Hydrido(methyl)carbene Complex of Platinum(IV)

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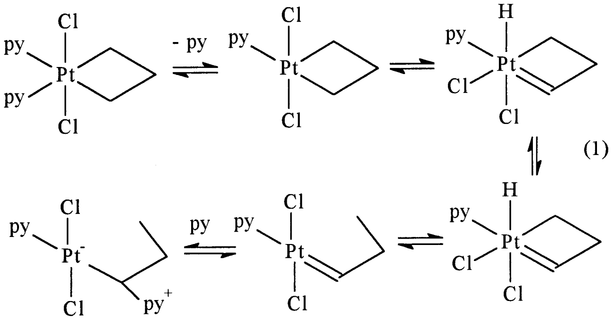
Received July 9, 2002

A hydrido(methyl)(carbene)platinum(IV) complex, using a stabilized Arduengo carbene, has been formed and characterized at low temperature by NMR. The electron-rich carbene complex $[PtMe_2\{C_3H_2N_2(CH_2\text{-}2\text{-}py)_2\}]$ reacts with MeX (X = I or CF_3SO_3) to give $[PtMe_3\{C_3H_2N_2(CH_2\text{-}2\text{-}py)_2\}]X$ and is protonated at low temperature to give $[PtHMe_2\{C_3H_2N_2(CH_2\text{-}2\text{-}py)_2\}]X$, X = CF_3SO_3, BF_4, or CF_3CO_2. At room temperature $[PtHMe_2\{C_3H_2N_2(CH_2\text{-}2\text{-}py)_2\}]^+$ undergoes irreversible reductive elimination of methane and dimerizes to give a binuclear bis{methyl(carbene)platinum(II)} complex cation $[Pt_2Me_2\{C_3H_2N_2(CH_2\text{-}2\text{-}py)_2\}_2]^{2+}$.

Introduction

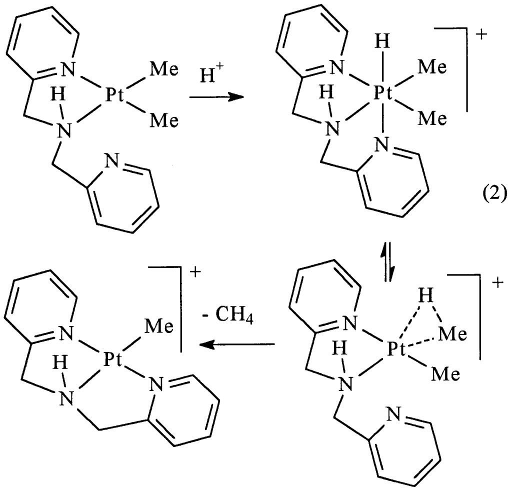
Carbene complexes of transition metals are important as reagents or intermediates in many catalytic and stoichiometric reactions, including C−H activation chemistry.[1] Platinum(II) carbene complexes have been studied extensively,[2] and some platinum(IV) derivatives are also known,[3,4] including a few that also contain alkylplatinum functional groups.[4] Hydrido(alkyl)carbeneplatinum complexes have been suggested as reaction intermediates, especially in reactions of platinacycloalkanes in which α-elimination is preferred over the more common β-elimination reaction in alkyl complexes of transition metals (eq 1);



(1)

similar α-elimination reactions may be involved in platinum-catalyzed petroleum reforming,[5] and such carbene compounds are also possible intermediates in C−H bond activation by carbene complex catalysts.[1] Such complexes have not been directly detected in the past, and so the evidence for their formation as transient intermediates, though convincing, is necessarily based on indirect evidence.[1−5] This article reports the direct detection and some relevant chemistry of the first model hydrido(alkyl)carbeneplatinum(IV) complex, using a stabilized Arduengo carbene, for these elusive intermediates. Of course, it must be recognized that these Arduengo carbenes, by being stabilized in a heterocyclic ring, are different from the simple carbenes (e.g., eq 1) that are proposed as reaction intermediates.[5] Arduengo carbenes are recognized as having strong σ-donor properties, similar to those of aryl groups, and are becoming important as ligand components of active catalysts.[1,6]

This research arose in part from an interest in methyl(hydrido)platinum(IV) complexes as intermediates in methane activation.[7] Flexible tridentate nitrogen donor ligands, such as $(2\text{-}pyCH_2)_2NH$ (BPMA), have yielded moderately stable dimethyl(hydrido)platinum(IV) complexes that equilibrate with a methane complex before irreversible loss of methane occurs (eq 2).



