

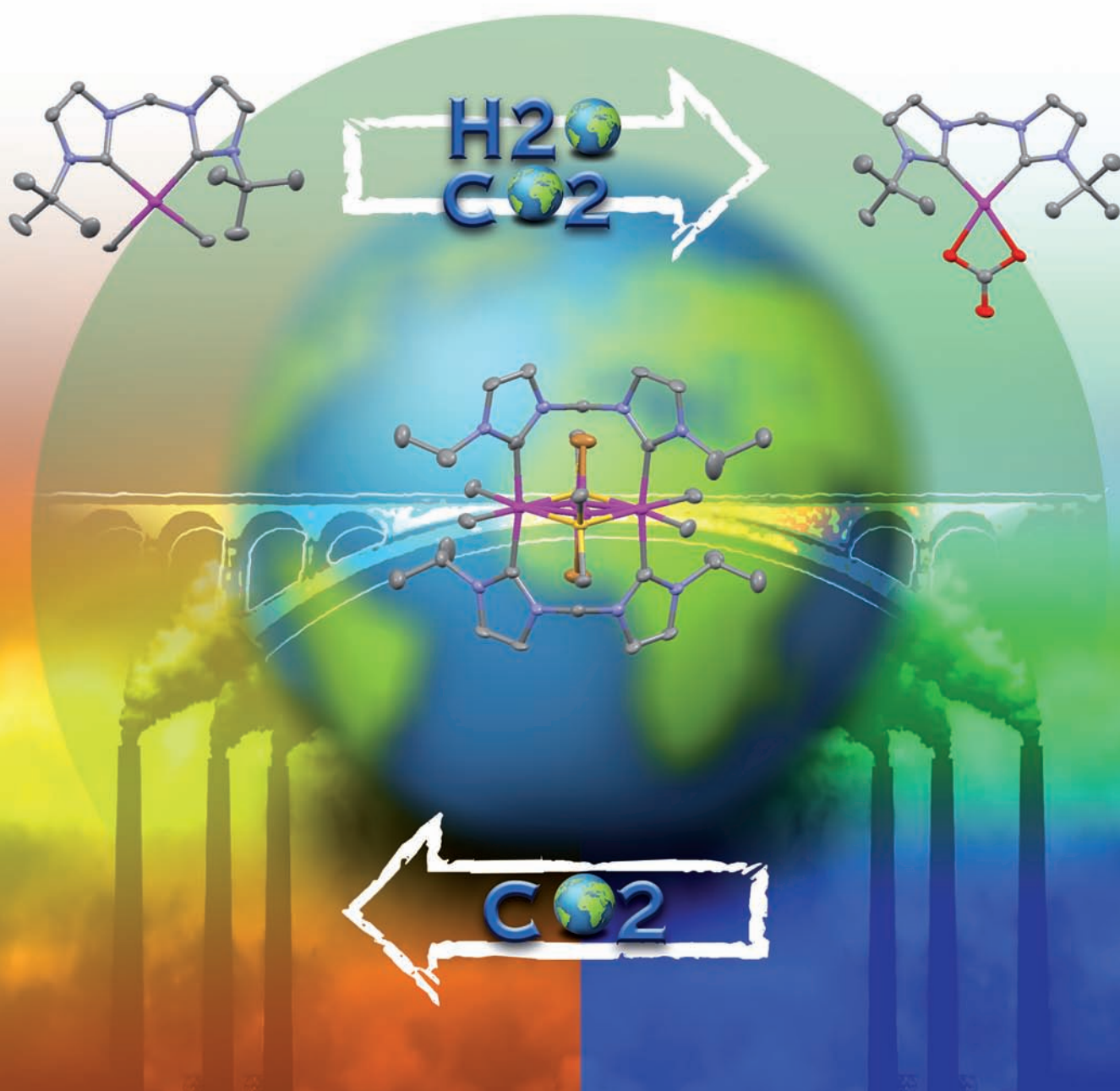
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Organoplatinum(II) complexes containing chelating or bridging bis(*N*-heterocyclic carbene) ligands: formation of a platinum(II) carbonate complex by aerial CO₂ fixation†‡Sirous Jamali,^{*a} Dalibor Milić,^b Reza Kia,^c Zahra Mazloomi^a and Hallimeh Abdolahi^a

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The preparation of two new bis(*N*-heterocyclic carbene) platinum(II) complexes, in which NHC rings are joined by a CH₂ linker group, is described. While, the chelate complex [PtMe₂(bis-NHC1)], **1**, was formed with large *tert*-butyl wingtips, the *iso*-propyl *N*-substituent analogue favors formation of the cluster complex [Pt₂Me₄(μ-SMe₂)(μ-bis-NHC2)]₂(μ-Ag₂Br₂), **2**, in which two binuclear platinum(II) complexes are linked together by an Ag₂Br₂ unit. The chelating platinum complex **1** undergoes aerial CO₂ fixation and forms platinum(II) carbonate complex [Pt(CO₃)(bis-NHC1)], **3**.

