcH)(BF₄) (73.6 mg, 0.400 mmol) in acetone (5 mL) with stirring. After 3 h at ambient temperature the reaction mixture was filtered, and the resulting solution was concentrated to 2 mL under reduced pressure. Layering with Et₂O (5 mL) resulted in the formation of an oil which was dried in a vacuum: ¹H NMR (400 MHz, (CD₃)₂CO) δ −0.06 (s+d, ²*J*ₚₜ,ₕ = 62.7 Hz, 3H, PtC*H*₃), 3.65 (s+d, ⁴*J*ₚₜ,ₕ = 2 Hz, 6H, NC*H*₃ *trans* Me), 3.82 (s+d, ⁴*J*ₚₜ,ₕ = 4.6 Hz, 12H, NC*H*₃ *trans* NHC), 4.03 (s, 6H, (*N,N*-hcH)⁺ NC*H*₃), 7.13 (s+d, 2H, ⁴*J*ₚₜ,ₕ = 6.2 Hz, C*H trans* Me), 7.21 (s+d, ⁴*J*ₚₜ,ₕ = 8.9 Hz, 4H, C*H trans* NHC) 7.66 (s, 6H, (*N,N*-hcH)⁺ N(C*H*)₂N); ¹³C NMR (100 MHz, CD₃OD) δ −16.9 (s+d, ¹*J*ₚₜ,c = 498.0 Hz, Pt*C*H₃), 36.5 (s, (*N,N*-hcH)⁺ N*C*H₃), 37.5 (s+d, ³*J*ₚₜ,c = 41.4 Hz, N*C*H₃), 37.7 (s+d, ³*J*ₚₜ,c = 30.7 Hz, N*C*H₃), 122.8 (s+d, ³*J*ₚₜ,c = 27.7 Hz, *C*H *cis* Me), 122.8 (s+d, ³*J*ₚₜ,c = 19.2 Hz, *C*H *trans* Me), 122.7 (s, (*N,N*-hcH)⁺ N(C*H*)₂N), 137.0 (t, (*N,N*-hcH)⁺ N(C*D*)N), 175.5 (s+d, ¹*J*ₚₜ,c = 1020.5 Hz, Pt*C trans* NHC), 178.3 (s+d, ¹*J*ₚₜ,c = 776.5 Hz, Pt*C trans* Me).

Preparation of *trans*-[PtMeI(*N,N*-hc)₂] (8). To a suspension of [(PtMe₃I)₄] (2) (50.1 mg, 0.100 mmol) in acetone (10 mL) were added KOAc (78.5 mg, 0.800 mmol) and a solution of (*N,N*-hcH)(BF₄) (73.6 mg, 0.400 mmol) in acetone (5 mL) with stirring. After 3 h at ambient temperature all solvents were removed under reduced pressure, K₂CO₃ (138 mg, 1.00 mmol) was added, and the mixture was extracted with benzene (10 mL). The volume of the solution was reduced to 5 mL. Layering with *n*-pentane (5 mL) resulted, within 12 h, in the formation of pale yellow, air-stable crystals which were filtered, washed with *n*-pentane (3 × 1 mL), and dried in a vacuum: yield 48 mg (90%); *T*dec = 220 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.20 (s+d, ²*J*ₚₜ,ₕ = 93.0 Hz, 3H, PtC*H*₃),

(27) Baldwin, J. C.; Kaska, W. C. *Inorg. Chem.* **1975**, *14*, 2020.
(28) Clegg, D. E.; Hall, J. R.; Swile, G. A. *J. Organomet. Chem.* **1972**, *38*, 403.
(29) Matsumoto, T.; Yamamoto, H.; Inoue, S. *J. Am. Chem. Soc.* **1984**, *106*, 4829.
(30) Swallow, A. G.; Truter, M. R. *Proc. R. Soc. A* **1960**, *254*, 205.

3.91 (s+d, $^4J_{Pt,H}$ = 4.2 Hz, 6H, NCH_3), 6.77 (s+d, $^4J_{Pt,H}$ = 8.3 Hz, 4H, CH); ^{13}C NMR (100 MHz, CDCl$_3$) δ −22.1 (s+d, $^1J_{Pt,C}$ = 760.7 Hz, PtCH_3), 37.0 (s+d, $^3J_{Pt,C}$ = 44.6 Hz, NCH_3), 120.6 (s+d, $^3J_{Pt,C}$ = 28.4 Hz, CH), 179.2 (s+d, $^1J_{Pt,C}$ = 1031.2 Hz, PtC). Anal. Calcd for C$_{11}$H$_{19}$N$_4$IPt: C, 24.96; H, 3.62; N, 10.59. Found: C, 25.13; H, 3.73; N, 10.28.

