Mono- vs Bis(carbene) Complexes: A Detailed Study on Platinum(II)−Benzimidazolin-2-ylidenes

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The reaction of $PtBr_2$ with NaOAc and 1,3-diisopropylbenzimidazolium bromide (**A**) in DMSO afforded the mixed monocarbene−DMSO complex *cis*-[$PtBr_2$(DMSO)(^{i}Pr$_2$-bimy)] (*cis*-**1**) and the bis(carbene) complex *trans*-[$PtBr_2$(^{i}Pr$_2$-bimy)$_2$] (*trans*-**2**). The DMSO ligand in *cis*-**1** can be easily replaced by stronger donors such as triphenylphosphine and pyridine to give novel benzannulated monocarbene complexes *trans*-[$PtBr_2$(^{i}Pr$_2$-bimy)(PPh_3)] (*trans*-**3**), *cis*-[$PtBr_2$(^{i}Pr$_2$-bimy)(PPh_3)] (*cis*-**3**), and *trans*-[$PtBr_2$(^{i}Pr$_2$-bimy)-(Pyridine)] (*trans*-**4**), respectively. All compounds have been fully characterized by multinuclei NMR spectroscopies and mass spectrometry (ESI, FAB). X-ray diffraction studies on single crystals of *cis*-**1**, *trans*-**2**, *cis*-**3**, and *trans*-**4** revealed a square-planar geometry and a fixed orientation of the N-isopropyl substituents with the C−H protons pointing to the metal center to maximize interesting and rare C−H···Pt preagostic interactions. These interactions are also retained in solution, as indicated by the large downfield shift of the isopropyl C−H protons in the ^{1}H NMR spectrum compared to that in the precursor salt **A**.

Introduction

The chemistry of N-heterocyclic carbenes (NHCs) and their transition metal complexes is currently a "hot topic" in organometallic chemistry and homogeneous catalysis and will continue to play a major role in these areas.[1] In particular, NHC complexes of group 10 metals are of great interest due to their potential catalytic applications. For example, palladium(II) carbene complexes derived from imidazole and imidazoline precursors have been successfully developed as highly active precatalysts for C−C coupling reactions such as Mizoroki−Heck and Suzuki−Miyaura couplings as well as CO−olefin copolymerization.[1] In contrast to the extensive studies on palladium NHC complexes, less attention has been paid to the synthesis of platinum NHC complexes and their use in catalysis.[2] In particular, platinum complexes bearing benzimidazolin-2-ylidenes are surprisingly rare.[3] Among the few reported examples, the template-controlled cascade reaction forming a homoleptic Pt(II)−tetracarbene complex is especially worth mentioning.[3a] Our interest in benzannulated NHCs is driven by their interesting properties as a consequence of their intermediate position between imidazole- and imdazoline-derived analogues.[4] Recently, we reported the syntheses and reactivities of several Pd(II) complexes with the bulky 1,3-diisopropylbenzimidazolin-2-ylidene ligand (^{i}Pr$_2$-bimy), which also exhibited interesting and rare preagostic C−H···Pd interactions.[5a,b] As a continuation of our research on benzannulated NHCs,[5] we herein describe the synthesis and structural characterization of platinum(II) complexes of this unique ligand.

Results and Discussion

Synthesis of Platinum(II) Complexes. Recently, Strassner and co-workers reported a general synthetic method toward platinum(II) complexes bearing chelating dicarbene ligands, which involves in situ deprotonation of diimidazolium salts with commercially available Pt(acac)$_2$ (acac = acetylacetonate) in DMSO.[6] Surprisingly, our attempt to synthesize a Pt(II) bis-(benzimidazolin-2-ylidene) complex using this method proved unsuccessful. The reaction of Pt(acac)$_2$ with 2 equiv of 1,3-diisopropylbenzimidazolium bromide (^{i}Pr$_2$-bimyH$^+$Br$^-$) (**A**) in DMSO at 90 °C gave a reaction mixture, from which only the DMSO-coordinated monocarbene complex *cis*-[$PtBr_2$(DMSO)-(^{i}Pr$_2$-bimy)] (*cis*-**1**) was isolated in a low yield of 18% together

