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# Synthesis, Structure and Stability of New $Pt^{II}$–Bis(N-Heterocyclic Carbene) Complexes

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The use of metal acetates has allowed the synthesis of NHC complexes without isolation of the free carbene. This route is very useful in cases where the metal acetates are readily available and has been used, for example, for the synthesis of bis(N-heterocyclic carbene) complexes of palladium(II). In the case of platinum, however, the corresponding acetate is not commercially available and is difficult to synthesize. Previously published syntheses require either an external base (e.g. NaOAc or KO*t*Bu) or a transmetalation step. Here we present a new general synthetic pathway for platinum–bis(carbene) complexes using platinum(II) acetylacetonate as a commercially available metal precursor. Aromatic substituents greatly enhance the stability of the metal complexes against acidic media.


## Introduction

In the last decade N-heterocyclic carbene (NHC) complexes of transition metals have found applications in many fields of chemistry. Metal complexes of imidazoline-2-ylidenes have recently been shown to be extremely versatile and stable catalysts for a wide range of reactions, including C–C coupling reactions,[1,2] olefin metathesis,[3–6] hydroformylation,[7,8] and, most recently, CH activation.[9,10] The key for this development has been the number of improved synthetic methods for the preparation of NHC complexes, which have been summarized in recent reviews.[11–13]

Metal acetates allow the synthesis of NHC complexes without isolation of the free carbene. Palladium(II) acetate in wet dimethyl sulfoxide (DMSO) at elevated temperatures directly forms carbene complexes with imidazolium salts. Even methylene-bridged bis(imidazolium) salts can be converted into the corresponding bis(carbene) complexes in high yields (85–90%).[14–16] We and others have been particularly interested in these chelate ligands as a way of extending the area to more complex ligands and more stable complexes.[17–23] Here we present a new general synthetic pathway towards platinum–bis(carbene) complexes with aromatic substituents, which greatly enhance the stability of the corresponding platinum carbene complexes.

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Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

## Results and Discussion

### Preparation of the Platinum(II)–Bis(carbene) Complexes

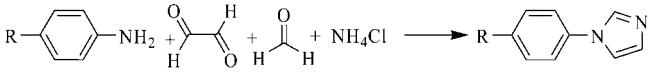
The previously reported syntheses of platinum–NHC complexes involve the preparation of either platinum precursors or free carbenes, which usually have to be handled under an inert gas atmosphere.[24–27] Since the acidic methylene protons in bis(imidazolium) salts might be attacked under common deprotonation conditions, a pathway via the free bis(carbenes) is only possible by using sterically demanding bases, but the yields are only moderate.[28,29] To circumvent the need for multi-step pathways we recently introduced a new synthetic route using the corresponding platinum(II) halide salts and sodium acetate as an external base for the synthesis of the metal complexes. However, the use of external bases like sodium acetate often leads to the formation of small amounts of platinum black, which produces lower yields in the reaction and is difficult to remove from the product.[22]

If platinum(II) acetylacetonate is used as metal precursor, no formation of platinum black is observed during the reaction. Like the platinum(II) halides used in our first protocol,[22] it is commercially available and can be handled in air. Furthermore, there are two major advantages for the use of platinum(II) acetylacetonate compared to platinum(II) halides. First, only platinum(II) halides with the same halides as the imidazolium salts can be used in the reaction to avoid anion scrambling in the complex, and platinum(II) halides are also much more expensive than platinum(II) acetylacetonate. Secondly, different from our

older procedure, no other external base has to be added since the basicity of the acetylacetonate anion is sufficient to deprotonate the imidazolium salt. When platinum(II) halides are used as metal precursors, sodium acetate has to be added to the reaction mixture, which leads to the formation of sodium halide salts during the reaction which have to be removed by washing the product with water several times.[22] In this case only pentan-2,4-dione emerges during the reaction, and this can be removed in vacuo along with the solvent. We were able to synthesize several new platinum–N-heterocyclic bis(carbene) complexes with different substituents at the aromatic ring following this method.

The synthesis of these new ligands can be accomplished in only two steps. First, the aromatic-substituted imidazoles were synthesized according to Scheme 1 from substituted anilines, which are commercially available in great diversity: 4-nitroaniline for **1a**, 4-chloroaniline for **1b**, 4-bromoaniline for **1c**, 4-methoxyaniline for **1d**, and ethyl 4-aminobenzoate for **1e**. The aromatic amine, glyoxal and formaldehyde are converted into an aromatic-substituted imidazole in a one-pot reaction. Additionally to the imidazoles prepared by Zhang et al.,[30] we extended this method to anilines substituted by different halogens. Both electron-donating and -withdrawing substituents are tolerated, although the yields of product are quite different (Table 1).