Preparation of *trans*-[PtMe(py)(*N,N*-hc)$_2$](CF$_3$COO) (9(CF$_3$-COO)). To a solution of *trans*-[PtMeI(*N,N*-hc)$_2$] (**8**) (106 mg, 0.200 mmol) in acetone (10 mL) was added Ag(CF$_3$COO) (44.2 mg, 0.200 mmol). After complete precipitation of AgI at ambient temperature (12 h), the reaction mixture was filtered. Pyridine (15.8 mg, 0.200 mmol) was added to the solution, which was subsequently concentrated to 2 mL under reduced pressure. Layering with Et$_2$O (5 mL) resulted, within 12 h, in the formation of colorless crystals, which were filtered, washed with Et$_2$O (3 × 1 mL), and dried in a vacuum: yield 95 mg (80%); F_P = 130−140 °C; ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO) δ 0.17 (s+d, $^2J_{Pt,H}$ = 84.1 Hz, 3H, PtCH_3), 4.01 (s, 12H, NCH_3), 7.26 (s+d, $^4J_{Pt,H}$ = 7.0 Hz, 4H, CH), 7.42 (m, 2H, py), 8.91 (m, 1H, py), 8.56 (m+d·m, $^3J_{Pt,H}$ = 22 Hz, 2H, py); ^{13}C NMR (126 MHz, (CD$_3$)$_2$CO) δ −33.8 (s+d, $^1J_{Pt,C}$ = 662.0 Hz, PtCH_3), 36.2 (s+d, $^3J_{Pt,C}$ = 40.3 Hz, NCH_3), 122.0 (s+d, $^3J_{Pt,C}$ = 27.8 Hz, CH), 126.3 (s+d, $^3J_{Pt,C}$ = 18−22 Hz, py), 137.6 (s, py), 152.3 (s+d, $^2J_{Pt,C}$ = 10−15 Hz, py), 177.5 (s+d, $^1J_{Pt,C}$ = 1072.0 Hz, PtC).

Reaction of [PtMe$_3$I(py)$_2$] (3) with a Stoichiometric Amount (a) and an Excess (b) of (*N,N*-hcH)(BF$_4$)/KOAc. To a solution of [PtMe$_3$I(py)$_2$] (**3**) (99.0 mg, 0.200 mmol) in acetone (10 mL) was added AgOAc (33.4 mg, 0.200 mmol). After complete precipitation of AgI at ambient temperature (12 h), the reaction mixture was filtered. KOAc (**a**, 39.4 mg, 0.400 mmol; **b**, 117.8 mg, 1.200 mmol) and a solution of (*N,N*-hcH)(BF$_4$) (**a**, 36.8 mg, 0.200 mmol; **b**, 110 mg, 0.600 mmol) in acetone (2 mL) were added to the solution. After 1 h at ambient temperature the reaction mixture was filtered, and the resulting solution was concentrated to 2 mL under reduced pressure. Layering with Et$_2$O (5 mL) resulted in the formation of an oil, which was dried in a vacuum.

(**a**): ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO) δ 0.11 (s+d, $^2J_{Pt,H}$ = 57.1 Hz, 3H, PtCH_3 **10**), 1.18 (s+d, $^2J_{Pt,H}$ = 67.2 Hz, 9H, **11** PtCH_3), 3.76 (s, $^4J_{Pt,H}$ = 3 Hz, 6H, **10** NCH_3 *trans* Me), 3.86 (s, $^4J_{Pt,H}$ = 4 Hz, 6H, **10** NCH_3 *trans* py), 7.14 (s+d, 2H, **10** CH *trans* Me), 7.22 (s+d, 2H, **10** CH *trans* py), 7.54 (m, 2H, **10** py), 7.70 (m, 6H, **22** py), 8.01 (m, 1H, **10** py), 8.18 (m, 3H, **22** py), 8.61 (m+d·m, $^3J_{Pt,H}$ = 16 Hz, 6H, **22** py), 8.77 (m+d·m, $^3J_{Pt,H}$ = 32 Hz, 2H, **10** py); ^{13}C NMR (100 MHz, (CD$_3$)$_2$CO) δ −6.2 (s+d, $^1J_{Pt,C}$ = 531.7 Hz, **10** PtCH_3), 36.4 (s+d, $^3J_{Pt,C}$ = 30.1 Hz, **10** NCH_3), 36.9 (s+d, $^3J_{Pt,C}$ = 51.6 Hz, **10** NCH_3), 121.8 (s+d, $^3J_{Pt,C}$ = 40.8 Hz, **10** N(CH)$_2$N *trans* Me), 122.2 (s+d, $^3J_{Pt,C}$ = 20.4 Hz, **10** N(CH)$_2$N *trans* py), 126.2 (s+d, $^3J_{Pt,C}$ = 31.2 Hz, **10** py), 138.0 (s, **10** py), 152.2 (s+d, $^2J_{Pt,C}$ = 17.2 Hz, **10** py). {**11** is [PtMe$_3$(py)$_3$]$^+$; **10** is *cis*-[PtMe(py)(*N,N*-hc)$_2$]$^+$.}