(2)

It was of interest to study how replacement of the central nitrogen atom of BPMA with a carbene donor having a much stronger trans-influence than the NH

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[1] For example: (a) Hillier, A. C.; Lee, H. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2001**, *20*, 4246. (b) Lee, S.; Beare, N. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 8410. (c) Albrecht, M.; Crabtree, R. H.; Mata, J.; Peris, E. *Chem. Commun.* **2002**, 32. (d) Muehlhofer, M.; Strassner, T.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1745.

[2] Frankel, R.; Kniczek, J.; Ponikwar, W.; Noth, H.; Polborn, K.; Fehlhammer, W. P. *Inorg. Chim. Acta* **2001**, *312*, 23. (b) McGuinness, D. S.; Yates, B. F.; Cavell, K. J. *Chem. Commun.* **2001**, 355. (c) Ferguson, G.; Li, Y.; McAlees, A. J.; McCrindle, R.; Zang, E. *J. Organomet. Chem.* **2001**, *617*−*618*, 671. (d) Lai, S.-W.; Chan, M. C. W.; Wang, Y.; Lam, H.-W.; Peng, S.-M.; Che, C.-M. *J. Organomet. Chem.* **2001**, *617*−*618*, 133. (e) Cucciolito, M. E.; Panunzi, A.; Ruffo, F.; Albano, V. G.; Monari, M. *Organometallics* **1999**, *18*, 3482. (f) Zhang, S.-W.; Motoori, F.; Takahashi, S. *J. Organomet. Chem.* **1999**, *574*, 163.

[3] Hartshorn, A. J.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1978**, 348. (b) Chatt, J.; Richards, R. L.; Royston, G. H. D. *J. Chem. Soc., Dalton Trans.* **1976**, 599. (c) Walker, R.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1975**, 272. (d) Balch, A. L. *J. Organomet. Chem.* **1972**, *37*, C19.

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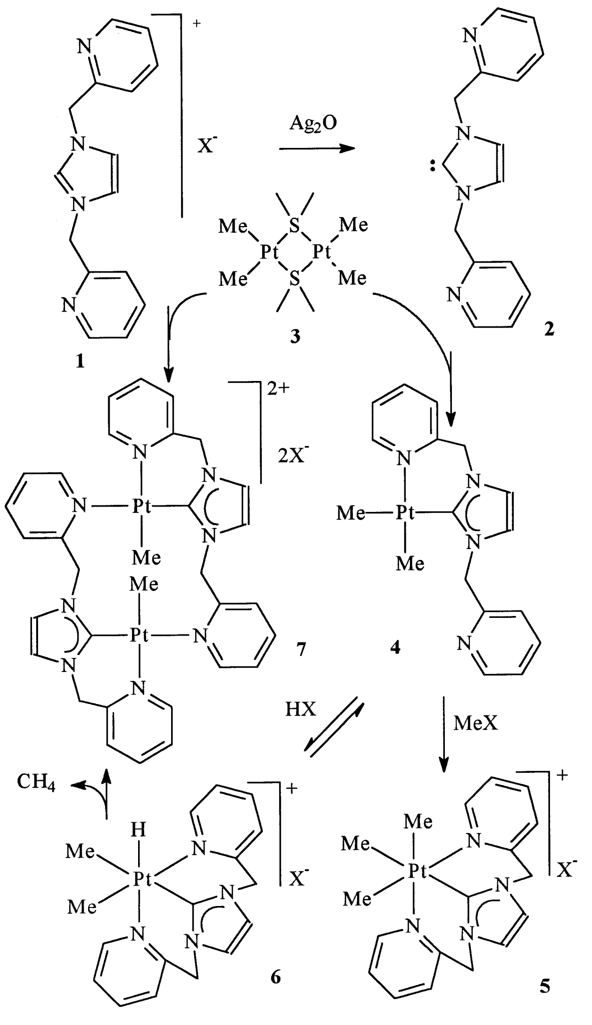
Scheme 1