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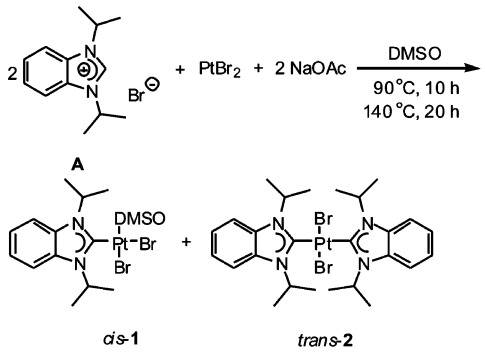
Scheme 1. Synthesis of Pt(II) Complexes *cis*-1 and *trans*-2



with unreacted starting materials. The desired bis(carbene) complex could not be obtained. To avoid the formation of DMSO complex *cis*-**1**, we explored the reaction in acetonitrile under reflux conditions. However, no carbene complexes were detected, and again, ~90% of $Pt(acac)_2$ was recovered. The reaction of $PtBr_2$ with **A** and NaOAc in acetonitrile under reflux was also attempted to no avail even after 30 h. The failure of these attempts is probably due to the difficulty in the deprotonation of salt **A** resulting from the +*I*-effect and the steric bulk of the N-isopropyl substituents as observed in the formation of Pd(II) complexes of the same ligand.[5b] It also demonstrates the different reactivity of benzimidazolium salts compared to the commonly used imidazolium or imidazolinium precursors.

Only the reaction of $PtBr_2$ with 2 equiv of **A** and NaOAc as an external base in DMSO, as illustrated in Scheme 1, afforded the bis(carbene) complex *trans*-[$PtBr_2$(^{i}Pr$_2$-bimy)$_2$] (*trans*-**2**), however, as a minor product in only 3% yield. As the major product, we isolated the mixed monocarbene−DMSO complex *cis*-**1** in an improved yield of 55%. Isolation of *trans*-**2** was straightforward and involved only a simple filtration step due to its low solubility in DMSO. It is also only sparingly soluble in DMF, but can be dissolved in halogenated solvents. The DMSO filtrate, on the other hand, contained mainly the monocarbene complex *cis*-**1**. The preferred formation of *cis*-**1** over *trans*-**2** in this reaction is presumably due to the steric bulk of the isopropyl substituents as well as the affinity of the relatively soft DMSO sulfur atom for the soft Pt center, which in turn hampers the attack of a second carbene ligand. Both complexes *cis*-**1** and *trans*-**2** are stable toward air and moisture. Furthermore, complex *cis*-**1** shows better solubility than *trans*-**2** in most polar organic solvents such as $CHCl_3$, CH_2Cl_2, CH_3-CN, DMF, and DMSO.

The formation of *cis*-**1** and *trans*-**2** was confirmed by ^{1}H NMR spectroscopy. The absence of the NCHN proton characteristic for salt **A** in the spectra of both *cis*-**1** and *trans*-**2** indicates a successful coordination of the carbene ligand ^{i}Pr$_2$-bimy to the platinum(II) centers. In addition, both complexes exhibit interesting C−H···Pt preagostic interactions,[7] as indicated by significant downfield shifts of their isopropyl C−H resonances upon coordination from 5.21 ppm in the precursor salt **A** to 6.27 ppm in *cis*-**1** and to 6.52 ppm in *trans*-**2**, respectively. These C−H···Pt interactions are also corroborated by the geometric parameters observed in the solid-state structures of the two complexes (vide infra). Noteworthy, such preagostic interactions seem to be characteristic for this ligand, as they have also been observed in palladium(II) complexes.[5a,b] The ^{1}H NMR signal for the methyl groups of the DMSO ligand in *cis*-**1** arises at 3.61 ppm as a singlet with platinum satellites of ^3J(Pt,H) = 21.5 Hz. Such a chemical shift and coupling constant are typical for sulfur-bonded sulfoxide complexes.[8] The ^{13}C NMR signal of these methyl groups appearing at 47.1 ppm also shows pronounced coupling to the platinum atom with ^2J(Pt,C) = 70.57 Hz. Coordination of the DMSO molecule in *cis*-**1** is further confirmed by a strong S=O stretching band at 1134 cm^{-1} in the IR spectrum (cf. 1050 cm^{-1} for free DMSO).[9]

Furthermore, two doublets of equal intensity at 1.75 and 1.74 ppm are observed for the carbene ligand in the ^{1}H NMR spectrum of *cis*-**1**, suggesting two inequivalent CH_3 groups of the N-isopropyl substituents. Correspondingly, two singlets at 20.6 and 20.4 ppm for these CH_3 groups are found in the ^{13}C NMR spectrum pointing to a sterically hindered rotation of the Pt−$C_{carbene}$ bond in the more congested cis configuration. In contrast, these CH_3 groups are equivalent in complex *trans*-**2**, giving rise to only one doublet at 1.81 ppm and confirming the trans configuration of this complex. Moreover, there is also a notable difference in the ^{13}C NMR resonances of the isopropyl C−H groups in the two complexes. Although their chemical shifts are found in the same range with values of 54.3 ppm for *cis*-**1** and 53.1 ppm for *trans*-**2**, respectively, only the former shows Pt satellites with a constant of ^3J(Pt,C) = 31.2 Hz. Finally, the carbene signals in *cis*-**1** and *trans*-**2** resonate at 153.6 and 176.5 ppm, respectively. The absence of Pt satellites for the carbene signal in monocarbene complexes is common and likely due to the low intensity of this signal.[3a,9] On the other hand, the absence of the Pt−$C_{carbene}$ coupling in the dicarbene complex *trans*-**2** can probably be attributed to its low solubility. Furthermore, the carbene resonance in *trans*-**2** appears more upfield compared to that of the palladium analogue *trans*-[$PdBr_2$(^{i}Pr$_2$-bimy)$_2$] (180.0 ppm). A similar but more pronounced upfield shift of the carbene resonance upon replacement of Pd by Pt has been reported by others.[9,10]

