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Synthesis and structural characterization of novel bridged platinum(II) biscarbene complexes

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Dedicated to Professor Dr J. Strähle on the occasion of his 65th birthday

Abstract

Novel bridged platinum(II) biscarbene complexes are reported: 1,1′-dimethyl-3,3′-methylene-4-diimidazolin-2,2′-diylidene platinum(II) (**3**) and 1,1′-dimethyl-3,3′-ethylene-4-diimidazolin-2,2′-diylidene platinum(II) complexes **4** are directly accessible in high yields starting from platinum halides. The one-pot synthesis obviates the need for multi-step reactions via metal precursors or free carbenes. An X-ray crystal structure of 1,1′-dimethyl-3,3′-methylene-4-diimidazolin-2,2′-diylidene platinum(II) dibromide (**3b**) confirmed the structural similarity to the known corresponding palladium complexes. Since free 1,1′-di-*R*-3,3′-methylene-4-diimidazolin-2,2′-diylidenes are only available in low yields this synthetic route provides an easy access to the corresponding carbene complexes.

Keywords: Platinum(II) biscarbene complexes; NHC; X-ray structures

1. Introduction

In the last decade N-heterocyclic carbenes (NHC) have been the subject of intense research in the field of organometallic chemistry. Because of their extraordinary properties they have found access to a great variety of catalytic processes which include C–C-coupling reactions [1–3], olefin metathesis [4–7], hydroformylation [8,9], polymerization reactions [10,11] and CH-activation [12]. The key for this development have been improved synthetic methods for the preparation of NHC complexes, which have been reported in recent reviews [13,14].

While the NHC complex formation via multi component reaction only plays an inferior role, many attempts were made to improve the deprotonation reaction and isolate free carbenes for consecutive reactions. A breakthrough was the isolation of the first free 1,3-di-*R*-4-imidazolin-2-ylidene by Arduengo et al. in 1991 [15]. With free carbenes a huge number of NHC complexes was now accessible which could not be synthesized before due to a lack of basic metal precursors.

But since free NHCs are sensitive to air and moisture and therefore hard to handle, alternative routes for the in-situ formation of NHC complexes have been developed, like the ammonia- and the alcoholate-method [16,6].

Metal acetates also allow the synthesis of NHC complexes without isolation of the free carbene. Palladium(II) acetate in wet dimethyl sulphoxide at elevated temperatures reacts via the deprotonation of the imidazolium salt. This route is very useful in cases where the metal acetates are easily available and was used for the synthesis of palladium(II) NHC complexes, which have shown to be active in the CH-activation of methane [12].

Even methylene bridged bisimidazolium salts (Scheme 1) can be converted to the corresponding biscarbene complexes in high yields (85–90%) [10,11,17].

Since the acidic methylene protons in bisimidazolium salts are also attacked under common deprotonation conditions, a pathway via free biscarbenes is only

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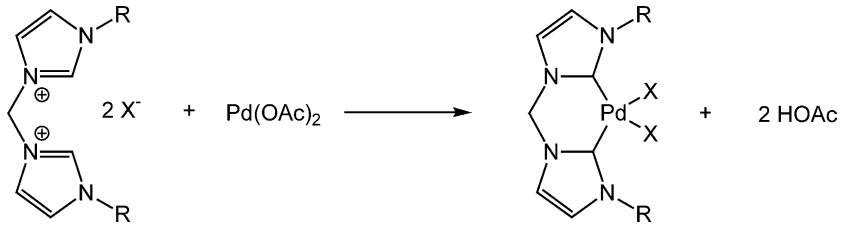


Scheme 1. The 'acetate route'.

possible by using sterically extremely demanding bases, but the yields are moderate [18,19].

For the syntheses of platinum NHC complexes so far either platinum precursor molecules or free carbenes had to be prepared, which usually have to be handled under inert gas atmosphere [20–25]. To circumvent multi step pathways we developed a new synthetic route. While platinum acetate is not commercially available and difficult to synthesize [26,27], the corresponding halide salts are readily available.

We would like to report a synthetic route to novel platinum NHC complexes via an in-situ method, which eliminates the need for the metal precursors or metal acetates and will be useful for all cases where the metal acetates are not readily available.