(**b**): ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO) δ −0.06 (s+d, $^2J_{Pt,H}$ = 62.7 Hz, 3H, **7** PtCH_3), 0.11 (s+d, $^2J_{Pt,H}$ = 57.1 Hz, 3H, **10** PtCH_3), 3.65 (s+d, $^4J_{Pt,H}$ = 3 Hz, 6H, **7** NCH_3 *trans* Me), 3.76 (s+d, $^4J_{Pt,H}$ = 3 Hz, 6H, **10** NCH_3 *trans* Me), 3.82 (s+d, $^4J_{Pt,H}$ = 5 Hz, 12H, **7** NCH_3 *trans* NHC), 3.86 (s+d, $^4J_{Pt,H}$ = 4 Hz, 6H, **10** NCH_3 *trans* py), 7.12 (s+d, 2H, $^4J_{Pt,H}$ = 6 Hz, **7** CH *trans* Me), 7.14 (s+d, 2H, $^4J_{Pt,H}$ = 5 Hz, **10** CH *trans* Me), 7.20 (s+d, $^4J_{Pt,H}$ = 9 Hz, 4H, **7** CH *trans* NHC), 7.22 (s+d, 2H, $^4J_{Pt,H}$ = 12 Hz, **10** CH *trans* py), 7.54 (m, 2H, **10** py), 8.01 (m, 1H, **10** py), 8.77 (m+d·m, $^3J_{Pt,H}$ = 32 Hz, 2H, **10** py); ESI-MS *m/z* (obsd/calcd for **10**/**7**, %) 480 (63/82), 481 (100/100), 482 (73/81), 483 (10/14), 484 (13/19), 485 (3/4), 497 (62/82), 498 (100/100), 499 (73/81), 500 (12/14), 501 (18/19), 502 (3/4). {**7** is [PtMe(*N,N*-hc)$_3$]$^+$; **10** is *cis*-[PtMe(py)(*N,N*-hc)$_2$]$^+$.}

Preparation of [PtMe$_3$(*N,O*-hc)$_3$](BF$_4$) (12(BF$_4$)). To a solution of [PtMe$_3$(OCMe$_2$)$_3$](BF$_4$) (**1**(BF$_4$)) (50.1 mg, 0.100 mmol) in acetone (10 mL) were added KOAc (78.5 mg, 0.800 mmol) and a solution of (*N,O*-hcH)(BF$_4$) (68.4 mg, 0.400 mmol) in acetone (5 mL) with stirring. After 3 h at ambient temperature all solvents

were removed under reduced pressure, K$_2$CO$_3$ (138 mg, 1.00 mmol) was added, and the mixture was extracted with CH$_2$Cl$_2$ (10 mL). The volume of the solution was reduced to 5 mL. Layering with *n*-pentane (5 mL) resulted, within 12 h, in the formation of colorless, air-stable crystals, which were filtered, washed with *n*-pentane (3 × 1 mL), and dried in a vacuum: yield 23 mg (40%); T_{dec} = 218 °C; ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO) δ −0.68 (s+d, $^2J_{Pt,H}$ = 55.6 Hz, 9H, PtCH_3), 2.19 (s+d, $^4J_{Pt,H}$ = 3.3 Hz, 9H, NCH_3), 6.28 (m, 3H, CH), 6.95 (m, 3H, CH); ^{13}C NMR (50 MHz, CD$_3$OD) δ −8.8 (s+d, $^1J_{Pt,C}$ = 494.7 Hz, PtCH_3), 35.0 (s+d, $^3J_{Pt,C}$ = 3 Hz, NCH_3), 122.0 (s+d, $^3J_{Pt,C}$ = 9.9 Hz, CH), 143.4 (s+d, $^3J_{Pt,C}$ = 14.9 Hz, CH), 184.5 (s+d, $^1J_{Pt,C}$ = 662.9 Hz, PtC).

