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Homoleptic chelating *N*-heterocyclic carbene complexes of palladium and nickel☆

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Abstract

Homoleptic, dicationic nickel(II) complexes with two *cis*-chelating *N*-heterocyclic carbene ligands have been prepared via high yielding, air-stable procedures. Homoleptic and heteroleptic dicationic tetra(carbene) palladium(II) analogues are accessible by the reaction of [*cis*-$CH_2\{\overline{N(H)C{=}C(H)N(Me)C}\}_2Pd(OAc)_2$] with one diazolium diiodide salt precursor or by reacting [*cis*-$CH_2\{\overline{N(H)C{=}C(H)N(Me)C}\}_2PdI_2$] with two equivalents of NaOAc and the corresponding diazolium diiodide salts. ^{1}H- and ^{13}C-NMR as well as X-ray crystallographic data are discussed.

Keywords: Palladium; Nickel; Heterocyclic carbene

1. Introduction

Novel metal complexes of imidazoline-2-ylidenes have attained enormous attention as a new structure principle for both redox active and redox neutral homogeneous catalytic reactions [1]. In contrast to the corresponding phosphine complexes, ligand dissociation has never been observed so that these catalysts do not require an excess of ligand. Furthermore, *N*-heterocyclic carbene based catalysts display unusually high thermal stability and keep their activity even under extreme catalytic reaction conditions. These properties make them suitable for chiral modifications [2] and catalyst immobilisation [3].

Recently, we focused our interest on olefin/CO-copolymerisation reactions catalyzed by solvent stabilized, dicationic *cis*-chelating Pd(II) carbene complexes [4] and developed an improved synthesis for these compounds [5].

Our attempts to include Ni(II) analogues in our studies resulted exclusively in the formation of dicationic tetra(carbene) species. In the present paper, we report on our synthetic studies of Ni(II)- and Pd(II)-tetra(carbene) species prepared by the salt method or in situ carbene generation. An improved synthesis of homoleptic palladium complexes, that has already been described in the literature [6], is presented.

2. Experimental section

2.1. General procedures

All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon or nitrogen. All solvents were used as received as technical grade solvents. [*cis*-$CH_2\{\overline{N(H)C{=}C(H)N(Me)C}\}_2PdBr_2$], [*cis*-$CH_2\{\overline{N(H)C{=}C(H)N(Me)C}\}_2PdI_2$] and all imidazolium salts were prepared according to literature

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procedures [7–9]. Other chemicals were obtained from Aldrich and used as received. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a JOEL JNM-GX 400 spectrometer in $CDCl_3$, d_6-DMSO and D_2O and referenced to the residual ^{1}H resonances of the solvents. Elemental analyses were performed by the microanalytical laboratory in our institute. Melting points were determined in glass capillaries under air. IR spectra were recorded on a FT-IR Perkin Elmer 1680 spectrometer. Mass spectra were recorded on a Varian MAT 311a spectrometer using FAB ionisation (xenon/*p*-nitrobenzylalcohol matrix). GC/MS were obtained on a Hewlett-Packard 5890 instrument.

2.2. Synthesis of bis{1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene}nickel(II) diiodide ***(1a)****, bis{1,1′-diisopropyl-3,3′-methylenediimidazoline-2,2′-diylidene}nickel(II) diiodide* ***(1b)****, bis{1,1′-dicyclohexyl-3,3′-methylenediimidazoline-2,2′-diylidene}nickel(II) diiodide* ***(1c)*** *and bis{1,1′-dimethyl-3,3′-methyleneditriazoline-2,2′-diylidene}nickel(II) diiodide* ***(1d)***

A stirred DMSO solution (5 ml) of the corresponding diazolium salt (1.00 mmol) and anhydrous $Ni(OAc)_2$ (177 mg, 1.00 mmol) was heated at 60°C for 12 h and then at 130°C for a further 2 h, during which time the reaction solution had turned to a pale yellow solution from being initially green. The remaining DMSO was then removed in vacuo at 70°C to give a yellow solid which was washed with MeOH to give the crude product. Recrystallisation from DMSO/MeOH gave the product as yellow crystals. Yields: 589 mg (0.90 mmol, 90%), **1a**; 715 mg (0.92 mmol, 92%), **1b**; 872 mg (0.93 mmol, 93%), **1c**; 607 mg (0.91 mmol, 91%), **1d**.