Carbene ligands, mainly the *N*-heterocyclic carbenes (NHCs), are regarded as important ligands that have attracted the attention of numerous chemists due to their applications in organometallic chemistry and homogeneous catalysis.¹ There has also been significant interest in the synthesis of new carbene ligands, their metal complexes and exploiting the remarkable structural and bonding properties of these compounds.² In this area, a large number of carbene ligand frameworks with tunable electronic and steric parameters have been prepared in the past decade.³ Poly(*N*-heterocyclic carbene) ligands are an interesting subclass of NHCs

that allow the preparation of organometallic compounds with a variety of geometries and chemical reactivities.⁴ An interesting type of bis(NHC) ligands comprises pairs of NHC rings that are joined by a -(CH₂)_{*n*}- linker group. Several studies have been recently published in order to rationalize the preference for chelating *versus* bridging coordination mode of bis-NHC ligands. It seems that the main factors that determine the coordination mode of the bis-NHC ligand are the length of the linker between the two azole rings, *N*-substituents and the nature of the counterion. The effect of all these parameters on the coordination mode of the bis-NHC ligands, as observed in a family of complexes of type [Rh(bis-NHC)(COD)]⁺, was described previously.⁵

Carbon dioxide enters the air by burning fossil fuels such as oil, natural gas and coal. The rate of annual global emission of CO₂ into the air is roughly proportional to the global rate of energy consumption. Greenhouse gases such as carbon dioxide trap radiation upwelling from the earth's surface and the expected result is global warming and an unprecedented rate of climate change.⁶ Thus, the development of methods for reduction of the atmospheric concentration of CO₂ would be highly desirable. Among these methods, the chemical fixation of atmospheric CO₂ is especially attractive and transition metal complexes are well established as successful compounds for CO₂ fixation.⁷ Here we report the synthesis and structural characterization of complexes [PtMe₂(bis-NHC1)], **1**, and [Pt₂Me₄(μ-SMe₂)(μ-bis-NHC2)]₂(μ-Ag₂Br₂), **2**, in which bis-NHC1, 1,1'-methylene-3,3'-bis[*N*-(*tert*-butyl)imidazol-2-ylidene] and bis-NHC2, 1,1'-methylene-3,3'-bis[*N*-(*iso*-propyl)imidazol-2-ylidene], act as chelating and bridging ligands, respectively. Also, it is demonstrated that the fixation reaction of CO₂ from air to **1** at room temperature gives the corresponding platinum carbonate complex [Pt(CO₃)(bis-NHC1)], **3**. Treatment of silver carbene complex, [Ag₂(bis-NHC1)Br₂], *in situ* generated from the corresponding bis(imidazolium) dibromide salt and Ag₂O,^{5,8} with 1/2 equiv. of [Pt₂Me₄(μ-SMe₂)₂] in CH₂Cl₂ at room temperature allowed the isolation of bis(carbene)platinum complex [Pt(Me)₂(bis-NHC)], **1**, in moderate yields (Scheme 1). Complex **1** is a white solid that is stable in acetone solution for several hours.

The ¹³C NMR spectrum of **1** displays the characteristic resonance for the carbene carbon atoms connected to the platinum center at δ 185.8 ppm with ¹J_{PtC} = 778.2 Hz.⁹ This coupling constant is in the range of previously reported ¹J_{PtC} observed for monodentate-NHC methylplatinum complexes.⁹ The two