Reaction of [PtMe$_3$(OCMe$_2$)$_3$](BF$_4$) (1(BF$_4$)) with a Substoichiometric Amount of (a) (*N,N*-hcH)(BF$_4$)/KOAc and (b) (*N,O*-hcH)(BF$_4$)/KOAc. To a solution of [PtMe$_3$(OCMe$_2$)$_3$](BF$_4$) (**1**(BF$_4$)) (0.100 mmol) in acetone-d_6 (2 mL) were added KOAc (19.6 mg, 0.200 mmol) and (*N,N*-hcH)(BF$_4$) (9.2 mg, 0.050 mmol) or (*N,O*-hcH)(BF$_4$) (8.5 mg, 0.050 mmol) for (a) or (b), respectively. The resulting reaction mixture was filtered and characterized by NMR spectroscopy.

(**a**): yield (spectroscopic) 30%; ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO) δ 0.48 (s+d, $\nu_{1/2}$ = 18 Hz, $^2J_{Pt,H}$ = 45.9 Hz, 3H, **13** PtCH_3 *trans* C), 0.87 (s+d, $\nu_{1/2}$ = 6 Hz, $^2J_{Pt,H}$ = 77.6 Hz, **1** PtCH_3), 1.10 (s+d, $\nu_{1/2}$ = 10 Hz, $^2J_{Pt,H}$ = 79.5 Hz, 6H, **13** PtCH_3 *trans* O), 1.81 ($\nu_{1/2}$ = 5 Hz, CH_3COO), 3.78 ($\nu_{1/2}$ = 4 Hz, 6H, **13** NCH_3), 7.18 ($\nu_{1/2}$ = 4 Hz, 2H, **13** CH). {**13** is [PtMe$_3$Y$_2$(*N,N*-hc)]^z, where Y = OAc, OCMe$_2$; z = 1, 0, −1).

(**b**): yield (spectroscopic) 10%; ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO) δ 0.57 (s+d, $^2J_{Pt,H}$ = 51.9 Hz, 3H, **14** PtCH_3 *trans* C), 0.84 (s+d, $^2J_{Pt,H}$ = 76.8 Hz, **1** PtCH_3), 1.09 (s+d, $^2J_{Pt,H}$ = 80.1 Hz, 6H, **14** PtCH_3 *trans* O), 1.81 (br, CH_3COO), 3.94 (s+d, $^4J_{Pt,H}$ = 3.3 Hz, 3H, **14** NCH_3), 7.60 (d, 1H, **14** CH), 8.20 (d, 1H, **14** CH). {**14** is [PtMe$_3$Y$_2$(*N,O*-hc)]^z, where Y = OAc, OCMe$_2$; z = 1, 0, −1).

Preparation of [PtMe$_3$(acac)(*N,X*-hc)] (X = N, 16; X = O, 17; X = S, 18). To a solution of [{PtMe$_3$(acac)}$_2$] (**15**) (67.9 mg, 0.100 mmol) in acetone (10 mL) were added KOAc (39.3 mg, 0.400 mmol) and a solution of (*N,N*-hcH)(BF$_4$) (36.8 mg, 0.200 mmol), (*N,O*-hcH)(BF$_4$) (68.4 mg, 0.400 mmol), or (*N,S*-hcH)(BF$_4$) (74.8 mg, 0.400 mmol) for **16**, **17**, or **18**, respectively, with stirring. After 3 h at ambient temperature all solvents were removed under reduced pressure, K$_2$CO$_3$ (138 mg, 1.00 mmol) was added, and the mixture was extracted with benzene (10 mL). The volume of the solution was reduced to 5 mL. Layering with *n*-pentane (5 mL) resulted, within 12 h, in the formation of colorless, air-stable crystals, which were filtered, washed with *n*-pentane (3 × 1 mL), and dried in a vacuum.