group of BPMA would affect this chemistry. The results are reported below.

Results and Discussion

The new chemistry is outlined in Scheme 1. Following literature precedent,[8] the carbene precursor 1,3-di(2-picolyl)imidazolium ion, **1**, as the chloride salt was treated with silver oxide to yield the carbene 1,3-di(2-picolyl)imidazolin-2-ylidene, **2**, as a silver(I) complex. Carbene transfer to platinum(II) was then effected by reaction with the dimethylplatinum complex, **3**, by displacement of the weakly bound dimethyl sulfide ligands to give the dimethyl(carbene)platinum(II) complex **4**. Complex **4** is a thermally stable solid, but in solution, it was somewhat air-sensitive. It was characterized by its ^{1}H NMR spectrum in acetone-d_6, which contained two methylplatinum resonances at $\delta = 0.74$ [^2J(PtH) = 90 Hz, PtMe trans to N] and 0.29 [^2J(PtH) = 61 Hz, PtMe trans to C] and separate resonances for the free and coordinated pyridyl groups. The spectrum was similar in CD_3OD solution at low temperature, but peaks were broad at room temperature as a result of unresolved fluxionality. The ^{13}C NMR spectrum also indicates that the carbene exerts a strong trans-influence since the magnitude of ^1J(PtC) for the methylplatinum group trans to carbene (640 Hz) was considerably less than for that trans to pyridyl (830 Hz). The complex **4** contains a free pyridyl group, and it appears to form a weak complex with the silver chloride formed during the synthesis. Samples analyzed as (**4**)$_2$·AgCl, but crystals for structure determination could not be obtained, so the nature of the binding of AgCl is uncertain. The silver halide was easily lost during subsequent reactions, when the pyridyl group coordinated to platinum.

Complex **4** is electron-rich at the platinum(II) center, and the complex is reactive toward oxidative addition. Methyl iodide and methyl triflate each react to give the same trimethylplatinum(IV) cation, **5**, as the iodide or triflate salt, in which the NCN ligand **2** is *fac*-tridentate. The stereochemistry is defined by the presence of two methylplatinum resonances in the ^{1}H NMR spectrum in a 2:1 ratio for methyl groups trans to pyridyl [$\delta = 1.16$, ^2J(PtH) = 73 Hz] and carbene [$\delta = 0.73$, ^2J(PtH) = 47 Hz], respectively. There was only one set of pyridyl resonances since the two pyridyl groups are equivalent in **5**. The analogous reaction with CD_3I gave **5**-d_3 with the CD_3 group trans to pyridyl. Complex **5** is stable for at least one month in solution at room temperature and demonstrates the ability of the *fac*-tridentate ligand **2** to stabilize organoplatinum(IV) compounds. In addition, **5**-d_3 did not undergo scrambling of the CH_3 and CD_3 groups over several days at room temperature (as shown by the 1:1 intensity ratio of the two MePt resonances), showing that the carbene has the unusual property of locking in the stereochemistry at platinum(IV).[7,9]