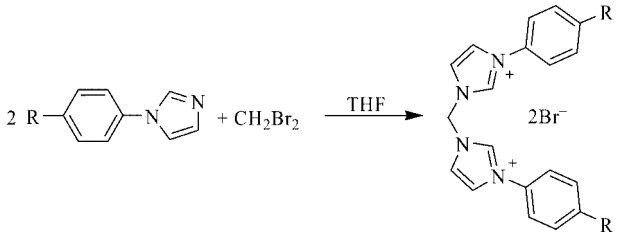
Scheme 1. Synthesis of imidazoles with different aromatic substituents [R = $NO_2$ (**1a**), R = Cl (**1b**), R = Br (**1c**), R = $OCH_3$ (**1d**), R = $COOCH_2CH_3$ (**1e**)].

Table 1. Isolated yields of **1a**–**1e**.

| | **1a** | **1b** | **1c** | **1d** | **1e** |
|---|---|---|---|---|---|
| Yield | 28.0% | 77.0% | 60.7% | 75.0% | 73.7% |

The low yield for **1a** can be explained by its lower solubility in organic solvents, so the extraction of the product is the limiting factor here. This reaction gives access to a wide range of N-substituted imidazoles with different functional groups at the aromatic ring, thereby allowing us to fine-tune the electronic situation in the N-heterocyclic carbene ligand.

These N-substituted imidazoles can be converted in good yields into the corresponding bis(imidazolium) salts by a nucleophilic substitution reaction with dibromomethane (Scheme 2). The reaction also works with diiodomethane,



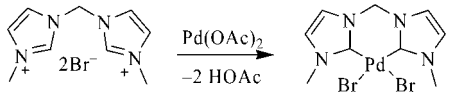
Scheme 2. Synthesis of the imidazolium salts [R = $NO_2$ (**2a**), R = Cl (**2b**), R = Br (**2c**), R = $OCH_3$ (**2d**), R = $COOCH_2CH_3$ (**2e**)].

as reported previously.[22] The preparation of the imidazoles and the following bridging step of two of these imidazoles with dibromomethane are compatible with a wide range of functional groups at the aromatic ring. Yields are given in Table 2.

Table 2. Isolated yields of **2a**–**2e**.

| | **2a** | **2b** | **2c** | **2d** | **2e** |
|---|---|---|---|---|---|
| Yield | 94.8% | 64.0% | 84.0% | 88.7% | 86.4% |

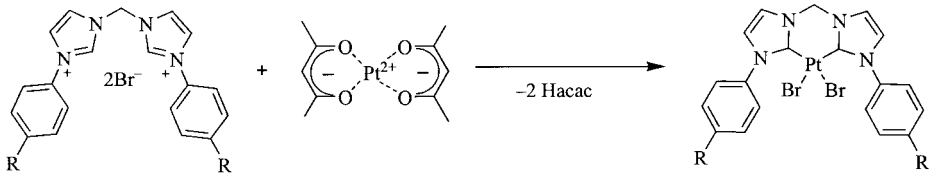
Finally, we succeeded in synthesizing the platinum–bis(carbene) complexes under very mild conditions, thus proving the application of our new compounds as suitable NHC ligands for late transition metals. In this case, the traditional metalation procedure involving deprotonation of the imidazolium precursor with strong bases produces unwanted side reactions because of the acidic protons in the bridging $CH_2$ group and in the functional groups at the aromatic ring.[31] Milder procedures were therefore needed that are compatible with more sensitive functionalities. Base-sensitive methylene-bridged bis(imidazolium) salts can be converted into the corresponding palladium–bis(carbene) complexes by treatment with $Pd(OAc)_2$ in wet dimethyl sulfoxide (DMSO) at elevated temperatures in high yields (Scheme 3).[14–16] This route is very useful in cases where the metal acetates are easily available. In the case of platinum, however, the corresponding acetate is not available and is difficult to synthesize.[32,33] So until now platinum(II) halides had to be used and sodium acetate had to be added to the reaction mixture as an external base, leading to the formation of sodium halides as by-products during the reaction.[22] Here we present a new synthetic approach that uses platinum(II) acetylacetonate as a commercially available metal precursor and base for the deprotonation of the imidazolium salt. The synthesis of the platinum complexes is illustrated in Scheme 4 and yields of the syntheses are given in Table 3.



Scheme 3. Synthesis of bridged palladium complexes from imidazolium salts and palladium(II) acetate.