Single crystals suitable for X-ray diffraction were obtained from a $CHCl_3$ solution for *cis*-**1** or from a CH_2Cl_2 solution for *trans*-**2**. Their molecular structures are depicted in Figure 1 and 2, selected bond parameters are summarized in Table 1, and crystallographic data are listed in Table 2. Complex *cis*-**1** crystallizes as solvate **1**·2$CHCl_3$ with the space group *P*2(1)/*m*. Its molecular structure shows the expected square-planar arrangement around the platinum center with the NHC and DMSO ligands cis to each other. The latter coordinates to the platinum center through the sulfur atom, as indicated by the ^{1}H NMR and IR spectra. Upon coordination, the sulfur atom in the DMSO molecule adopts a tetrahedral configuration with angles ranging from 102.0(6)° to 117.0(3)°. The carbene ring plane is perfectly perpendicular to the PtCSBr coordination plane with a dihedral angle of 90 °C due to symmetry. The Pt−$C_{carbene}$[3a,6,7,10c,11] and

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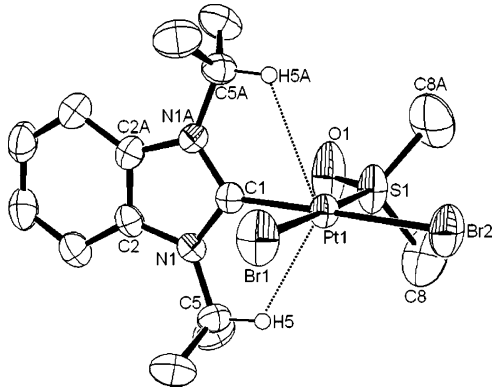


Figure 1. Molecular structure of complex *cis*-**1**·2$CHCl_3$ showing 50% probability ellipsoids; solvent molecules and hydrogen atoms except for H5 and H5A are omitted for clarity.

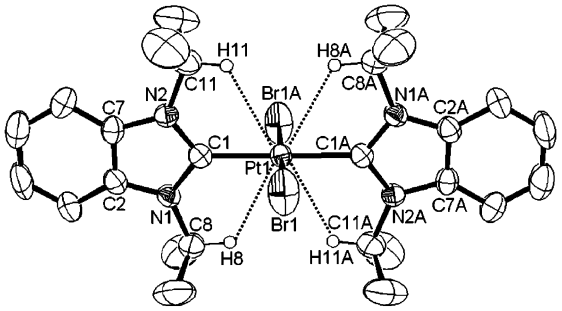
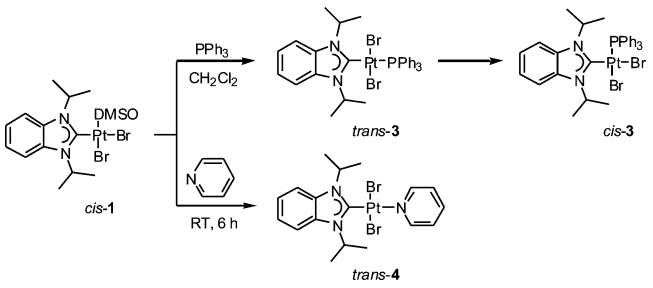


Figure 2. Molecular structure of complex *trans*-**2** showing 50% probability ellipsoids; hydrogen atoms, except for H8, H8A, H11, and H11A are omitted for clarity.

Scheme 2. Synthesis of Pt(II) Complexes *trans*-3, *cis*-3, and *trans*-4



Pt−S[12] bond lengths amount to 1.979(6) and 2.196(2) Å, respectively, and are in the expected range. Furthermore, the Pt−Br2 bond trans to the NHC (2.4628(9) Å) is longer than the Pd−Br1 bond trans to the DMSO (2.4294(10) Å), confirming a stronger trans influence of the NHC.