2. Results and discussion

Using the halide salts we developed a new direct, easy synthetic route for platinum(II) NHC complexes, combining the advantages of readily available starting materials with the in-situ deprotonation of the imidazolium salts and avoiding free carbenes or expensive syntheses of air-sensitive organometallic precursors.

We found that sodium acetate does not compete in carbene complex formation. In order to avoid halogen scrambling during the reaction, the platinum(II) halides were reacted with imidazolium salts bearing the same halide counter anions. The methylene bridged species 3,3′-dimethyl-1,1′-methylene-diimidazolium diiodide (**1a**) and 3,3′-dimethyl-1,1′-methylene-diimidazolium dibromide (**1b**), as well as 3,3′-dimethyl-1,1′-ethylene-diimidazolium diiodide (**2**) have been synthesized by a known procedure [28], additional data of the characterization is given in Section 6.

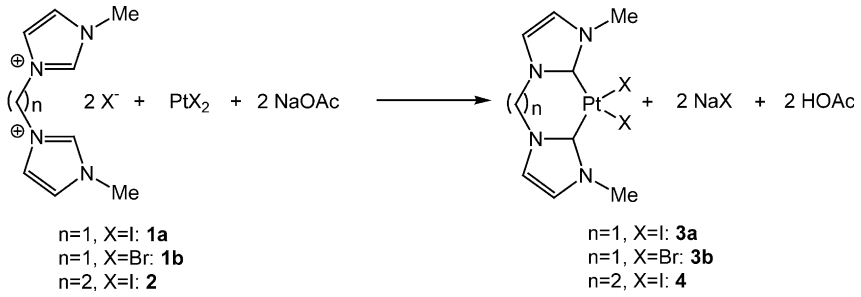
In the complex synthesis with platinum(II) iodide one equivalent of **1a** and sodium acetate, respectively, were solved in dimethyl sulphoxide and heated to 75 °C (Scheme 2). After one hour, the dark color originating from platinum(II) iodide disappears and a yellow solution is obtained. After subjection to the work-up procedure described below, **3a** was isolated in 70.1% yield. The same procedure was used for the reactions of **1b** with platinum(II) bromide, leading to **3b** in 64.2% yield (Fig. 1, Table 1).

^{1}H-NMR spectra of the product solutions reveal that the characteristic signals for the acidic proton in the imidazolium salt at 9.65 ppm for **1a** and 9.83 ppm for **1b** have disappeared. Furthermore the ^{13}C spectra show a significant shift for the carbon atom in position 2, indicating the formation of the NHC complexes **3a** and **3b**.

In addition the ^{1}H signals of the methylene groups of **3a** and **3b** split into two signals, which has already been reported for several palladium(II) NHC complexes bearing bridged NHC ligands. The new synthetic method was also successful for the synthesis of the ethylene bridged complex **4**. Again the ^{1}H signals of the bridging ethylene group split up, indicating the formation of the desired product.

3. X-ray structure determination of complex 3b

Details of the X-ray experiment, data reduction, and final structure refinement calculation are summarized in Table 2. Crystals of complex **3b** suitable for an X-ray structure determination were grown from a saturated solution of **3b** in acetonitrile. Preliminary examination and data collection were carried out on a CAD4 diffractometer (Nonius) at the window of a sealed tube (NONIUS FR590; 51 kV; 35 mA; 1.8 kW) and graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 25 high angle reflections. Data collection was performed at 293 K with an exposure time of maximum 60 s per reflection (omega scans; scan width: $(1.10+0.15 \tan \Theta)^\circ \pm 25\%$ to each side of the reflection to determine the background). A total number of 10 100 reflections were collected. Raw data were corrected for Lorentz and polarization effects [29]. Corrections for absorption (based on psi-scans) and decay effects were applied [30]. After merging a sum of 2850 independent reflections remained and were used for all calculations. The structure was solved by a combination of direct methods and difference Fourier syntheses [31]. All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were placed in calculated positions ($d_{C-H} = 0.93$, 0.96, 0.97 Å). Isotropic displacement parameters were calculated



Scheme 2. Synthesis of bridged Pt–NHC complexes.