To obtain these complexes in good yields it is necessary to follow the synthetic protocol described below. It is crucial that the halide salt of the bis(imidazolium) compound is completely converted into the platinum–monocarbene species by slowly heating the reaction mixture over several hours first to 60 °C, thereby deprotonating only one of the imidazolium rings, otherwise a substantial amount of platinum black formation is observed.[22] The reaction mixture should then be heated up to 130 °C to deprotonate the second imidazolium ring. This is consistent with the earlier findings of Herrmann et al. regarding palladium–bis(carbene) complexes,[34] but had not been observed for platinum carbenes before.




Scheme 4. Synthesis of the platinum complexes [R = $NO_2$ (**3a**), R = Cl (**3b**), R = Br (**3c**), R = $OCH_3$ (**3d**), R = $COOCH_2CH_3$ (**3e**)].

Table 3. Isolated yields of **3a**–**3e**.

| | 3a | 3b | 3c | 3d | 3e |
|---|---|---|---|---|---|
| Yield | 62.1% | 86.8% | 67.0% | 69.9% | 71.8% |

### Solid-State Structures and NMR Studies of the Platinum(II)–Bis(carbene) Complexes

Important geometrical parameters of the solid-state structures are shown in Table 4 and the Supporting Information. Details of the structure determinations are given in the Experimental Section.

Table 4. Selected bond lengths and bond and torsional angles of **3b**–**3e**.

| | 3b | 3c | 3d | 3e |
|---|---|---|---|---|
| Pt–C1 | 1.968(12)×2 | 1.968(5)×2 | 1.961(6) | 1.967(12) |
| Pt–C11 | | | 1.971(6) | 1.976(13) |
| Pt–Br1 | 2.4685(16)×2 | 2.4833(6)×2 | 2.4926(7) | 2.4746(13) |
| Pt–Br2 | | | 2.4831(7) | 2.4812(14) |
| C1–N1 | 1.366(16)×2 | 1.351(7)×2 | 1.349(8) | 1.377(15) |
| C11–N3 | | | 1.333(8) | 1.359(15) |
| C1–Pt–C1A/C11 | 86.4(5) | 84.9(2) | 84.4(3) | 85.6(5) |
| C1–Pt–Br1 | 92.2(4) | 92.75(15) | 92.34(18) | 93.1(4) |
| C1–N2–C5–C10 | 137.0(12) | –147.0(5) | 128.0(7) | –143.8(12) |

The molecular structures of complexes **3b**–**3e** are nearly identical with each other and with **4**; they contain a bowl-shaped NHC ligand. A DMSO solvent molecule, which covers the cavity, is found inside this bowl in all structures. The solid-state structure of complex **3d** is given in Figure 1 as an example, although the DMSO solvent molecule has been omitted for clarity. Pictures of the solid-state structures of the other complexes are given in the Supporting Information.

The Pt–carbene-C distances of the aromatic-substituted complexes **3b**–**3e** are equivalent within the margin of error. The biggest differences between these structures are found in the torsional angles of the plane of the aromatic rings towards the plane of the imidazole rings. Figure 2 shows a superposition of all four crystal structures; the DMSO and methanol solvent molecules found in the crystal structures have been omitted for clarity. The figure shows that the coordination environment of the metal center is highly preserved and so there are nearly no differences in the steric situation of the metal, even though the complexes crystallize in different space groups.

Although structurally quite similar these complexes have different electronic properties at the metal center, as can be seen from the $^{13}C$ NMR spectra. The effects of the different

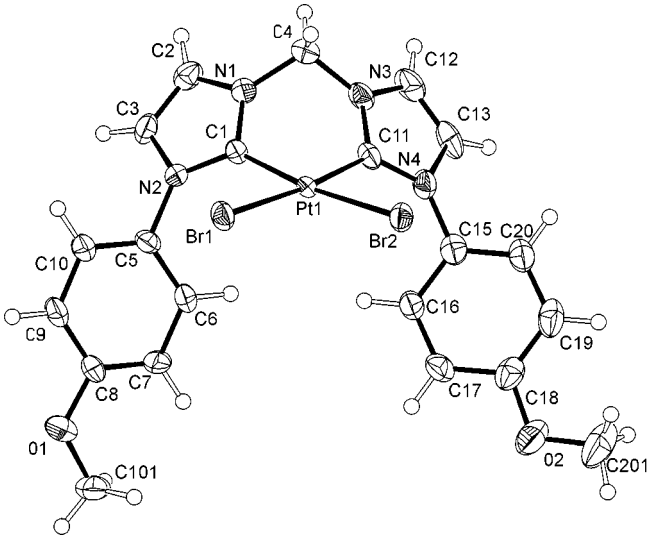



Figure 1. ORTEP-style plot of the solid-state structure of compound **3d**. Thermal ellipsoids are drawn at the 50% probability level. The disordered DMSO molecule in the crystal has been omitted for clarity.