In complex **2** the platinum center is coordinated by two carbene and two bromo ligands in a trans fashion. Both carbene ring planes are oriented almost perpendicular to the PtC_2Br_2 plane with a dihedral angle of 87.72°. The Pd−C bonds in *trans*-**2** amount to 2.015(4) Å and are, as expected, longer than that in *cis*-**1**. Finally, it is noteworthy that all C−H protons of the isopropyl groups in both *cis*-**1** and *trans*-**2** show a fixed orientation toward the metal center, resulting in relatively short C−H···Pt distances of 2.747 Å in the former and 2.734 and 2.706 Å in the latter complex, respectively. These structural properties support the aforementioned C−H···Pt preagostic interactions as indicated by ^{1}H NMR spectroscopy.[8]

Reactivity Studies of Complex *cis*-1. *cis*-**1** is stable in coordinating solvents such as CH_3CN and DMF. However, in the presence of stronger donors, the DMSO ligand can be easily replaced. This is demonstrated by the reaction of *cis*-**1** with triphenylphosphine (PPh_3) and pyridine, as shown in Scheme 2.

When *cis*-**1** and 1 equiv of PPh_3 were dissolved in CH_2Cl_2 at room temperature, complex *trans*-[$PtBr_2$(^{i}Pr_2-bimy)(PPh_3)] (*trans*-**3**) was first formed, as indicated by ^{1}H and ^{31}P NMR spectroscopy. *trans*-**3** was found to slowly convert to its thermodynamically more stable cis isomer. However, this isomerization process is sluggish at ambient temperature. An attempt to facilitate this process was made by heating the reaction mixture in refluxing CH_2Cl_2. But even after 15 h this trans−cis isomerization did not achieve completeness and a mixture of *trans*-**3** and *cis*-**3** was obtained in a ratio of 1.6:1, as suggested by the integration of their ^{1}H NMR signals. We have observed a faster isomerization in the palladium analogue, where the trans complex completely converts to its cis isomer in CH_2Cl_2 under reflux after 15 h.[5a] The slower isomerization process for Pt(II) mixed carbene−phosphine complexes compared to their palladium analogues has also been reported by Lappert for trialkylphosphines.[13] However, c*is*-**3** can be isolated from the product mixture due to its lower solubility in THF than *trans*-**3**. On the other hand, isolation of pure *trans*-**3** was not feasible due to its aforementioned isomerization to *cis*-**3**.

The formation of *cis*-**3** was supported by its positive-mode FAB mass spectrum, where a peak at $m/z = 739$ corresponding to the $[M - Br]^+$ fragment was observed. The ^{1}H NMR spectrum of *cis*-**3** in $CDCl_3$ shows a characteristic multiplet at 6.09 ppm for the C−H proton and two doublets of equal intensity at 1.63 and 0.86 ppm for the CH_3 groups of the N-isopropyl substituents. In its ^{31}P NMR spectrum, a single peak at 10.0 ppm with platinum satellites of ^2J(Pt,P) = 3848 Hz was observed, confirming the successful substitution of DMSO by PPh_3. Furthermore, the ^{13}C NMR resonance of the carbene atom in *cis*-**3** appears at 161.0 ppm as a doublet due to its coupling to the phosphine with ^2J(P,C) = 5.5 Hz.

Single crystals of *cis*-**3** were obtained from a CH_2Cl_2/hexane solution, and its molecular structure is depicted in Figure 3. The platinum center in *cis*-**3** is surrounded by one carbene, one phosphine, and two bromo ligands in a nearly perfect square-planar fashion with the former two cis to each other. The Pt−$C_{carbene}$ and Pt−P bond lengths amounting to 1.973(4) and 2.2327(11) Å, respectively, are unexceptional.[10c,11] It is maybe worth mentioning that the commonly observed stronger trans influence of NHCs over tertiary phosphine ligands is not demonstrated in *cis*-**3**, as the two Pt−Br bonds are of the same length (2.4815(5) Å).

In contrast to the reaction of *cis*-**1** with PPh_3, the substitution of DMSO by pyridine yielded only the trans-configured product *trans*-[$PtBr_2$(^{i}Pr_2-bimy)(pyridine)] (*trans*-**4**). When 1 equiv of pyridine was added into a solution of *cis*-**1** in $CDCl_3$ at ambient temperature, only signals corresponding to *cis*-**1**, *trans*-**4**, unreacted pyridine, and released DMSO were present in the spectra. Figure 4 shows the time-dependent ^{1}H NMR spectra in the range 6.76−6.12 ppm (C−H resonances of N-isopropyl groups), illustrating the progress of the reaction. This reaction is irreversible and complete after ∼18 h. No changes were found in the ^{1}H NMR spectrum afterward, suggesting that no trans−