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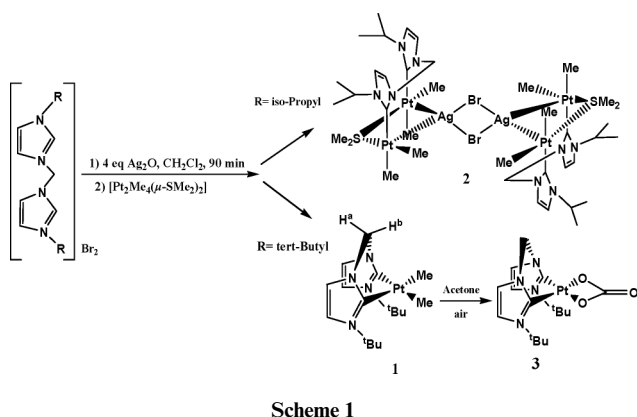
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‡ Crystal data for **1**: C₁₇H₃₀N₄Pt, orthorhombic, *Pna*2₁, *a* = 11.5536(2) Å, *b* = 18.5617(3) Å, *c* = 8.6213(2) Å, *V* = 1848.88(6) Å³, *T* = 150(1) K, *Z* = 4, *F*(000) = 952, *R*₁ = 0.0218, *wR*₂ = 0.0419, *GOF* = 1.055, collected reflections = 27179, independent reflections = 5842 (*R*_{int} = 0.0332).

Crystal data for **2**: C₄₇H₉₄Ag₂Br₂N₈O₃Pt₂S₂, triclinic, *P* $\bar{1}$, *a* = 9.8360(3) Å, *b* = 12.2936(4) Å, *c* = 13.7271(4) Å, α = 74.311(3)°, β = 85.741(2)°, γ = 79.721(3)°, *V* = 1571.80(8) Å³, *T* = 150(1) K, *Z* = 1, *F*(000) = 964, *R*₁ = 0.0279, *wR*₂ = 0.0486, *GOF* = 0.871, collected reflections = 12100, independent reflections = 7113 (*R*_{int} = 0.0335).

Crystal data for **3**: C₁₆H₃₀N₄O₆Pt, monoclinic, *P*2₁/*c*, *a* = 8.8501(2) Å, *b* = 17.2896(4) Å, *c* = 13.1079(2) Å, β = 94.015(2)° *V* = 2000.78(7) Å³, *T* = 120(2) K, *Z* = 4, *F*(000) = 1120, *R*₁ = 0.0386, *wR*₂ = 0.0698, *GOF* = 1.004, collected reflections = 13622, independent reflections = 6565 (*R*_{int} = 0.0332).



equivalent carbon atoms of the methyl ligands appeared as a singlet signal at $\delta -7.7$ ppm with $^1J_{\text{PtC}} = 606.1$ Hz. The presence of two equivalent Pt–Me ligands in complex **1** is supported by a singlet resonance in the ^1H NMR spectrum (acetone- d_6) at $\delta 0.23$ ppm, which is flanked by ^{195}Pt satellite signals ($^2J_{\text{PtH}} = 67.5$ Hz), due to the Me protons. The protons H^a and H^b of the methylene linker appear as an AB pattern at $\delta 5.3$ and 6.1 ppm with $^2J_{\text{HH}} = 12.2$ Hz respectively indicating that the six-membered chelate ring of bis-NHC ligand is not planar and adopts a boat conformation (Scheme 1). The H^b resonance in the ^1H NMR spectrum of **1** is shifted downfield by 0.8 ppm *versus* H^a and shows a coupling with the platinum center ($J_{\text{PtH}} = 19.5$ Hz) (Fig. 1a). These NMR data suggest a weak electrostatic interaction between the methylene linker proton H^b and the platinum metal center and therefore not an agostic interaction, which is characterized by an upfield ^1H NMR chemical shift.¹⁰ Crystals of complex **1** were obtained by the slow diffusion of ether into an acetone solution of **1** under a CO_2 -free atmosphere in a refrigerator for a week. A view of the molecular structure of **1** is depicted in Fig. 2. As anticipated by NMR analysis, the bis-NHC ligand adopts a bidentate coordination mode through the C(carbene) atoms, forming a six-membered chelate ring with the bite angle $83.0(1)^\circ$. The Pt–C(carbene) bond distances of $\text{C}(21)\text{--Pt}(1) = 2.039(3)$ Å and $\text{C}(22)\text{--Pt}(1) = 2.049(3)$ Å lie in the range of previously reported Pt(II)–C(NHC) bond lengths^{9,11} and the NHC ring planes are tilted by an average of 56.6° from the coordination plane.