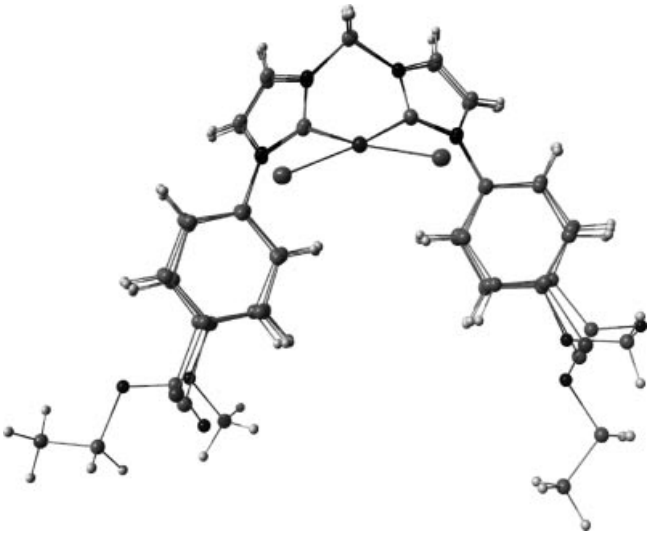


Figure 2. Superposition of the solid-state structures of **3b**–**3e**. Solvents omitted for clarity.

aromatic substituents $R_1$ on the $^{13}C$ chemical shifts for the carbene carbon atoms are shown in Figure 3. Therefore it is possible to fine-tune the electronic situation at the metal center by varying the functional groups at the aromatic ring. Electron-withdrawing groups like $NO_2$ or halogens at the aromatic ring lead to a shift of the $^{13}C$ signal of the

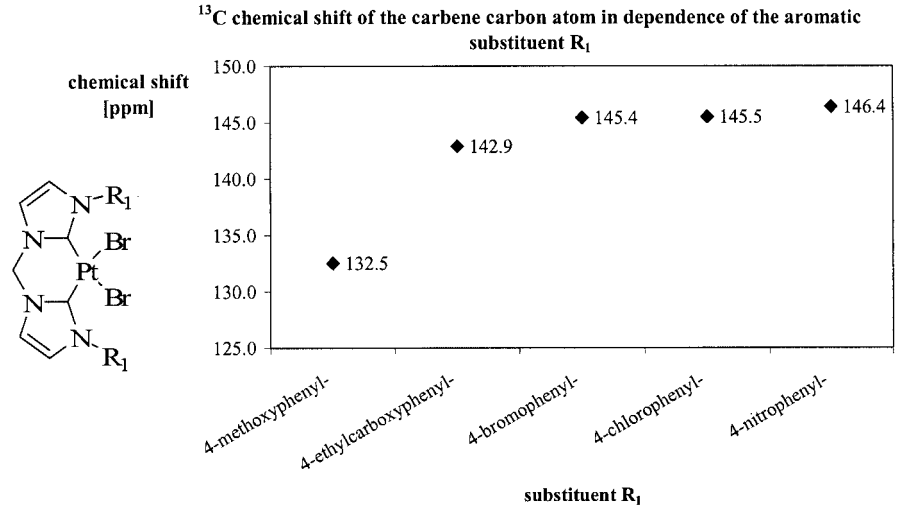



Figure 3. Dependence of the $^{13}C$ chemical shift of the carbene carbon atom on the aromatic substituents $R_1$.

carbene C to lower field, which is indicative of a higher partial negative charge at the carbene carbon atoms of the complex. As expected, the electron-withdrawing effects of a 4-chlorophenyl and a 4-bromophenyl group at the imidazole are nearly equivalent. On the other hand, electron-donating groups like the methoxy group at the aromatic ring lead to a high-field shift of the $^{13}C$ signal of the carbene carbon atom.

This type of complex also shows an unusually high thermal stability combined with a surprising resistance to acidic media. We have observed this stability previously for palladium(II)–NHC complexes like 1,1′-dimethyl-3,3′-methylene-4-diimidazoline-2,2′-diylidenepalladium(II) dibromide (**4**), which are catalysts for the activation of methane, while the analogous platinum(II)–NHC complex **5** decomposes quickly in trifluoroacetic acid (Figure 4).[9,10,22]

**4** **5**

Figure 4. Methyl-substituted bis-NHC complexes of palladium (**4**) and platinum (**5**).