[PtMe$_3$(acac)(*N,N*-hc)] (**16**): yield 61 mg (70%); T_{dec} = 160 °C; ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO) δ 0.28 (s+d, $^2J_{Pt,H}$ = 52.3 Hz, 3H, CH_3 *trans* C), 0.98 (s+d, $^2J_{Pt,H}$ = 76.4 Hz, 6H, CH_3 *trans* O), 1.76 (s, 6H, CH_3 acac), 3.81 (s+d, 6H, $^4J_{Pt,H}$ = 2.0 Hz, NCH_3), 4.96 (s+d, $^4J_{Pt,H}$ = 1.6 Hz, 1H, CH acac), 7.09 (s+d, $^4J_{Pt,H}$ = 3.3 Hz, 2H, CH *N,N*-hc); ^{13}C NMR (126 MHz, CDCl$_3$) δ −17.7 (s+d, $^1J_{Pt,C}$ = 731.3 Hz, CH_3 *trans* O), 2.2 (s+d, $^1J_{Pt,C}$ = 547.0 Hz, CH_3 *trans* C), 25.5 (s+d, $^3J_{Pt,C}$ = 8.6 Hz CH_3 acac), 33.4 (s+d, $^3J_{Pt,C}$ < 5 Hz NCH_3), 96.4 (s+d, $^3J_{Pt,C}$ = 30.7 Hz, CH acac), 119.1 (s+d, $^3J_{Pt,C}$ = 15.4 Hz, CH *N,N*-hc), 175.7 (s+d, $^1J_{Pt,C}$ = 658.3 Hz, PtC *N,N*-hc), 182.2 (s+d, $^2J_{Pt,C}$ = 13.4 Hz, C=O acac). Anal. Calcd for C$_{13}$H$_{24}$N$_2$O$_2$Pt: C, 35.86; H, 5.56; N, 6.43. Found: C, 35.88; H, 5.78; N, 6.48.

[PtMe$_3$(acac)(*N,O*-hc)] (**17**): yield 61 mg, 60%; T_{dec} = 146 °C; ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO) δ 0.34 (s+d, $^2J_{Pt,H}$ = 53.1 Hz, 3H, CH_3 *trans* C), 0.98 (s+d, $^2J_{Pt,H}$ = 75.5 Hz, 6H, CH_3 *trans* O), 1.77 (s, 6H, CH_3 acac), 3.85 (s+d, 3H, $^4J_{Pt,H}$ = 3.3 Hz, NCH_3), 5.06 (s+d, $^4J_{Pt,H}$ < 2 Hz, 1H, CH acac), 7.50 (d+dd, $^3J_{H,H}$ = 1.2 Hz, $^4J_{Pt,H}$ < 2 Hz, 1H, CH *N,O*-hc), 8.14 (d+dd, $^3J_{H,H}$ = 1.2 Hz, $^4J_{Pt,H}$ < 2 Hz, 1H, CH *N,O*-hc); ^{13}C NMR (126 MHz, CDCl$_3$) δ −14.9 (s+d, $^1J_{Pt,C}$ = 725.5 Hz, CH_3 *trans* O), 5.3 (s+d, $^1J_{Pt,C}$ = 563.1 Hz, CH_3 *trans* C), 28.2 (s+d, $^3J_{Pt,C}$ = 8−9 Hz, CH_3 acac), 34.6 (s+d, $^3J_{Pt,C}$ < 5 Hz, NCH_3), 100.0 (s+d, $^3J_{Pt,C}$ = 31.1 Hz, CH

Table 6. Crystallographic and Structure Refinement Data for **9**(CF₃COO), **16**, and **20**(BF₄)

	9(CF₃COO)	16	20(BF₄)
empirical formula	C₁₈H₂₄F₃N₅O₂Pt	C₁₃H₂₄N₂O₂Pt	C₁₇H₂₂BF₄N₃OPt
formula weight	594.51	435.43	566.28
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	8.4462(9)	8.464(2)	8.4311(7)
b (Å)	22.760(2)	13.213(3)	12.433(3)
c (Å)	11.106(1)	14.322(3)	19.069(2)
β (Å)	91.10(1)	95.57(2)	96.350(7)
V (Å³)	2134.5(4)	1594.1(6)	1986.7(5)
Z	4	4	4
D_{calc} (g/cm³)	1.850	1.814	1.893
μ (mm⁻¹)	6.622	8.799	7.110
$F(000)$	1152	840	1088
independent reflections	4075	3096	3506
no. of obsd reflections [$I > 2\sigma(I)$]	3251	2501	2864
data/restraints/parameters	4075/0/262	3096/0/164	3506/0/249
goodness-of-fit	1.144	1.072	1.100
R_1 [$I > 2\sigma(I)$], R_1 (all data)	0.0528, 0.0665	0.0662, 0.0752	0.0406, 0.0534
wR_2 [$I > 2\sigma(I)$], wR_2 (all data)	0.1206, 0.1300	0.1554, 0.1626	0.0975, 0.1056
largest diff peak/hole (e Å⁻³)	4.099/−2.020	4.446/−5.286	1.493/−1.958