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Table 1. Selected Bond Lengths [Å] and Angles [deg] for Complexes *cis*-1, *trans*-2, *cis*-3, and *trans*-4

	cis-**1**·2CHCl$_3$	*trans*-**2**	*cis*-**3**	*trans*-**4**·THF
Pt1−C1	1.979(6)	2.015(4)	1.973(4)	1.958(4)
Pt1−Br1	2.4294(10)	2.4268(4)	2.4815(5)	2.4253(5)
Pt1−Br2	2.4628(9)		2.4815(5)	2.4188(5)
Pt1−S1	2.196(2)			
Pt1−P1			2.2327(11)	
Pt1−N3				2.085(4)
N1−C1	1.348(5)	1.354(4)	1.354(5)	1.355(5)
N1−C2	1.391(6)	1.397(4)	1.378(5)	1.397(5)
N1−C5	1.469(6)			
N1−C8		1.479(4)	1.498(5)	1.478(5)
N2−C1		1.357(4)	1.345(5)	1.351(5)
N2−C7		1.387(5)	1.391(5)	1.383(5)
N2−C11		1.476(5)	1.493(5)	1.483(5)
C2−C2A	1.372(10)			
C2−C7		1.396(5)	1.390(6)	1.390(6)
C−H···Pt	2.7474(6)	2.7341(1), 2.7059(1)	2.7107(2), 2.7796(2)	2.7197(2), 2.7275(2)
C1−Pt1−Br1	85.67(19)	89.38(10)		90.60(12)
C1−Pt1−Br1A		90.62(10)		
Br1−Pt1−Br2	90.12(4)		90.490(18)	
C1−Pt1−S1	92.18(19)			
S1−Pt1−Br2	92.03(6)			
C1−Pt1−Br2			84.71(12)	89.19(12)
C1−Pt1−P1			93.06(12)	
P1−Pt1−Br1			91.61(3)	
N3−Pt1−Br1				89.98(10)
N3−Pt1−Br2				90.31(10)
coordination plane/ carbene ring dihedral angle	90	87.72	88.46	79.72

cis isomerization took place under the NMR monitoring conditions. This observation is in line with a weaker trans influence of the pyridine ligand compared to PPh_3 (vide supra). The ^{1}H NMR spectrum of *trans*-**4** shows the presence of the pyridine ligand, of which the 2,6-py-H resonance is shifted downfield by 0.5 ppm compared to that of the free pyridine. Upon ligand substitution, the C−H resonances of the N-isopropyl groups shift downfield to 6.59 ppm (cf. 6.27 ppm in *cis*-**1**) probably pointing to a more electron-rich Pt center, which strengthens preagostic interactions. The ^{13}C NMR signal of the carbene atom in *trans*-**4** appears at 149.7 ppm, which is more upfield by 9.8 ppm than that found in the palladium analogue *trans*-[PdBr$_2$(*i*Pr$_2$-bimy)(pyridine)].

The formation of *trans*-**4** was further confirmed by X-ray diffraction analyses on single crystals obtained by slow evaporation of a concentrated THF solution. Its molecular structure depicted in Figure 5 shows the expected trans configuration with a nearly perfect square-planar coordination geometry. The deviation angle of the carbene ring from the PtCNBr$_2$ coordination plane is 79.72° and smaller than those found in complexes **1**−**3**. Furthermore, the pyridine ring plane is twisted from the perpendicular orientation with respect to the PdCNBr$_2$ coordination plane in a torsion angle of 59.47°. The Pt1−N3 bond length of 2.085(4) Å is in the expected range. The fixed orientation of the C−H protons of the N-isopropyl substituents toward the platinum center results in short C−H···Pt distances of 2.720

Table 2. Selected X-ray Crystallographic Data for Complexes *cis*-1, *trans*-2, *cis*-3, and *trans*-4