With the introduction of aromatic ligands and the novel platinum(II) acetylacetonate synthesis presented here, we have been able to make several new platinum–bis(carbene) complexes with increased stability against strongly acidic conditions. While the analogous *N*-methyl-substituted complex **5** is stable towards air and moisture even at elevated temperatures, it decomposes within minutes to platinum black in trifluoroacetic acid.[9] However, the new complex **3b** does not decompose even after weeks in TFA or at elevated temperatures of up to 90 °C in the presence of strong oxidants like $K_2S_2O_8$. Complex **3e** can also be heated to 110 °C in 2 N HCl solution for 4 h with no change in the NMR spectrum. Neither reprotonation to the imidazolium salt nor hydrolysis of the ester functionality are observed under these conditions.

## Conclusion

We have shown that platinum(II)–bis(carbene) complexes with various aromatic substituents can be synthesized following our new protocol with platinum(II) acetylacetonate as metal precursor. Together with our new aromatic ligands with various substituents, acid-stable platinum(II)–bis(carbene) complexes are now synthetically available in great diversity. The electronic situation at the metal center can be fine-tuned by varying the functional groups at the aromatic ring without changing the steric situation of the metal center. This is important for future applications of these complexes in various catalytic reactions, since many known homogeneous catalytic processes depend on a particular electronic situation at the metal center.

## Experimental Section

**General Procedures:** Solvents of 99.5% purity were used throughout this study. Platinum(II) acetylacetonate (98%) was purchased from Acros. All other chemicals were obtained from common suppliers and used without further purification. Ligands **2a**–**2e** were prepared according to the procedures given in the Supporting Information. $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker AC 300 P, Jeol JNM GX-270, or Jeol JNM GX-400 spectrometer. As the $^1H$ and $^{13}C$ NMR spectra of one compound were not always measured on the same spectrometer, spectrometer frequencies of the measurements are given. The spectra were referenced internally to the resonances of the solvent ($^1H$, $^{13}C$). Elemental analyses were performed by the microanalytical laboratory at our institute using an EuroVektor Euro EA-300 Elemental Analyzer. Mass spectra were recorded with a Finnigan MAT 90 spectrometer.

**Synthesis of Platinum(II) Complex 3a:** 1,1′-Bis[1-(4-nitrophenyl)]-3,3′-methylenimidazolium dibromide (**2a**; 280.5 mg, 0.51 mmol) and platinum(II) acetylacetonate (200 mg, 0.51 mmol) were dissolved in 3 mL of dimethyl sulfoxide in a nitrogen-flushed Schlenk tube and heated for 2 h to 60 °C, 2 h to 80 °C, 2 h to 100 °C, and 1 h to 130 °C. At approximately 80 °C the reaction mixture became a clear, yellow solution. After removal of the solvent in vacuo the resulting residue was washed twice with 5 mL of diethyl ether and

5 mL of dichloromethane. The product was obtained as a yellow powder. Yield: 0.236 g (62.1%). $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 6.31 (d, $J$ = 14.4 Hz, 1 H, NC$H_2$N), 6.38 (d, $J$ = 14.4 Hz, 1 H, NC$H_2$N), 7.79 (d, $J$ = 9.0 Hz, 2 H, NC$H_2$CH$_2$N), 7.97–8.03 (m, 4 H, arom. H), 8.36 (d, $J$ = 9.0 Hz, 2 H, NCH$_2$C$H_2$N), 8.51–8.55 (m, 4 H, arom. H) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 62.4 (N$C$H$_2$N), 121.0 (N$C$HCHN), 122.6 (NCH$C$HN), 124.5 (C2, C6 of C$_6$H$_4$NO$_2$), 125.5 (C3, C5 of C$_6$H$_4$NO$_2$), 126.4 (C1 of C$_6$H$_4$NO$_2$), 146.4 ($C$–Pt), 146.8 ($C$–NO$_2$). $C_{19}H_{14}Br_2N_6O_4Pt$·0.5DMSO (745.24 + 39.07): calcd. C 30.63, H 2.18, N 10.72; found C 30.94, H 2.46, N 10.79. MS (FAB): $m/z$ = 584.2 [M – 2Br]$^+$, 462.2 [M – 2Br – C$_6$H$_4$NO$_2$]$^+$, 341.2 [M – 2Br – 2C$_6$H$_4$NO$_2$]$^+$, 147.3 [M – 2Br – Pt – 2C$_6$H$_4$NO$_2$]$^+$.