acac), 122.0 (s+d, $^3J_{Pt,C}$ = 10.4 Hz, C*H N,O*-hc), 143.2 (s+d, $^3J_{Pt,C}$ = 16.7 Hz, C*H N,O*-hc), 185.9 (s+d, $^2J_{Pt,C}$ = 13.8 Hz, *C*=O acac), 201.4 (s+d, $^1J_{Pt,C}$ = 699.0 Hz, Pt−*C N,O*-hc). Anal. Calcd for C₁₂H₂₁N₁O₃Pt: C, 34.12; H, 5.01; N, 3.32. Found: C, 34.22; H, 5.25; N, 3.44.

[PtMe₃(acac)(*N,S*-hc)] (**18**): yield 53 mg, 60%; *T*dec = 182 °C; ¹H NMR (400 MHz, (CD₃)₂CO) δ 0.42 (s+d, $^2J_{Pt,H}$ = 53.5 Hz, 3H, C*H₃ trans* C), 0.98 (s+d, $^2J_{Pt,H}$ = 75.5 Hz, 6H, C*H₃ trans* O), 1.76 (s, 6H, C*H₃* acac), 4.16 (s+d, 3H, $^4J_{Pt,H}$ = 2.5 Hz, NC*H₃*), 4.97 (s+d, $^4J_{Pt,H}$ = 2.6 Hz, 1H, C*H* acac), 7.80 (d+dd, $^3J_{H,H}$ = 3.5 Hz, $^4J_{Pt,H}$ = 3.4 Hz, 1H, C*H N,S*-hc), 7.95 (d+dd, $^3J_{H,H}$ = 3.5 Hz, $^4J_{Pt,H}$ = 2.6 Hz, 1H, C*H N,S*-hc); ¹³C NMR (126 MHz, CDCl₃) δ −13.8 (s+d, $^1J_{Pt,C}$ = 729.0 Hz, C*H₃ trans* O), 4.6 (s+d, $^1J_{Pt,C}$ = 562.0 Hz, C*H₃ trans* C), 28.6 (s+d, $^3J_{Pt,C}$ = 8.6 Hz C*H₃* acac), 40.9 (s+d, $^3J_{Pt,C}$ = 7.5 Hz NC*H₃*), 100.0 (s+d, $^3J_{Pt,C}$ = 31.1 Hz, C*H* acac), 122.9 (s+d, $^3J_{Pt,C}$ = 12.7 Hz, C*H N,S*-hc), 137.3 (s+d, $^3J_{Pt,C}$ = 19.9 Hz, C*H N,S*-hc), 185.6 (s+d, $^2J_{Pt,C}$ = 13.2 Hz, *C*=O acac), 215.4 (s+d, $^1J_{Pt,C}$ = 581.6 Hz, Pt−*C N,S*-hc). Anal. Calcd for C₁₂H₂₁NO₂SPt: C, 32.87; H, 4.83. Found: C, 33.53; H, 4.59.

Preparation of [PtMe₃(bpy)(*N,X*-hc)](BF₄) (X = N, 19(BF₄); X = O, 20(BF₄)). To a solution of [PtMe₃(acac)(*N,N*-hc)] (**16**) (131 mg, 0.300 mmol) or [PtMe₃(acac)(*N,O*-hc)] (**17**) (127 mg, 0.300 mmol) for **19** and **20**, respectively, in acetone (10 mL) were added bipyridine (46.8 mg, 0.300 mmol) and a solution of H(BF₄) in Et₂O (51%, 43 μL, 0.30 mmol) with stirring. The resulting solution was concentrated to 3 mL. Layering with *n*-pentane (5 mL) resulted, within 12 h, in the formation of colorless, air-stable crystals, which were filtered, washed with *n*-pentane (3 × 1 mL), and dried in a vacuum.