The reaction of **4** with protic acids (HBF_4, CF_3CO_2H, CF_3SO_3H) in acetone-d_6 at −78 °C gave the hydrido(dimethyl)carbene complex cation **6** ($X = BF_4$, CF_3CO_2, CF_3SO_3, Scheme 1), whose stereochemistry was defined by its ^{1}H NMR spectrum. In particular, the couplings to ^{195}Pt defined the presence of a hydride [$\delta = -20.18$, ^1J(PtH) = 1438 Hz], a methyl group [$\delta = 1.05$, ^2J(PtH) = 70 Hz] trans to pyridyl, and a methyl group [$\delta = 0.70$, ^2J(PtH) = 44 Hz] trans to carbene. None of the alternate isomer with hydride trans to carbene was detected at any stage, again indicating that this carbene ligand can lock in the stereochemistry at platinum(IV). Complex **6** is stable for at least 1 week at −78 °C, but it decomposes within 7 h at −60 °C and within 1 h at −40 °C, as monitored by NMR, by reductive elimination of methane. The thermal stability of complex **6** stabilized by the *fac*-tridentate NCN donor ligand is considerably lower than for similar complexes with NNN donors.[7] The carbene is clearly a strong donor, as shown by the low coupling constant ^2J(PtH) = 44 Hz to the trans methyl group, but the carbene group still has a lower

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(4) Zhang, S.-W.; Takahashi, S. *Organometallics* **1998**, *17*, 4757. (b) Rendina, L. M.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 1030. (c) Chisholm, M. H.; Clark, H. C.; Johns, W. S.; Ward, J. E. H.; Yasufuku, K. *Inorg. Chem.* **1975**, *14*, 900.

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(6) Jafarpour, L.; Nolan, S. P. *J. Organomet. Chem.* **2001**, *617*−*618*, 17.

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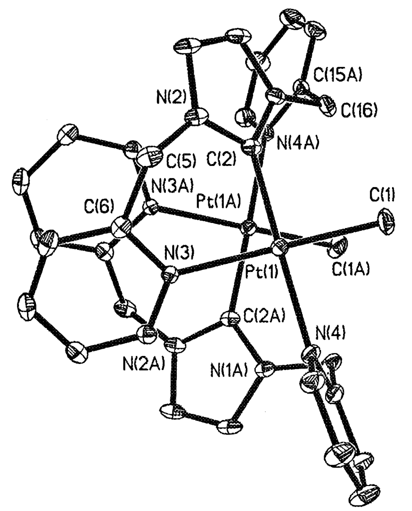


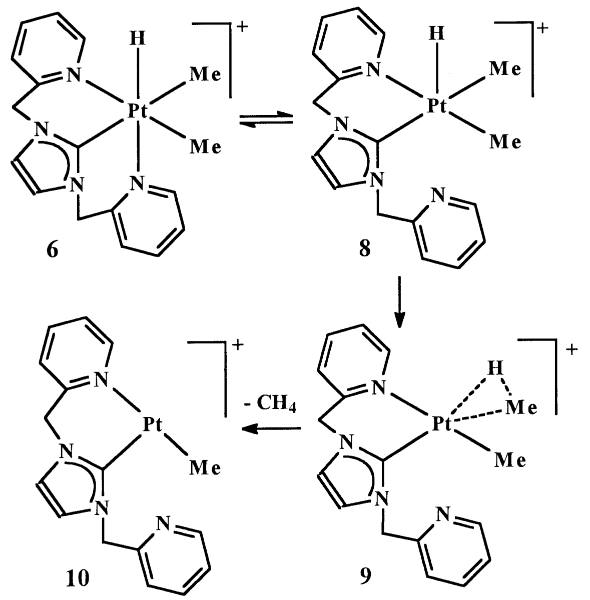
Figure 1. View of the structure of the dicationic complex **7**.

ability compared to amine or pyridyl to stabilize the hydrido(methyl)platinum(IV) unit.[7] The reductive elimination of methane is irreversible, as shown by the formation of CH_3D only, with no deuterium incorporation into methylplatinum groups, when the reaction was carried out with CF_3SO_3D in CD_3OD solvent, whereas such reactions with NNN donor ligands often give the range of isotopomers CH_nD_{4-n}.[7]