	cis-**1**·2CHCl$_3$	*trans*-**2**	*cis*-**3**	*trans*-**4**·THF
formula	$C_{17}H_{26}Br_2Cl_6N_2OPtS$	$C_{26}H_{36}Br_2N_4Pt$	$C_{31}H_{33}Br_2N_2PPt$	$C_{22}H_{31}Br_2N_3OPt$
fw	874.07	759.50	819.47	708.41
color, habit	colorless, long rod	colorless, block	colorless, block	colorless, block
cryst size [mm]	0.60×0.46×0.14	0.28×0.24×0.16	0.40×0.24×0.20	0.30×0.20×0.08
temp [K]	243(2)	295(2)	223(2)	223(2)
cryst syst	triclinic	orthorhombic	monoclinic	orthorhombic
space group	*P*2(1)/*m*	*Pbca*	*P*2(1)/*n*	*Pbca*
a [Å]	9.547(3)	17.2381(9)	10.5275(5)	17.1196(7)
b [Å]	10.589(3)	9.5180(5)	17.5069(8)	9.7318(4)
c [Å]	14.693(4)	17.8717(9)	16.5319(7)	29.7136(11)
α [deg]	90	90	90	90
β [deg]	104.055(6)	90	94.7690(10)	90
γ [deg]	90	90	90	90
V [Å^3]	1440.9(7)	2932.2(3)	3036.3(2)	4950.4(3)
Z	2	4	4	8
D_c [g cm^{-3}]	2.015	1.720	1.793	1.901
radiation used	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ [mm^{-1}]	8.284	7.530	7.328	8.915
θ range [deg]	2.20−27.47	2.28−27.49	1.70−27.50	1.81−27.50
no. of unique data	9829	19 674	21 495	33 569
max., min. transmn	0.3901, 0.0827	0.3788, 0.2269	0.3219, 0.1576	0.5357, 0.1751
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0352$, $wR_2 = 0.0926$	$R_1 = 0.0269$, $wR_2 = 0.0610$	$R_1 = 0.0319$, $wR_2 = 0.0753$	$R_1 = 0.0305$, $wR_2 = 0.0636$
R indices (all data)	$R_1 = 0.0405$, $wR_2 = 0.0947$	$R_1 = 0.0538$, $wR_2 = 0.0692$	$R_1 = 0.0412$, $wR_2 = 0.0783$	$R_1 = 0.0444$, $wR_2 = 0.0675$
goodness-of-fit on F^2	1.089	0.992	1.053	1.022
peak/hole [e Å^{-3}]	2.580/−1.058	0.735/−0.558	1.685/−1.178	1.019/−0.970

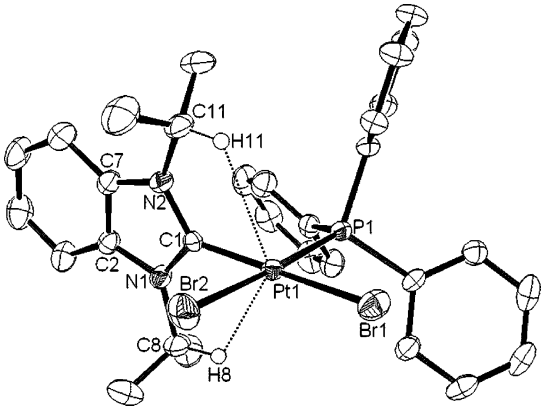

Figure 3. Molecular structure of complex *cis*-**3** showing 50% probability ellipsoids; hydrogen atoms except for H8 and H11 are omitted for clarity.

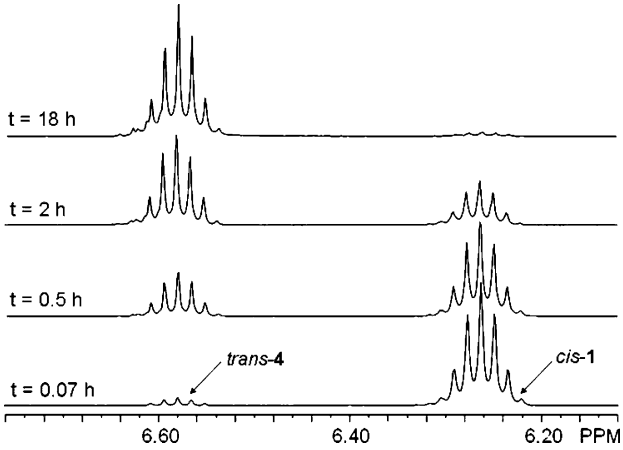

Figure 4. Time-dependent ^{1}H NMR spectra illustrating the reaction of *cis*-**1** with equivalent pyridine.

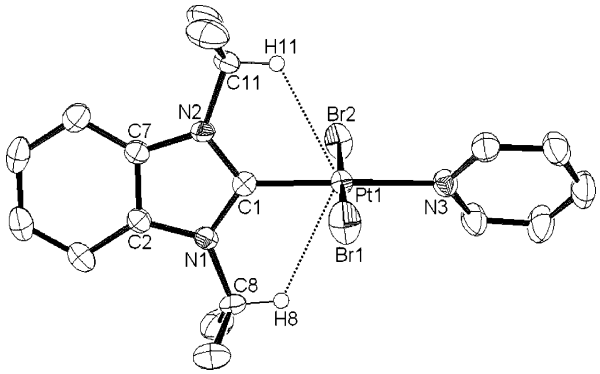

Figure 5. Molecular structure of complex *trans*-**4** showing 50% probability ellipsoids; solvent molecules and hydrogen atoms except for H8 and H11 are omitted for clarity.

and 2.728 Å, again suggesting the C−H···Pt preagostic interactions. Other parameters are unexceptional and require therefore no further comments.