[PtMe₃(bpy)(*N,N*-hc)](BF₄) (**19**(BF₄)): yield 140 mg (80%); *T*dec = 148 °C; ¹H NMR (400 MHz, (CD₃)₂CO) δ 0.05 (s+d, $^2J_{Pt,H}$ = 53.3 Hz, 3H, PtC*H₃ trans* C), 1.29 (s+d, $^2J_{Pt,H}$ = 69.3 Hz, 6H, PtC*H₃ trans* N), 3.42 (s+d, $^4J_{Pt,H}$ = 2.3 Hz, 6H, NC*H₃*), 7.08 (s+d, $^4J_{Pt,H}$ = 3.7 Hz, 2H, C*H N,N*-hc), 7.96 (m, 2H, bpy), 8.41 (m, 2H, bpy), 8.78 (m, 2H, bpy), 9.24 (m, 2H, bpy); ¹³C NMR (100 MHz, (CD₃)₂CO) δ −5.1 (s+d, $^1J_{Pt,C}$ = 660.7 Hz, PtC*H₃ trans* N), 5.8 (s+d, $^1J_{Pt,C}$ = 503.8 Hz, PtC*H₃ trans* C), 38.7 (s+d, $^3J_{Pt,C}$ = 4.4 Hz, NC*H₃*), 125.5 (s+d, $^3J_{Pt,C}$ = 14.7 Hz, C*H N,N*-hc), 126.8 (s+d, $^3J_{Pt,C}$ = 8.1 Hz, C*H* bpy), 129.3 (s+d, $^3J_{Pt,C}$ = 14.4 Hz, C*H* bpy), 142.3 (s+d, $^4J_{Pt,C}$ = 3.7 Hz, C*H* bpy), 150.1 (s+d, $^2J_{Pt,C}$ = 14.7 Hz, C*H* bpy), 157.3 (s+d, $^2J_{Pt,C}$ = 2.9 Hz, C*H* bpy), 169.5 (s+d, $^1J_{Pt,C}$ = 652.6 Hz, Pt*C N,N*-hc). Anal. Calcd for C₁₈H₂₅N₄PtBF₄: C, 37.29; H, 4.35. Found: C, 37.30; H, 4.97.

[PtMe₃(bpy)(*N,O*-hc)](BF₄) (**20**(BF₄)): yield 136 mg (80%); *T*dec = 203 °C; ¹H NMR (400 MHz, (CD₃)₂CO) δ 0.06 (s+d, $^2J_{Pt,H}$ = 54.2 Hz, 3H, PtC*H₃ trans* C), 1.27 (s+d, $^2J_{Pt,H}$ = 69.7 Hz, 6H,

PtC*H₃ trans* N), 3.67 (s+d, $^4J_{Pt,H}$ = 3.1 Hz, 6H, NC*H₃*), 7.46 (s+d, $^4J_{Pt,H}$ = 1.0 Hz, 1H, C*H N,O*-hc), 7.95 (m, 2H, bpy), 8.04 (s+d, $^4J_{Pt,H}$ = 0.8 Hz, 1H, C*H N,O*-hc), 8.40 (m, 2H, bpy), 8.79 (m, 2H, bpy), 9.13 (m, 2H, bpy); ¹³C NMR (100 MHz, (CD₃)₂CO) δ −5.9 (s+d, $^1J_{Pt,C}$ = 652.0 Hz, PtC*H₃ trans* N), 3.8 (s+d, $^1J_{Pt,C}$ = 514.0 Hz, PtC*H₃ trans* C), 36.6 (s+d, $^3J_{Pt,C}$ = 3.4 Hz, NC*H₃*), 124.1 (s+d, $^3J_{Pt,C}$ = 11.2 Hz, C*H N,O*-hc), 126.7 (s+d, $^3J_{Pt,C}$ = 8.2 Hz, C*H* bpy), 129.5 (s+d, $^3J_{Pt,C}$ = 14.0 Hz, C*H* bpy), 142.1 (s+d, $^4J_{Pt,C}$ = 3.4 Hz, C*H* bpy), 144.9 (s+d, $^3J_{Pt,C}$ = 15.0 Hz, C*H N,O*-hc), 149.3 (s+d, $^2J_{Pt,C}$ = 14.2 Hz, C*H* bpy), 156.7 (s+d, $^2J_{Pt,C}$ = 3.4 Hz, C*H* bpy), 192.8 (s+d, $^1J_{Pt,C}$ = 688.9 Hz, *C*). Anal. Calcd for C₁₇H₂₂N₃OPtBF₄: C, 36.03; H, 3.91. Found: C, 36.17; H, 4.24.