The product formed by reductive elimination of methane from **6** is the interesting binuclear methyl(carbene)-platinum(II) complex **7** (Scheme 1). Complex **7** was also formed by direct reaction of the 1,3-di(2-picolyl)imidazolium ion, **1**, with the dimethylplatinum complex, **3**, as shown in Scheme 1. The complex was identified by its NMR spectra and also by a structure determination (Figure 1). The analogous palladium(II) complex is known but exists as a mixture of a monomer and a dimer, whose exact structure was not defined but which is presumably isostructural with **7**.[10] The selective formation of complex **7** is almost certainly for electronic reasons, with a strong preference for the *cis*-methyl-(carbene) stereochemistry at platinum(II), and the binuclear complex has a face-to-face structure with the platinum atoms separated by 3.67 Å and the angle between the planes of the platinum atoms of 17°. The formation of **7** can also be rationalized in terms of mechanism. Dissociation of the pyridyl group trans to hydride gives a five-coordinate intermediate, **8**,[9] which is likely to undergo reductive elimination by coupling of the hydride with the methylplatinum group that is trans to carbene rather than the more strongly bonded methylplatinum group trans to pyridyl (Scheme 2). The methane complex **9**, with methane trans to the carbene, then loses free methane faster than it can equilibrate back to the hydrido(methyl) precursor **8** (Scheme 2). Dimerization of the platinum(II) product **10** naturally forms **7**.

Although the carbene ligand in the hydrido(methyl)-carbene complex **6** is a “stabilized” one, the stereochemistry and reaction selectivity is fully consistent with that proposed, on the basis of indirect evidence,[5] for short-lived intermediates. In particular, the carbene appears to promote easy, irreversible C−H reductive elimination. Hence complex **6** can be considered as a crude model for reactive hydrido(alkyl)(carbene)platinum(IV) intermediates.

Scheme 2



Experimental Section

Reactions were carried out under inert atmosphere by using Schlenk or drybox techniques. NMR spectra were recorded by using a Varian Inova 400 MHz or Mercury 400 MHz spectrometer. The complex $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and imidazolium salt $[C_3H_3N_2(CH_2\text{-}2\text{-}py)_2]Cl$ were prepared by using the literature methods.[10,11]

$[PtMe_2(\kappa^2\text{-}N,C\text{-}C_3H_2N_2(CH_2\text{-}2\text{-}py)_2]$, 4. A mixture of $[C_3H_3N_2(CH_2\text{-}2\text{-}py)_2]Cl$ (515 mg, 1.80 mmol) and Ag_2O (415 mg, 1.79 mmol) in dry methanol (10 mL) was stirred in the dark for 25 min, followed by addition of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (580 mg, 1.01 mmol). After 3 h, activated carbon was added and the mixture was filtered through Celite. The red solution was evaporated, and the red-orange solid product was washed with diethyl ether (20 mL) and dried under vacuum. Yield: 486 mg, 57%. NMR in acetone-d_6: $\delta(^1H) = 8.96$ [d, 1H, $^3J(HH) = 6$ Hz, $^3J(PtH) = 27$ Hz, coord py]; 8.48 [d, 1H, $^3J(HH) = 4$ Hz, free py]; 7.95 [dd, 1H, $^3J(HH) = 8$ Hz, coord py]; 7.65 [dd, 1H, $^3J(HH) = 8$ Hz, free py]; 7.60 [d, 1H, $^3J(HH) = 8$ Hz, coord py]; 7.34 [dd, 1H, $^3J(HH) = 6$ Hz, 8 Hz, coord py]; 7.21 [d, 1H, $^3J(HH) = 8$ Hz, free py]; 7.20 [dd, ^1H, $^3J(HH) = 8$ Hz, 4 Hz, free py]; 7.30 [d, 1H, $^3J(HH) = 2$ Hz, Im C_2H_2]; 7.06 [d, 1H, $^3J(HH) = 2$ Hz, Im C_2H_2]; 5.42 [s, 2H, CH_2]; 5.18 [br, 2H, CH_2]; 0.74 [s, 3H, $^2J(PtH) = 90$ Hz, PtMe trans to py]; 0.29 [s, 3H, $^2J(PtH) = 61$ Hz, PtMe trans to Im]; $\delta(^{13}C) = 157.91$, 154.29 [py]; 152.03 [$J(PtC) = 16$ Hz, py]; 149.39, 136.79, 136.74 [py]; 125.27 [$J(PtC) = 19$ Hz, py]; 124.37, 122.60, 121.70 [py]; 120.37 [im]; 119.97 [$J(PtC) = 25$ Hz, im]; 55.15 [$J(PtC) = 50$ Hz, CH_2]; 54.06 [CH_2]; 4.42 [$J(PtC) = 640$ Hz, PtMe trans im]; -25.69 [$J(PtC) = 830$ Hz, PtMe trans py]. This complex was difficult to purify since it was air-sensitive and did not crystallize easily. It also occluded the silver chloride formed, probably by coordination to the free pyridine group. Anal. Calcd for $C_{17}H_{20}N_4Pt{\cdot}0.5AgCl$: C, 37.2; H, 3.9; N, 10.2. Found: C, 36.8; H, 3.9; N, 9.7. The presence of AgCl in soluble samples was confirmed by XPS.