Conclusion

The monocarbene complex *cis*-**1** and the bis(carbene) complex *trans*-**2** have been prepared by the reaction of $PtBr_2$ with NaOAc and the sterically bulky 1,3-diisopropylbenzimidazolium bromide precursor **A** in DMSO. Substitution of DMSO in *cis*-**1** with triphenylphosphine and pyridine afforded the novel benzannulated monocarbene complexes *trans*-**3**, *cis*-**3**, and *trans*-**4**, respectively. The trans−cis isomerization in the former reaction indicated that a cis arrangement in such complexes is thermodynamically favored. Furthermore, X-ray single-crystal diffraction analyses of complexes *cis*-**1**, *trans*-**2**, *cis*-**3**, and *trans*-**4** revealed that all these complexes show a fixed orientation of C−H protons in the N-isopropyl substituents toward the metal center, suggesting interesting C−H···Pt preagostic interactions. The large downfield shift of these protons in the ^{1}H NMR spectrum indicates that these interactions are retained in solution. The results of this work further show that benzimidazolium precursors behave indeed differently compared to their well-known imidazolium analogues, in this case leading preferably to monocarbene rather than bis(carbene) complexes. Research in our laboratories is underway to establish a general route to benzannulated bis(carbene) complexes of Pt(II) and to expand the scope of Pt(II)−benzimidazolin-2-ylidenes in catalysis.

Experimental Section

General Considerations. Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture. All solvents were used as received. $PtBr_2$ was purchased from Strem. All chemicals were used as received without any further treatment if not noted otherwise. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AMX 500 spectrometer, and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^{1}H, ^{13}C) or externally to 85% H_3PO_4 (^{31}P). Mass spectra were measured using a Finnigan MAT LCQ (ESI) and Finnigan/MAT 95XL-T (FAB) spectrometer. Infrared spectra were recorded with a Varian 3100 FT-IR spectrometer using KBr pellets. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

***cis*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(dimethylsulfoxide)platinum(II) (*cis*-1) and *trans*-Dibromo-bis(1,3-diisopropylbenzimidazolin-2-ylidene)platinum(II) (*trans*-2).** A mixture of salt **A** (170 mg, 0.6 mmol), $PtBr_2$ (106 mg, 0.3 mmol), and $NaOAc\cdot 3H_2O$ (82 mg, 0.6 mmol) in DMSO (5 mL) was stirred at 90 °C for 10 h. The initially orange reaction mixture turned to a yellow solution. Further heating at 140 °C for 20 h afforded some yellow precipitate, which was filtered off and washed with small portions of DMSO and diethyl ether. It was then dried in vacuo to give *trans*-**2** as a yellow powder (6 mg, 0.008 mmol, 3%). Removal of the solvent from the filtrate via vacuum distillation and subsequent washing of the resulting residue with H_2O (4 × 30 mL) afforded crude *cis*-**1**, which after drying in vacuo was isolated as an off-white solid. Slow evaporation of a concentrated $CHCl_3$ solution of the crude product afforded *cis*-**1** as white crystals (102 mg, 0.16 mmol, 55%). *cis*-**1**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (dd, 2 H, Ar−H), 7.28 (dd, 2 H, Ar−H), 6.27 (m, ^3J(H,H) = 7.0 Hz, 2 H, NC*H*$(CH_3)_2$), 3.61 (s, ^3J(Pt,H) = 21.5 Hz, 6 H, $(CH_3)_2$SO), 1.75 (d, ^3J(H,H) = 7.0 Hz, 6 H, CH_3), 1.74 (d, ^3J(H,H) = 7.0 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): 153.6 (s, NCN), 132.8, 123.2, 113.5 (s, Ar−C), 54.3 (^3J(Pt,C) = 31.2 Hz, N*C*H$(CH_3)_2$), 47.1 (s, ^2J(Pt,C) = 70.6 Hz, $(CH_3)_2$SO), 20.6, 20.4 (s, CH_3). IR (KBr pellet) $\tilde{\nu}$ 1134 (s, S=O) cm^{-1}. Anal. Calc for $C_{15}H_{24}Br_2N_2OPtS$: C, 28.36; H, 3.81; N, 4.41. Found: C, 28.33; H, 3.49; N, 4.57%. MS (ESI): *m*/*z* 1191 $[2M - Br]^+$. *trans*-**2**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (dd, 4 H, Ar−H), 7.21 (dd, 4 H, Ar−H), 6.52 (m, ^3J(H,H) = 7.0 Hz, 4 H, NC*H*$(CH_3)_2$), 1.81 (d, ^3J(H,H) = 7.0 Hz, 24 H, CH_3). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): 176.5 (s, NCN), 133.6, 122.1, 112.9 (s, Ar−C), 53.1 (s, N*C*H$(CH_3)_2$), 21.1 (s, CH_3). Anal. Calc for $C_{26}H_{36}Br_2N_4Pt$: C, 41.12; H, 4.78; N, 7.38. Found: C, 41.53; H, 5.18; N, 7.44. MS (FAB): *m*/*z* 760 $[M]^+$.