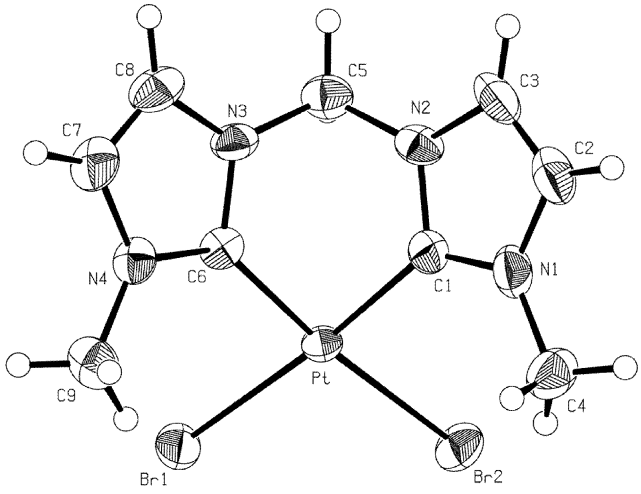


Fig. 1. ORTEP [34] representation of complex **3b** in the solid state. Thermal ellipsoids are drawn at the 50% probability level.

Table 1
Selected interatomic distances (Å) and angles (°) for complex **3b**

Bond distances	
Pt–Br1	2.4976(11)
Pt–Br2	2.4883(13)
Pt–C1	1.963(10)
Pt–C6	1.950(10)
Bond angles	
Br1–Pt–Br2	91.14(4)
Br1–Pt–C1	175.0(3)
Br1–Pt–C6	92.5(3)
Br2–Pt–C1	92.2(3)
Br2–Pt–C6	173.3(3)
C1–Pt–C6	83.8(4)

from the parent carbon atom ($U_H = 1.2U_C$). Full-matrix least-squares refinements were carried out by minimizing $\Sigma\, w(F_o^2 - F_c^2)^2$ with a SHELXL-97 weighting scheme and stopped at maximum shift/err < 0.001 [32]. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography* [33]. All other calculations (including ORTEP graphics) were done with the program PLATON [34]. Calculations were performed on a PC workstation (Intel Pentium II) running LINUX.

Table 2
Crystallographic data for complex **3b**

	3b
Chemical formula	$C_9H_{12}Br_2N_4Pt$
Formula weight	531.11
Temperature (K)	293
Color/shape	Pale yellow/plate
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
a (Å)	8.5813(8)
b (Å)	15.9405(7)
c (Å)	10.4418(12)
β (°)	112.385(7)
V (Å^3)	1320.7(2)
Z	4
ρ_{calc} (g cm^{-3})	2.671
μ (mm^{-1})	16.655
$F(000)$	968
Crystal size (mm)	$0.46 \times 0.28 \times 0.15$
θ-Range (°)	2.47–25.93
Data collected	$-10 \le h \le 10$, $-19 \le k \le 19$, $-12 \le l \le 12$
Reflections collected	10 100
Reflections observed [$I > 2\sigma(I)$]	2100 (observed)
Independent reflections	2580 (all) [$R_{int} = 0.0907$]
Parameters refined	148
R_1 (observed/all)	0.0439/0.0604
wR_2 (observed/all)	0.0897/0.0963
Goodness-of-fit (observed/all)	1.030/1.030
Max/min $\Delta\rho$ (e Å^{-3})	+3.89/−3.73

4. Conclusion

We present a new synthetic pathway which directly leads to novel platinum(II) biscarbene complexes starting from inexpensive and easily available platinum(II) halides. The reactions with sodium acetate and imidazolium salts can be carried out without special precautions concerning atmosphere and solvents. This was demonstrated for several bridged biscarbene complexes, which can be synthesized in high yields under these reaction conditions.

5. Experimental

5.1. Reagents

Platinum(II) bromide (98%) and platinum(II) iodide (98%) were purchased from Aldrich, platinum(II) chloride was a generous donation from Degussa. Dibromomethane (>99%), diiodomethane (>99%) and diiodoethane (>99%) were supplied by Merck, while methyl imidazole was available from Fluka. Solvents were purchased from common suppliers and used without further purification.

5.2. Reactions

5.2.1. 1,1′-Dimethyl-3,3′-ethylene-diimidazolium diiodide (**2**)

In an ACE pressure tube 1.00 g (12.2 mmol) methyl imidazole and 1.89 g (6.7 mmol) diiodoethane are solved in 5 ml THF and heated to 130 °C for 16 h. After cooling to room temperature (r.t.) the resulting precipitate is filtered off and washed twice with 5 ml THF. The product is dried under vacuum, yielding 2.13 g (78.3%) of a yellow powder.