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[PtMe$_3$(κ^3-N,N′,C-C$_3$H$_2$N$_2$(CH$_2$-2-py)$_2$]I, 5a. To a solution of complex **4** (122 mg, 0.257 mmol) in dry THF (10 mL) was added MeI (18 μl, 0.289 mmol). A tan-colored precipitate formed rapidly. After stirring for 2 h, pentane (20 mL) was added, and the solid residue was separated and dried under vacuum. It was recrystallized from CH$_2$Cl$_2$/pentane. Yield: 78.1 mg, 50%. NMR in acetone-d_6: δ(^{1}H) = 9.27 [d, 1H, ^3J(HH) = 6 Hz, ^3J(PtH) = 14 Hz, py]; 8.09 [dd, 1H, ^3J(HH) = 7 Hz, 8 Hz, py]; 7.86 [d, 1H, ^3J(HH) = 8 Hz, py]; 7.64 [s, 2H, Im]; 7.63 [dd, 1H, ^3J(HH) = 6 Hz, 7 Hz, py]; 5.74 [br, 4H, CH$_2$]; 1.16 [s, 6H, ^2J(PtH) = 73 Hz, PtMe trans to py]; 0.73 [s, 3H, ^2J(PtH) = 47 Hz, PtMe trans to Im]. Anal. Calcd for C$_{18}$H$_{23}$IN$_4$Pt: C, 35.0; H, 3.7; N, 9.1. Found: C, 34.9; H, 3.8; N, 8.8.

The complex [PtMe$_3$(κ^3-N,N=,C−C$_3$H$_2$N$_2$(CH$_2$-2-py)$_2$]I, **5b**, was prepared similarly using methyl triflate. The ^{1}H NMR spectral parameters were identical with those for **5a**: δ(^{13}C) = 154.2 [J(PtC) = 5 Hz, py]; 151.43, 141.12 [py]; 127.97 [J(PtC) = 8 Hz, py]; 122.98 [J(PtC) = 14 Hz, Im]; 55.08 [J(PtC) = 10 Hz, CH$_2$]; 10.77 [J(PtC) = 519 Hz, PtMe trans im]; −11.92 [J(PtC) = 670 Hz, PtMe trans py].