***cis*-Dibromo(*N*,*N*-diisopropylbenzimidazolin-2-ylidene)(triphenylphosphine)platinum(II) (*cis*-3).** A mixture of complex **1** (64 mg, 0.1 mmol) and triphenylphosphine (26 mg, 0.1 mmol) in CH_2Cl_2 (5 mL) was stirred at ambient temperature for 6 h and then refluxed for 15 h. After removing the solvent in vacuo, 3 mL of THF was added to the residue. The precipitate obtained was filtered off and washed with another 3 mL of THF. It was then dried in vacuo to give *cis*-**3** as a white powder (29 mg, 0.035 mmol, 35%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (dd, 2 H, Ar−H), 7.38 (br, 15 H, Ar−H), 7.20 (dd, 2 H, Ar−H), 6.09 (m, ^3J(H,H) = 7.0 Hz, 2 H, NC*H*$(CH_3)_2$), 1.63 (d, ^3J(H,H) = 7.0 Hz, 6 H, CH_3), 0.86 (d, ^3J(H,H) = 7.0 Hz, 6 H, CH_3). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): 161.0 (d, ^2J(P,C) = 5.5 Hz, NCN), 134.9 (br, Ar−C), 133.8, 131.8, 129.1, 129.0, 123.4, 113.5 (s, Ar−C), 54.6 (s, N*C*H$(CH_3)_2$), 21.4, 19.7 (s, CH_3). ^{31}P{^{1}H} NMR (202.4 MHz, $CDCl_3$): δ 10.0 (^2J(Pt,P) = 3848 Hz, PPh_3). Anal. Calc for $C_{31}H_{33}Br_2N_2PPt$: C, 45.44; H, 4.06; N, 3.42. Found: C, 45.58; H, 4.42; N, 3.50. MS (FAB): *m*/*z* 739 $[M - Br]^+$.

***trans*-Dibromo(1,3-diisopropylbenzimidazolin-2-ylidene)(pyridine)platinum(II) (*trans*-4).** Complex **1** (64 mg, 0.1 mmol) was dissolved in pyridine (1 mL) and stirred at ambient temperature for 6 h. All volatiles were removed in vacuo to give a yellow solid. Crystallization from a CH_2Cl_2/hexane solution of this solid afforded the product as yellow crystals (54 mg, 0.085 mmol, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.13 (m, 2 H, 2,6-py-H), 7.78 (m, 1 H, 4-py-H), 7.59 (dd, 2 H, Ar−H), 7.36 (m, 2 H, 3,5-py-H), 7.19 (dd, 2 H, Ar−H), 6.59 (m, ^3J(H,H) = 6.9 Hz, 2 H, NC*H*$(CH_3)_2$), 1.77 (d, ^3J(H,H) = 6.9 Hz, 12 H, CH_3). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): 153.4 (s, Ar−C), 149.7 (s, NCN), 138.4, 133.8, 125.6, 122.8, 113.3 (s, Ar−C), 54.3 (s, N*C*H$(CH_3)_2$), 21.3 (s, CH_3). Anal. Calc for $C_{18}H_{23}N_3Br_2Pt$: C, 33.98; H, 3.64; N, 6.60. Found: C, 33.75; H, 3.95; N, 6.76. MS (FAB): *m*/*z* 637 $[M]^+$.

X-ray Diffraction Studies. Diffraction data for complexes *cis*-**1**, *trans*-**2**, *cis*-**3**, and *trans*-**4** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 243(2) (*cis*-**1**), 295(2) (*trans*-**2**), or 223(2) K (*cis*-**3** and *trans*-**4**) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected over the full sphere and were corrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least-squares on F^2 using SHELXL-97[14] with first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms. A summary of the most important crystallographic data is given in Table 2.

Acknowledgment. We thank the National University of Singapore for financial support (Grant No. R 143-000-268-112) and technical assistance from our department.

Supporting Information Available: Crystallographic data for *cis*-**1**, *trans*-**2**, *cis*-**3**, and *trans*-**4** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Sheldrick, G. M. *SHELXL-97*; Universität Göttingen: Germany, 1997.