**Synthesis of Platinum(II) Complex 3b:** 1,1-Bis[1-(4-chlorophenyl)]-3,3′-methylenimidazolium dibromide (**2b**; 500 mg, 0.94 mmol) and platinum(II) acetylacetonate (370 mg, 0.94 mmol) were dissolved in 10 mL of dimethyl sulfoxide in a nitrogen-flushed Schlenk tube and heated for 2 h to 40 °C, 2 h to 60 °C, 2 h to 80 °C, 2 h to 100 °C and 1 h to 130 °C. At 60 °C the reaction mixture became a clear, yellow solution. After removal of the solvent in vacuo the resulting residue was washed twice with 5 mL of ethanol. The product was obtained as a white powder. Yield: 0.591 g (86.8%). $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 6.10 (d, $J$ = 14.6 Hz, 1 H, NC$H_2$N), 6.31 (d, $J$ = 14.6 Hz, 1 H, NC$H_2$N), 7.64 (d, $J$ = 9.0 Hz, 4 H, arom. H), 7.73 (d, $J$ = 2.2 Hz, 2 H, NC$H$CHN), 7.77 (d, $J$ = 2.1 Hz, 2 H, NCHC$H$N), 7.81 (d, $J$ = 9.0 Hz, 4 H, arom. H) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 67.0 (N$C$H$_2$N), 121.4 (N$C$HCHN), 122.2 (NCH$C$HN), 127.0 (C2, C6 of C$_6$H$_4$Cl), 128.6 (C3, C5 of C$_6$H$_4$Cl), 132.3 ($C$–Cl), 138.2 (C1 of C$_6$H$_4$Cl), 145.5 ($C$–Pt) ppm. $C_{19}H_{14}Br_2Cl_2N_4Pt$·DMSO (724.13 + 78.13): calcd. C 31.44, H 2.51, N 6.98, S 4.00; found C 31.16, H 2.51, N 6.65, S 4.00. MS (FAB): $m/z$ = 643.3 [M – Br]$^+$, 563.3 [M – 2Br]$^+$, 176.3 [C$_9$H$_6$N$_2$Cl$^+$].

**Synthesis of Platinum(II) Complex 3c:** 1,1-Bis[1-(4-bromophenyl)]-3,3′-methylenimidazolium dibromide (**2c**; 315.0 mg, 0.51 mmol) and platinum(II) acetylacetonate (200.0 mg, 0.51 mmol) were dissolved in 3 mL of dimethyl sulfoxide in a nitrogen-flushed Schlenk tube and stirred for 2 h at room temperature. The reaction mixture was then heated for 2 h to 60 °C, 1 h to 85 °C, and finally 1 h to 110 °C. The solvent was then removed in vacuo until only 0.5 mL of the solvent remained. After the addition of 3 mL of water a white solid precipitated. The aqueous solution was filtered off and the resulting residue was washed twice with 5 mL of dichloromethane. The product was obtained as a white powder. Yield: 0.278 g (67.0%). $^1$H NMR (270 MHz, [D$_6$]DMSO): $\delta$ = 6.10 (d, $J$ = 12.7 Hz, 1 H, NC$H_2$N), 6.31 (d, $J$ = 12.4 Hz, 1 H, NC$H_2$N), 7.53–7.95 (m, 12 H, remaining H) ppm. $^{13}$C NMR (67.9 MHz, [D$_6$] DMSO): $\delta$ = 62.5 (N$C$H$_2$N), 120.7 (N$C$HCHN), 121.5 ($C$–Br), 122.2 (NCH$C$HN), 127.3 (C2, C6 of C$_6$H$_4$Br), 131.6 (C3, C5 of C$_6$H$_4$Br), 138.8 (C1 of C$_6$H$_4$Br), 145.4 ($C$–Pt) ppm. MS (FAB): $m/z$ = 733.0 [M – Br]$^+$, 653.1 [M – 2Br]$^+$, 572.2 [M – 3Br]$^+$, 419.5 [M – 3Br – C$_6$H$_4$Br]$^+$.