[PtHMe$_2$(κ^3-N,N′,C-C$_3$H$_2$N$_2$(CH$_2$-2-py)$_2$][CF$_3$SO$_3$], 6a. This was prepared by reaction of complex **4** (0.10 mmol) with CF$_3$SO$_3$H in acetone-d_6 at −78 °C in an NMR tube and characterized in situ. NMR at −80 °C: δ(^{1}H) = 9.32 [br, 1H, py]; 9.25 [br, 1H, py]; 8.17 [dd, 1H, ^3J(HH) = 7 Hz, py]; 8.10 [dd, 1H, ^3J(HH) = 6 Hz, py]; 7.87 [br, 2H, py]; 7.71 [br, 2H, py and Im]; 7.68 [s, 1H, Im]; 7.62 [dd, 1H, ^3J(HH) = 6 Hz, py]; 5.84 [d, 1H, ^2J(HH) = 15 Hz, CH$_2$]; 5.81 [d, 1H, ^2J(HH) = 16 Hz, CH$_2$]; 5.70 [d, 1H, ^2J(HH) = 16 Hz, CH$_2$]; 5.41 [d, 1H, ^2J(HH) = 15 Hz, CH$_2$]; 1.05 [s, 3H, ^2J(PtH) = 70 Hz, PtMe trans to py]; 0.70 [s, 3H, ^2J(PtH) = 44 Hz, PtMe trans to Im]; −20.18 [s, 1H, ^1J(PtH) = 1438 Hz, PtH]; δ(^{13}C) = 154.31, 152.86, 151.10, 150.66, 141.07, 140.91, 127.65, 126.70, 126.64, 126.62 [py]; 122.84, 121.88 [im]; 56.51 [J(PtC) = 26 Hz, CH$_2$]; 54.19 [CH$_2$]; −3.93 [J(PtC) = 481 Hz, PtMe trans im]; −23.11 [J(PtC) = 618 Hz, PtMe trans py].

[Pt$_2$Me$_2${μ-κ^3-N,N′,C-C$_3$H$_2$N$_2$(CH$_2$-2-py)$_2$}$_2$][PF$_6$]$_2$, 7a. A mixture of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (60.0 mg, 0.104 mmol) and [C$_3$H$_3$N$_2$(CH$_2$-2-py)$_2$][PF$_6$] (82.5 mg, 0.208 mmol) in THF (8 mL) was stirred for 4 days. Diethyl ether (20 mL) was added to precipitate the product as a pale tan solid. The solvent was removed, and the product was dried under vacuum. Yield: 74 mg, 59%. Colorless single crystals were grown from acetone. NMR in acetone-d_6: δ(^{1}H) = 8.93 [d, 1H, ^3J(HH) = 6 Hz, py]; 8.43 [d, 1H, ^3J(HH) = 8 Hz]; 8.29 [dd, 1H, ^3J(HH) = 8, 8 Hz]; 7.74 [d, 1H, ^3J(HH) = 2 Hz, py]; 7.59 [dd, 1H, ^3J(HH) = 8, 6 Hz]; 7.58−7.55 [m, 2H, py]; 7.50 [dd, 1H, ^3J(HH) = 8 Hz, py]; 7.32 [s, 1H, Im C$_2$H$_2$]; 7.29 [s, 1H, Im C$_2$H$_2$]; 5.69 [d, 1H, ^3J(HH) = 18 Hz, CH$_2$]; 5.65 [d, 1H, ^3J(HH) = 14 Hz, CH$_2$]; 5.63 [d, 1H, 18 Hz, CH$_2$]; 5.41 [d, 1H, 14 Hz, CH$_2$]; 0.89 [s, 3H, ^2J(PtH) = 80 Hz, PtMe]; δ(^{13}C) = 155.62, 153.50, 151.72, 150.06, 140.77, 139.73, 130.07, 126.55, 125.86, 125.71 [py]; 123.61, 120.39 [im]; 54.97, 54.69 [CH$_2$]; −22.26 [PtMe]. Anal. Calcd for C$_{32}$H$_{34}$F$_{12}$N$_8$P$_2$Pt$_2$: C, 31.7; H, 2.8; N, 9.2. Found: C, 31.5; H, 2.7; N, 9.0.