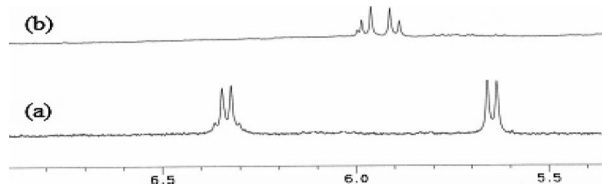


Fig. 1 The CH_2 linker region ^1H NMR spectra of (a) complex **1** and (b) complex **3**.

The hydrogen atom $\text{H}102$ of $\text{C}10$ (the methylene linker carbon atom) is at distance 2.91 Å from the platinum atom with the C–H–Pt angle of 89.4° . This confirms the presence of an electrostatic interaction between $\text{H}102$ proton and platinum center, as observed in the ^1H NMR spectrum of **1** and discussed above. The most interesting feature of complex **1** is its capability to fix aerial CO_2 at room temperature. Exposure of an acetone solution of the

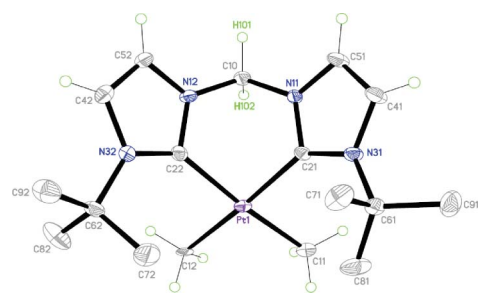


Fig. 2 The molecular structure of complex **1**, showing 40% probability displacement ellipsoids and the atomic numbering. The H atoms are shown as sphere of arbitrary radius. (except for the *tert*-butyl H atoms, which were omitted for clarity).

dimethylplatinum complex **1** to air for 24 h led to isolation of the platinum carbonate complex $[\text{Pt}(\text{CO}_3)(\text{bis-NHC})]$, **3**, as a white solid in 65% yield (Scheme 1). It seems that the carbonate ligand connected to platinum atom originates from hydration of aerial CO_2 to give H_2CO_3 , which in turn undergoes deprotonation in reaction with **1** and affords the stable bis-NHC platinum carbonate complex **3**. The presence of the carbonate ligand was confirmed by the ^{13}C NMR spectrum of complex **3**, which displayed the carbonate carbon atom as a singlet at $\delta 168$ ppm. This value of chemical shift falls in the same range ($165\text{--}170$ ppm) as those previously reported for platinum carbonate complexes.¹² The carbene carbon atoms appeared as a singlet at $\delta 140$ ppm with a considerably higher $^1J_{\text{PtC}}$ value close to 1318 Hz because of the lower *trans* influence of O atoms of carbonate ligand as compared with that of C atoms of the methyl ligands in complex **1**. The ^1H NMR spectrum of complex **3** in $\text{DMSO-}d_6$ displayed an AB pattern at $\delta 5.95$ and 5.87 with $^2J_{\text{HH}} = 12.6$ Hz for the methylene linker protons (Fig. 1b). Furthermore, no methyl proton resonances associated with the methyl ligands could be observed in the ^1H NMR spectrum of complex **3**. The IR spectrum of complex **3** displays a strong band at 1600 cm^{-1} , indicating that the carbonate ligand is bonded to the platinum atom as a bidentate ligand.¹³ Complete structural characterization of **3** as a carbonate complex was achieved by X-ray crystallographic analysis. The crystals of **3** suitable for X-ray crystallographic analyses were obtained by slow evaporation of an acetone solution of complex **1**. As shown in Fig. 3a, complex **3** adopts a slightly distorted square planar geometry (the Pt atom displaced $-0.09(1)$ Å from the coordination plane) and three water molecules in the asymmetric unit are bound to **3** *via* hydrogen bonds to the oxygen atoms of carbonate ligand. The Pt–C(carbene) bond lengths $1.959(5)$ and $1.969(4)$ Å are in the expected range of Pt(II)–C(NHCs) bonds.

The bite angle of the bis-NHC ligand $[\text{C}(22)\text{--Pt}(1)\text{--C}(21)]$ is $84.0(2)^\circ$ and the dihedral angle between the coordination plane of the complex and the NHC ring plane $[48.1(2)^\circ]$ is twisted significantly from the favored orthogonal arrangement. This might be caused by a steric clash between the *tert*-butyl groups of the carbene ligand. The yaw distortion, θ for two azole rings in complex **3** (with an average of 7.5°) is significantly smaller than that observed in **1** (12.5°). Further examination of the crystal structure of **3** also reveals that the molecules of complex **3** are connected into infinite 1-D extended chains along the $[100]$ direction through $\text{O}(\text{carbonate}) \cdots \text{H}\text{--O}\text{--H} \cdots \text{O}(\text{H})\text{--H}\text{--O}$ (carbonate) H-bonds (Fig. 3b).