**Synthesis of Platinum(II) Complex 3d:** 1,1-Bis[1-(4-methoxyphenyl)]-3,3′-methylenimidazolium dibromide (**2d**; 250.0 mg, 0.48 mmol) and platinum(II) acetylacetonate (188.3 mg, 0.48 mmol) were dissolved in 7 mL of dimethyl sulfoxide in a nitrogen-flushed Schlenk tube and stirred for 4 d at 60 °C. The solvent was then removed in vacuo and the product washed twice with 5 mL of water and twice with 5 mL of diethyl ether. The product was obtained as a white powder Yield: 0.240 g (69.9%). $^1$H NMR (300 MHz, [D$_6$] DMSO): $\delta$ = 3.86 (s, 6 H, OC$H_3$), 6.07 (d, $J$ = 14.6 Hz, 1 H, NC$H_2$N), 6.26 (d, $J$ = 14.6 Hz, 1 H, NC$H_2$N), 7.08 (m, 4 H, arom. H), 7.67 (s, 2 H, NC$H$CHN), 7.72 (s, 2 H, NCHC$H$N), 7.78 (m, 4 H, arom. H) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 55.3 (O$C$H$_3$), 62.4 (N$C$H$_2$N), 113.7 (arom. $C$H), 122.5 (N$C$HCHN), 126.1 (arom. $C$H), 126.3 (NCH$C$HN), 126.7 (C1 of C$_6$H$_4$OMe), 132.5 (Pt–$C$), 158.8 ($C$–OMe) ppm. $C_{21}H_{20}Br_2N_4O_2Pt$ (715.30): calcd. C 35.26, H 2.81, N 7.86; found C 35.34, H 2.87, N 7.52. MS (FAB): $m/z$ = 635.1 [M – Br]$^+$, 554.3 [M – 2Br]$^+$, 448.2 [M – 2Br – C$_6$H$_4$OCH$_3$]$^+$, 341.3 [M – 2Br – 2C$_6$H$_4$OCH$_3$]$^+$.

**Synthesis of Platinum(II) Complex 3e:** 1,1-Bis[1-(4-ethylcarboxyphenyl)]-3,3′-methylenimidazolium dibromide (**3e**; 100.0 mg, 0.165 mmol) and platinum(II) acetylacetonate (64.9 mg, 0.165 mmol) were dissolved in 6 mL of dimethyl sulfoxide in a nitrogen-flushed Schlenk tube and stirred for 3 h at 40 °C, 2 h at 60 °C, 2 h at 70 °C, 2 h at 100 °C, and 1 h at 130 °C. The solvent was removed in vacuo and the product washed once with 5 mL of ethanol. The product was obtained as a white powder. Yield: 0.095 g (72%). $^1$H NMR (300 MHz, [D$_6$]DMSO): $\delta$ = 1.43 (t, $J$ = 7.0 Hz, 6 H, CH$_2$C$H_3$), 4.40 (q, $J$ = 7.0 Hz, 4 H, C$H_2$CH$_3$), 6.14 (d, $J$ = 13.2 Hz, 1 H, NC$H_2$N), 6.35 (d, $J$ = 13.2 Hz, 1 H, NC$H_2$N), 7.84 (d, $J$ = 2.7 Hz, 2 H, NC$H$CHN);7.91 (d, $J$ = 2.7 Hz, 2 H, NCHC$H$N), 7.98 (d, $J$ = 8.4 Hz, 4 H, arom. H), 8.19 (d, $J$ = 8.4 Hz, 4 H, arom. H) ppm. $^{13}$C NMR (75 MHz, [D$_6$]DMSO): $\delta$ = 14.1 (CH$_2$$C$H$_3$), 61.1 ($C$H$_2$CH$_3$), 62.7 (N$C$H$_2$N), 120.3 (arom. $C$H), 125.2 (N$C$HCHN), 129.8 (arom. $C$H), 130.7 (NCH$C$HN), 138.4 (C1 of C$_6$H$_4$COOEt), 139.1 (C4 of C$_6$H$_4$COOEt), 142.9 (Pt–$C$), 165.3 ($C$OOEt) ppm. $C_{25}H_{26}Br_2N_4O_2Pt$·0.5DMSO (799.37 + 39.07): calcd. C 37.25, H 3.25, N 6.68, S 1.91; found C 37.15, H 3.38, N 6.29, S 2.11.

**X-ray Crystal-Structure Determination for 3b–3e:** Crystals suitable for an X-ray investigation were obtained either by allowing methanol to condense into a saturated solution of the metal complex in DMSO (**3b**, **3c**) or by slowly cooling a hot, saturated solution of the complex in DMSO (**3d**, **3e**). The crystals were stored under perfluorinated ether, transferred to a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area-detection system (Kappa-CCD; Nonius) with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å). Data collections were performed at 173 K (**3b**) or 198 K (**3c**–**3e**) in the $\Theta$ range 2.27° < $\Theta$ < 21.02° (**3b**) or 3.00° < $\Theta$ < 27.40° (**3c**–**3e**). The reflections were integrated, raw data were corrected for Lorentz, polarization, decay, and absorption effects. Due to the small size of the crystal the data set for **3d** was reduced to 25.00 and that of **3e** to 26.40. The absorption correction was applied using the PLATON DELABS algorithm for **3b** and SADABS for **3c**–**3e**. The independent reflections were used for all calculations after merging. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions as riding on the parent carbon atoms. During the final stage of the refinements it becomes evident that the crystal of **3b** contains unresolvable solvent molecules. This problem was cured by using the PLATON CALC SQUEEZE procedure. All other solvent molecules in **3c**–**3e** could be fully resolved. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final difference Fourier map showed high residual electron density peaks for **3b** (+1.610 and –2.096 e Å$^{-3}$) caused by the incomplete absorption correction and the incomplete removal of solvent molecules and **3c** (1.546 and –0.959 e Å$^{-3}$; distance to platinum 0.783 and 0.976 Å) caused by an incomplete absorption correction. Details of the structure determinations are given in Table 5. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography. All calcu-