3.3. X-ray Crystallography. Single crystals suitable for X-ray diffraction measurements were obtained by crystallization from benzene/*n*-pentane (2:1) (**16**) and CH₂Cl₂/*n*-pentane (2:1) (**9**(CF₃COO)/**20**(BF₄)). Intensity data were collected on a Stoe-IPDS instrument at 220(2) K (**9**(CF₃COO)/**16**) and on a STADI-4 instrument at 293(2) K (**20**(BF₄)) with Mo Kα radiation (λ = 0.7103 Å, graphite monochromator). Crystallographic data and data collection parameters for **9**(CF₃COO), **16** and **20**(BF₄) are given in Table 6. Absorption corrections were applied numerically (T_{min}/T_{max} = 0.12/0.26, **9**(CF₃COO); 0.04/0.18, **16**; 0.16/0.24, **20**(BF₄)). All structures were solved by direct methods with SHELX-86 and refined using full-matrix least-squares routines against F^2 with SHELX-97.[31,32] Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms with isotropic displacement parameters. Hydrogen atoms were added to their calculated position and refined according to the riding model.

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Center (CCDC) as Supplementary Publication No. CCDC-720320 (**9**(CF₃COO)),

(31) Sheldrick, G. M. *SHELXS-86 Program for Crystal Structures Solutions*; University of Göttingen: Göttingen, Germany, 1990.

(32) Sheldrick, G. M. *SHELXS-97 Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(33) Frisch, M. J.; et al. *Gaussian 03*, revision B.04; Gaussian, Inc.: Wallingford, CT, 2004.

(34) Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664.

(35) (a) Burke, K.; Perdew, J. P.; Wang, Y. In *Electronic Density Functional Theory: Recent Progress and New Directions*; Dobson, J. F., Vignale, G., Das, M. P., Eds.; Plenum Press: New York, 1998. (b) Perdew, J. P. In *Electronic Structure of Solids '91*; Ziesche, P., Eschrig, H., Eds.; Akademie Verlag: Berlin, 1991. (c) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671. (d) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1993**, *48*, 4978. (e) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533.

CCDC-720321 (**16**), and CCDC-720322 (**20**(BF$_4$)). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K. (fax +44 1223-336-033; E-mail deposit@ccdc.cam.ac.uk).

3.4. Computational Details. DFT calculations of compounds were carried out by the Gaussian03 program package[33] using the modified Perdew—Wang 1991 exchange functional by Adamo and Barone[34] plus the Perdew—Wang 1991 correlation functional[35] (MPWPW91). The 6-311G(d,p)[36] basis set as implemented in Gaussian03 was employed for C, H, N, and O atoms, while the relativistic pseudopotentials of the Ahlrichs group and related basis functions of TZVPP quality[37] were employed for Pt atoms. All systems were fully optimized without any symmetry restrictions. The resulting geometries were characterized as equilibrium structures or transition states, respectively, by the analysis of the force constants of normal vibrations. The connection of the located transition states to the equilibrium structures was confirmed by following the reaction path using the IRC algorithm as implemented in Gaussian03.[38,39] Solvent effects were considered according to the polarized continuum model.[20] The interaction energies were corrected for basis set superposition errors (BSSE) that were estimated with counterpoise-type calculations.[40]

Supporting Information Available: Complete ref 33; crystallographic data; tables of computational results (Cartesian coordinates and energies). This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) (a) Dewar, M. J. S.; Reynolds, C. H. *J. Comput. Chem.* **1986**, *7*, 140. (b) Raghavachari, K.; Pople, J. A.; Replogle, E. S.; Head-Gordon, M. *J. Phys. Chem.* **1990**, *94*, 5579.

(37) (a) Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, *294*, 143. (b) Leininger, T.; Nicklass, A.; Küchle, W.; Stoll, H.; Dolg, M.; Bergner, A. *Chem. Phys. Lett.* **1996**, *255*, 274. (c) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chem. Acc.* **1990**, *77*, 123.

(38) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(39) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(40) (a) Simon, S.; Duran, M.; Dannenberg, J. J. *J. Chem. Phys.* **1996**, *105*, 11024. (b) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(41) Stang, P. J.; Huang, Yo.-H. *J. Organomet. Chem.* **1992**, *431*, 247.

(42) Clark, H. C.; Jain, V. K.; Rao, G. S. *J. Organomet. Chem.* **1983**, *259*, 275.