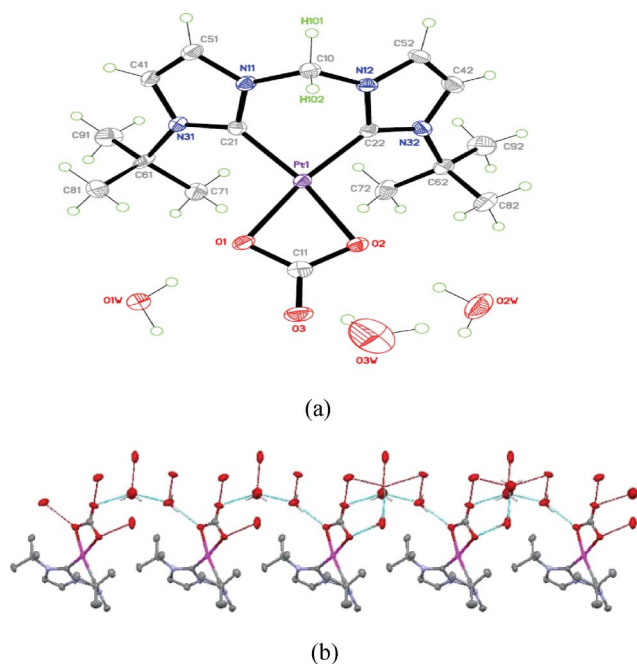


Fig. 3 (a) The molecular structure of complex 3, showing 40% probability displacement ellipsoids and the atomic numbering. The H atoms are shown as sphere of arbitrary radius. (b) A part of the crystal packing of complex 3 showing a 1-D infinite chain along the [100] direction through intermolecular hydrogen bonding. Only the H atoms involved in the H-bonding are shown.

As observed in the present and previously published works,⁵ the use of large *N*-substituent groups and short linker CH₂ group favors the chelating mode of bis(NHC) ligands. However, the reaction of 1/2 equiv. [Pt₂Me₄(μ-SMe₂)₂] with a mixture of methylene bis(*N*-(*iso*-propyl)imidazolium bromide) and Ag₂O in CH₂Cl₂ gave the hexanuclear cluster complex [Pt₂Me₄(μ-SMe₂)(μ-bis-NHC2)]₂(μ-Ag₂Br₂), **2** in 70% yield, in which bis(NHC2) acts as a bridging ligand (Scheme 1). Crystals of the acetone solvated of **2** were obtained by the slow diffusion of *n*-pentane into an acetone solution of complex **2** in a refrigerator. The complex crystallizes in a triclinic *P* $\bar{1}$ space group. The structure of **2** in the solid state (Fig. 4) indicates two binuclear platinum units [Pt₂Me₄(μ-SMe₂)(μ-bis-NHC2)] that are linked together by an Ag₂Br₂ entity to form centrosymmetric cluster complex **2**.

The complex contains two different types of Pt–Ag bonds, short and long. The bond distance for the short bonds, Pt(1)–Ag(1) or Pt(1A)–Ag(1A) = 2.8377(6) Å, is near to the sum of the metallic radii of Pt and Ag (2.83 Å), indicating the formation of a Pt–Ag dative bond; note that each bond is also supported by two secondary weak interactions of the Ag atom with the C atoms of the methyl ligands [C(12) or C(14)] that are coordinated to the Pt atom (dashed bonds in Fig. 4) with Ag–C distances of Ag(1)–C(12) = 3.000(7) Å and Ag(1)–C(14) = 3.075(7) Å. The long bonds, Pt(2)–Ag(1) or Pt(2A)–Ag(1A) = 2.8982(5) Å, are shorter than the sum of the van der Waals radii of Pt and Ag (3.45 Å), demonstrating the presence of Pt–Ag bonding interactions. The Pt–C bond distances of methyl ligands *trans* to C(carbene) atom, Pt(1)–C(12) = 2.087(5) Å and Pt(2)–C(14) = 2.097(5) Å are longer than the Pt–C bond distances of the methyl ligands *trans* to the dimethylsulfide ligand, Pt(1)–C(11) = 2.045(6) Å and Pt(2)–