^{1}H-NMR (400 MHz, 25 °C, d_6-Me_2SO): $\delta = 9.24$ (s, 2H, NCHN), 7.78 (s, 2H, NCH), 7.53 (s, 2H, NCH), 4.65 (s, 4H, CH_2CH_2), 3.74 ppm (s, 6H, CH_3). ^{13}C-NMR (100 MHz, 25 °C, d_6-Me_2SO): $\delta = 137.4$ (NCHN), 124.3 (NCH), 122.7 (NCHN), 48.7 (CH_2CH_2), 36.6 ppm (CH_3). EA: Anal. Calc.: C, 26.9; H, 3.6; N, 12.6. Found: C, 27.0; H, 3.6; N, 12.6%.

5.2.2. 1,1′-Dimethyl-3,3′-methylene-4-diimidazolin-2,2′-diylidene platinum(II) diiodide (**3a**)

Platinum(II) iodide (224 mg, 0.5 mmol), sodium acetate trihydrate (136 mg, 1.0 mmol) and 1,1′-dimethyl-3,3′-methylene-4-imidazolium diiodide (216 mg, 0.5 mmol) are solved in 6 ml Me_2SO and are heated to 75 °C. The dark suspension clears to a red–brown solution within 1 h. After further 2 h the solvent is evaporated and the residue washed twice with 2 ml portions of CH_2Cl_2. After extraction of the sodium salt with a small amount of water the residue is washed with THF and dried under high vacuum. Two hundred and nineteen milligram (70.1%) of a slightly yellow powder are obtained.

^{1}H-NMR (400 MHz, 25 °C, d_6-Me_2SO): $\delta = 7.52$ (s, 2H, NCH), 7.29 (s, 2H, NCH), 6.14 (d, 1H, NCH_2), 5.91 (d, 1H, NCH_2), 3.83 ppm (s, 6H, CH_3). ^{13}C-NMR (100 MHz, 25 °C, d_6-Me_2SO): $\delta = 143.4$ (NCN), 122.7 (NCH), 120.4 (NCH), 61.8 (CH_2), 37.3 ppm (CH_3). EA: Anal. Calc.: C, 17.3; H, 1.9; N, 9.0. Found: C, 17.8; H, 2.2; N, 9.5%. MS: *m/u* 498 [$M^+ - I$], 370 [$M^+ - 2I$], 289 [$M^+ - 2I - C_4H_5N_2$], 176 [$M^+ - 2I - Pt$].

5.2.3. 1,1′-Dimethyl-3,3′-methylene-4-diimidazolin-2,2′-diylidene platinum(II) dibromide (**3b**)

Platinum(II) bromide (200 mg, 0.56 mmol), sodium acetate trihydrate (153 mg, 1.12 mmol) and 1,1′-dimethyl-3,3′-methylene-4-imidazolium dibromide (190 mg, 1.12 mmol) are solved in 4 ml Me_2SO and are heated to 80 °C. After 2 h the solution is heated to 100 °C for 1 h. The mixture is cooled to r.t. and the solution filtered off from a small amount of platinum black that has formed. Afterwards the solvent is evaporated and the residue washed twice with 2 ml portions of CH_2Cl_2. After extraction of the sodium salt with a small amount of water the residue is washed with THF and dried under high vacuum. One hundred and ninety-one milligrams (64.2%) of a very light yellow powder are obtained.

^{1}H-NMR (400 MHz, 25 °C, d_6-Me_2SO): $\delta = 7.56$ (s, 2H, NCH), 7.33 (s, 2H, NCH), 6.23 (d, 1H, NCH_2), 5.94 (d, 1H, NCH_2), 3.83 ppm (s, 6H, CH_3). ^{13}C-NMR (100 MHz, 25 °C, d_6-dimethyl sulphoxide): $\delta = 144.8$ (NCN), 122.6 (NCH), 120.4 (NCH), 61.8 (CH_2), 36.3 ppm (CH_3). EA: Anal. Calc.: C, 20.3; H, 2.3; N, 10.5. Found: C, 20.4; H, 2.4; N, 10.3%. MS: *m/u* 531 [M^+], 451 [$M^+ - Br$], 369 [$M^+ - 2Br$].