Table 5. Selected parameters for the crystal-structure determination of **3b**–**3e**.

| | **3b** | **3c**·DMSO,·MeOH | **3d**·DMSO | **3e**·DMSO |
|---|---|---|---|---|
| Measured by | E.H. | S.A. | S.G. | S.A. |
| Crystal color and form | colorless needle | colorless needle | colorless needle | colorless fragment |
| Crystal size [$mm^3$] | 0.05 × 0.08 × 0.43 | 0.38 × 0.08 × 0.03 | 0.18 × 0.08 × 0.07 | 0.25 × 0.16 × 0.10 |
| Unit cell | orthorhombic | monoclinic | triclinic | monoclinic |
| Space group | *Pnma* (no. 62) | $P2_1/m$ (no. 11) | $P\bar{1}$ (no. 2) | $P2_1$ (no. 4) |
| $\Theta$ range [°] | 2.27–21.02 | 3.91–27.40 | 3.61–25.00 | 3.96–26.40 |
| $a$ [Å] | 13.2647(2) | 8.108(1) | 9.840(1) | 8.2480(3) |
| $b$ [Å] | 16.8268(3) | 17.395(1) | 10.050(1) | 17.8570(15) |
| $c$ [Å] | 10.6220(2) | 10.258(1) | 14.054(1) | 10.5310(7) |
| $\alpha$ [°] | | | 101.46(1) | |
| $\beta$ [°] | | 109.56(1) | 106.39(1) | 103.150(5) |
| $\gamma$ [°] | | | 95.43(1) | |
| $V$ [$Å^3$], $Z$ | 2370.86(7), 4 | 1363.3(2), 2 | 1289.9(2), 2 | 1510.38(17), 2 |
| $F_{000}$ | 1352 | 868 | 760 | 848 |
| Rflns. measured | 47273 | 18489 | 23987 | 20357 |
| Rflns. independent | 1336 | 3184 | 4533 | 6110 |
| Refined | 130-parameter full-matrix refinement | 168-parameter full-matrix refinement | 312-parameter full-matrix refinement | 373-parameter full-matrix refinement, 8 restraints (disordered solvent) |
| Refinement | least-squares refinement of 1336 reflections with Denzo/HKL | least-squares refinement of 3184 reflections with Collect/SADABS | least-squares refinement of 4533 reflections with Collect/SADABS | least-squares refinement of 6110 reflections with Collect/SADABS |
| Remaining electron density [e $Å^{-3}$] | +1.610, –2.096 (insuff. CALC SQEEZE) | +1.546, –0.959 (near platinum) | +0.668, –0.621 | +0.899, –0.596 |
| $R_1$[a] [$F_o > 4\sigma(F_o)$] | 0.0498 | 0.0283 | 0.0330 | 0.0379 |
| [all reflections] | 0.0530 | 0.0426 | 0.0568 | 0.0516 |
| $wR_2$[b] [$F_o > 4\sigma(F_o)$] | 0.1229 | 0.0560 | 0.0502 | 0.0741 |
| [all reflections] | 0.1252 | 0.0611 | 0.0537 | 0.0789 |
| GOF (on $F^2$)[a] | 1.172 | 1.137 | 0.995 | 1.065 |
| Diffractometer | Kappa CCD (Area Diffraction System; Nonius); Mo-$K_\alpha$; rotating anode | Kappa CCD (Area Diffraction System; Nonius); Mo-$K_\alpha$; sealed tube | Kappa CCD (Area Diffraction System; Nonius); Mo-$K_\alpha$; sealed tube | Kappa CCD (Area Diffraction System; Nonius); Mo-$K_\alpha$; sealed tube |

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

lations were performed with the programs PLATON, SIR92, SHELXL-97, and SADABS.[35–38]

CCDC-287338 (**3b**), -287341 (**3c**), -287339 (**3d**), and -287340 (**3e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting information** (see footnote on the first page of this article): Synthetic and analytical data of the aromatic substituted bis(carbene) ligands, as well as important data of the solid-state structures of **3b**–**3e**.

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