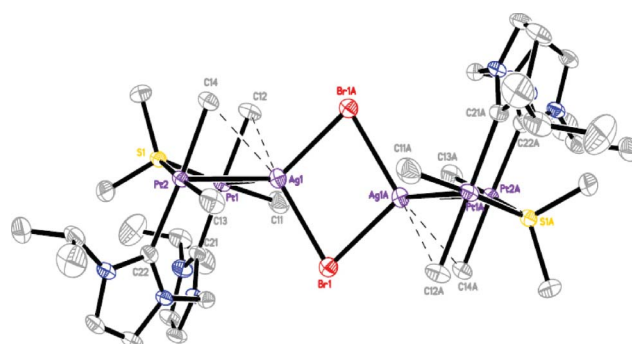


Fig. 4 The molecular structure of complex **2**, showing displacement ellipsoids at the 30% probability level. H-atoms were removed for clarity. The dashed lines show the close contacts between the designated atoms. Label “A” denotes atoms centrosymmetrically related to those in the other half of a molecule.

C(13) = 2.057(6) Å, indicating the carbene ligand exerts higher *trans* influence than the dimethylsulfide ligand. The ¹⁹⁵Pt NMR spectrum of **2** gave a broad resonance at δ –2420 ppm with no detectable coupling ¹J_{AgPt}. The ¹H NMR spectrum of complex **2** in acetone-*d*₆ solvent, shows two equal intensity signals at δ 0.34 and 0.25 ppm with ²J_{PtH} = 91 and 66 Hz due to the Me protons *trans* to dimethylsulfide and carbene ligands, respectively. The presence of a bridging dimethylsulfide ligand was shown by the appearance of the two equal intensity MeS resonances at δ 2.8 and 2.2 ppm in the ¹H NMR spectrum as two 1 : 8 : 18 : 8 : 1 quintets due to coupling to two adjacent ¹⁹⁵Pt atoms with ³J_{PtH} = 19.5 and 18.3 Hz, respectively. The ¹³C NMR spectrum of **2** showed a singlet resonance at δ 183.5 ppm due to the C atoms of the carbene ligand with no detectable ¹J_{PtC} coupling. Finally, there were two methylplatinum resonances in the ¹³C NMR spectrum at δ –11.9 and –7.9 ppm; the coupling ¹J_{PtC} = 736 Hz for the methyl groups *trans* to sulfur was greater than the value ¹J_{PtC} = 582 Hz for the methyl group *trans* to C atoms of carbene ligand. Electrospray ionization (ESI) mass spectrum (positive ions) of complex **2** shows a base peak at *m/z* 1022 (Fig. 5) assignable to the species [Pt₂Me₄(bis-NHC)₂-Ag]⁺ formed by the displacement of a labile dimethyl sulfide ligand with a bis-NHC2 ligand and cleavage of Ag–Br bonds. Examples of formation of bis(carbene)silver complexes (C–Ag–C), in the gas phase from silver NHCs with solid-state motifs of C–Ag–X and C–Ag–X₂ have been reported previously.¹⁴

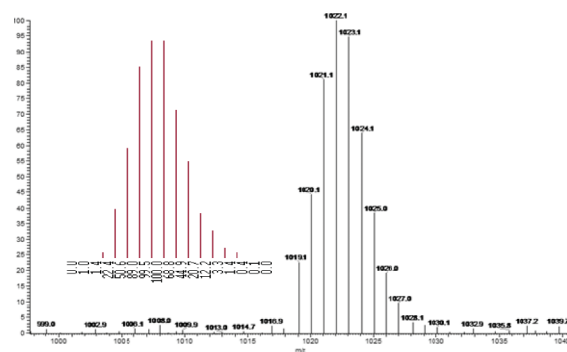


Fig. 5 Expanded ESI mass spectrum of complex **2** Inset: Simulated isotope pattern for the [Pt₂Me₄(bis-NHC)₂-Ag]⁺ cation.

Conclusions

In summary, we have prepared two new bis(*N*-heterocyclic carbene) platinum complexes in which the bis(*N*-heterocyclic carbene) acts as chelating or bridging ligand and forms mono- or multinuclear complexes **1** and **2**. The chelating complex **1** demonstrated the ability to fix aerial CO₂. Current efforts are focused on the synthesis, structure and reactivity of new bis(*N*-heterocyclic carbene) platinum complexes with different *N*-substituents and longer aliphatic linker chains.

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