[Pt$_2$Me$_2${μ-κ^3-N,N′,C-C$_3$H$_2$N$_2$(CH$_2$-2-py)$_2$}$_2$]Cl$_2$, 7b. A mixture of [C$_3$H$_3$N$_2$(CH$_2$-2-py)$_2$]Cl (213 mg, 0.743 mmol) and Ag$_2$O (173 mg, 0.749 mmol) in methanol (10 mL) was stirred in the dark for 25 min, followed by the addition of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (203 mg, 0.353 mmol). The mixture was stirred for 3 days, the solution was filtered through Celite, and the solvent was evaporated to give the product. Yield: 270 mg, 77%. Anal. Calcd for C$_{32}$H$_{34}$Cl$_2$N$_8$Pt$_2$: C, 38.7; H, 3.5; N, 11.3. Found: C, 38.4; H, 3.9; N, 11.0.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [Pt$_2$Me$_2$(pImp)$_2$][PF$_6$]$_2$, 7a

Pt(1)−C(2)	1.960(3)	N(1)−C(2)	1.355(5)
Pt(1)−C(1)	2.048(4)	N(1)−C(3)	1.378(5)
Pt(1)−N(4)	2.098(3)	C(2)−N(2)	1.345(5)
Pt(1)−N(3)	2.135(3)	N(2)−C(4)	1.388(5)
C(2)−Pt(1)−C(1)	92.7(2)	N(2)−C(2)−N(1)	104.8(3)
C(2)−Pt(1)−N(4)	176.9(1)	C(2)−N(1)−C(3)	109.9(3)
C(1)−Pt(1)−N(4)	86.9(2)	C(2)−N(2)−C(4)	111.4(3)
C(2)−Pt(1)−N(3)	88.3(1)	N(1)−C(2)−Pt(1)	133.3(3)
C(1)−Pt(1)−N(3)	174.5(2)	N(2)−C(2)−Pt(1)	121.9(3)
N(4)−Pt(1)−N(3)	91.7(1)		

Table 2. Crystal Data and Structure Refinement for [Pt$_2$Me$_2$(pImp)$_2$][PF$_6$]$_2$, 7a

empirical formula, fw	C$_{16}$H$_{17}$F$_6$N$_4$PPt, 605.40
temperature	200(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$C2/c$
cell dimens	a = 25.1989(3) Å b = 10.3131(2) Å c = 16.6591(3) Å β = 118.2870(8)°
volume, Z	3812.4(1) Å^3, 8
d(calc)	2.110 Mg/m^3
abs coeff	7.511 mm^{-1}
F(000)	2304
no. of reflns collected	10 634
no. of ind reflns	5591 [R(int) = 0.0336]
abs corr	integration
max. and min. transmn	0.3987 and 0.1531
no. of data/restraints/params	5591/0/290
goodness-of-fit on F^2	1.036
final R indices [$I > 2\sigma(I)$]	R1 = 0.0296, wR2 = 0.0644
R indices (all data)	R1 = 0.0467, wR2 = 0.0694

Structure Determination. A crystal of [Pt$_2$Me$_2${μ-κ^3-N,N′,C-C$_3$H$_2$N$_2$(CH$_2$-2-py)$_2$}$_2$][PF$_6$]$_2$, **7a**, was mounted on a glass fiber. Data were collected by using a Nonius Kappa-CCD diffractometer with COLLECT software (Nonius B.V., 1998). Crystal cell refinement and data reduction were carried out using DENZO and data were scaled by using SCALEPACK (Nonius B.V., 1998). The structure was solved by Patterson methods and refined by successive difference Fouriers, using SHELXTL V5.1 (Sheldrick, G. M.). Each of the [PF$_6$]$^-$ anions was disordered and modeled as a 65:35 disorder over two positions. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and were riding on their associated carbon atoms. Details of the crystal data and refinement are listed in Table 2.

Acknowledgment. We thank Dr. M. C. Jennings for the X-ray data and NSERC (Canada) for financial support. R.J.P. thanks the government of Canada for a Canada Research Chair.

Supporting Information Available: X-ray data for complex **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0205400