5.2.4. 1,1′-Dimethyl-3,3′-ethylene-4-diimidazolin-2,2′-diylidene platinum(II) diiodide (**4**)

Platinum(II) iodide (224 mg, 0.5 mmol), sodium acetate trihydrate (136 mg, 1.0 mmol) and 1,1′-dimethyl-3,3′-ethylene-4-imidazolium diiodide (223 mg, 0.5 mmol) are solved in 6 ml Me_2SO and are heated to 75 °C. The dark suspension clears to a red–brown solution within 1 h. After further 2 h the solvent is evaporated and the residue washed twice with 2 ml portions of CH_2Cl_2. After extraction of the sodium salt with a small amount of water the residue is washed with THF and dried under high vacuum. Two hundred and thirty-one milligrams (72.4%) of a slightly yellow powder are obtained.

^{1}H-NMR (400 MHz, 25 °C, d_6-Me_2SO): $\delta = 7.33$ (s, 2H, NCH), 7.29 (s, 2H, NCH), 5.16 (m, 2H, NCH_2), 4.44 (m, 2H, NCH_2), 3.79 ppm (s, 6H, CH_3). ^{13}C-NMR (100 MHz, 25 °C, d_6-dimethyl sulphoxide): $\delta = 143.0$ (NCN), 122.7 (NCH), 121.7 (NCH), 46.8 (CH_2), 37.4 ppm (CH_3). EA: Anal. Calc.: C, 18.8; H, 2.2; N, 8.8. Found: C, 18.8; H, 2.2; N, 9.5%.

6. Additional experimental data

6.1. 1,1′-Dimethyl-3,3′-methylene-diimidazolium diiodide (**1a**)

In an ACE pressure tube 1.00 g (12.2 mmol) methyl imidazole and 0.54 mL (6,7 mmol) diiodomethane are

solved in 5 mL tetrahydrofurane and heated to 130 °C for 16 h. After cooling to room temperature the resulting precipitate is filtered off and washed twice with 5 mL tetrahydrofurane. The product is dried under vacuum, yielding 1.91 g (72.3%) of a light yellow powder.

^{1}H NMR (400 MHz, 25 °C, d_6-dimethyl sulphoxide): $\delta = 9.65$ ppm (s, 2H, NCHN), 7.97 ppm (s, 2H, NCH), 7.79 ppm (s, 2H, NCH), 6.65 ppm (s, 2H, CH_2), 3.89 ppm (s, 6H, CH_3).

^{13}C NMR (100 MHz, 25 °C, d_6-dimethyl sulphoxide): $\delta = 138.4$ ppm (NCHN), 124.7 ppm (NCH), 122.3 ppm (NCHN), 58.5 ppm (CH_2), 36.7 ppm (CH_3).

6.2. 1,1′-Dimethyl-3,3′-methylene-diimidazolium dibromide (*1b*)

In an ACE pressure tube 1.00 g (12.2 mmol) methyl imidazole and 0.95 mL (6.7 mmol) dibromomethane are solved in 5 mL tetrahydrofurane and heated to 130 °C for 16 h. After cooling to room temperature the resulting precipitate is filtered off, washed twice with 5 mL tetrahydrofurane. The product is dried under vacuum, yielding 1.56 g (75.8%) of a white powder.

^{1}H NMR (400 MHz, 25 °C, d_6-dimethyl sulphoxide): $\delta = 9.83$ ppm (s, 2H, NCHN), 8.34 ppm (s, 2H, NCH), 7.82 ppm (s, 2H, NCH), 6.82 ppm (s, 2H, CH_2), 3.90 ppm (s, 6H, CH_3).

^{13}C NMR (100 MHz, 25 °C, d_6-dimethyl sulphoxide): $\delta = 138.0$ ppm (NCHN), 124.3 ppm (NCH), 121.9 ppm (NCHN), 57.8 ppm (CH_2), 36.2 ppm (CH_3). EA: calc.: C 32.0%, H 4.2% N 16.6%; found: C 31.9%, H 4.2%, N 16.6%.

7. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 187513 for complex **3b**. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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