Compound **1a**. M.p. 289°C (decomp.); ^{1}H-NMR (400 MHz; d_6-DMSO; 25°C; ppm): δ 7.63 (s, 4H, CH); 7.23 (s, 4H, CH); 6.47, 7.00 (AB, ^2J(H,H) = 16.35 Hz, 4H, NCH_2N); 3.10 (s, 12H, CH_3). ^{13}C{^{1}H}-NMR (100.53 MHz; d_6-DMSO; 25°C; ppm): δ 171.07 ($C_{carbene}$); 121.98 (CH); 120.72 (CH); 60.72 (NCH_2N); 35.04 (CH_3). MS (FAB, m/z (%)): 538 (100) $[M-I]^+$, 410 (39) $[M-2I]^+$. Anal. Found: C, 32.30; H, 4.06; N, 15.24%. Calc. for $C_{18}H_{24}N_8I_2Ni$ + 1 DMSO (743.07): C, 32.33; H, 4.07; N, 15.08%.

Compound **1b**. M.p. > 300°C; ^{1}H-NMR (400 MHz; d_6-DMSO; 25°C; ppm): δ 7.78 (s, 4H, CH); 7.44 (s, 4H, CH); 6.60, 6.81 (AB, ^2J(H,H) = 16 Hz, 4H, NCH_2N); 3.85 (sept., ^3J(H,H) = 2 Hz; 4H, CH); 1.30 (d, ^3J(H,H) = 2 Hz, 12H, CH_3); 1.21 (d, ^3J(H,H) = 2 Hz, 12H, CH_3). ^{13}C{^{1}H} (100.53 MHz; d_6-DMSO; 25°C; ppm): δ 171.26 ($C_{carbene}$); 122.42 (CH); 117.71 (CH); 51.65 (NCH_2N); 30.65 (NCH); 24.26 (CH_3); 20.92 (CH_3). MS (FAB, m/z (%)): 649 (100) $[M-I]^+$, 522 (45) $[M-2I]^+$. Anal. Found: C, 39.37; H, 5.80; N, 13.36%. Calc. for $C_{26}H_{40}N_8I_2Ni$ + 1 DMSO (855.29): C, 39.23; H, 5.64; N, 13.07%.

Compound **1c**. M.p. > 300°C; ^{1}H-NMR (400 MHz; d_6-DMSO; 25°C; ppm): δ 8.03 (s, 4H, CH); 7.56 (s, 4H, CH); 6.50, 6.75 (AB, ^2J(H,H) = 14 Hz, 4H, NCH_2N); 0.88–1.95 (m, 44H, C_6H_{11}). ^{13}C{^{1}H}-NMR (100.53 MHz; d_6-DMSO; 25°C; ppm): δ 173.08 ($C_{carbene}$); 123.85 (CH); 120.10 (CH); 60.57(NCH_2N); 36.50 (NCH); 31.02 (CH_2); 27.47 (CH_2); 26.51 (CH_2); 25.35 (CH_2); 24.73 (CH_2). MS (FAB, m/z (%)): 808 (100) $[M-I]^+$, 681 (76) $[M-2I]^+$. Anal. Found: C, 47.28; H, 6.40; N, 10.54%. Calc. for $C_{38}H_{56}N_8I_2Ni$ + 1 DMSO (1015.54): C, 47.31; H, 6.15; N, 11.03%.

Compound **1d**. M.p. > 300°C; ^{1}H-NMR (400 MHz; d_6-DMSO; 25°C; ppm): δ 8.81 (s, 4H, CH); 6.93, 7.85 (AB, ^2J(H,H) = 16 Hz, 4H, NCH_2N); 3.41 (s, 12H, CH_3). ^{13}C{^{1}H} (100.53 MHz; d_6-DMSO; 25°C; ppm): δ 173.73 ($C_{carbene}$); 125.30 (CH); 66.08 (NCH_2N); 35.04 (CH_3). MS (FAB, m/z (%)): 540 (100) $[M-I]^+$, 414 (56) $[M-2I]^+$. Anal. Found: C, 25.74; H, 3.30; N, 22.29%. Calc. for $C_{14}H_{20}N_{12}I_2Ni$ + 1 DMSO (747.02): C, 25.73; H, 3.51; N, 22.50%.

2.3. Synthesis of {1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene}palladium(II)diacetate ***2***

An acetonitrile solution (15 ml) of [{1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene}palladium(II)dibromide] (300 mg, 0.68 mmol) and Ag(OAc) (227 mg, 1.36 mmol) was heated at 60°C for 8 h. The solution was then filtered from the precipitated AgBr and the acetonitrile removed in vacuo to give the pure product as a white solid (248 mg, 91%). M.p. 95°C; ^{1}H-NMR (400 MHz; d_6-DMSO; 25°C; ppm): δ 7.58 (s, 2H, CH); 7.30 (s, 2H, CH); 6.32 (s, 2H, NCH_2N); 3.76 (s, 6H, NCH_3); 1.77 (s, 6H, CH_3). ^{13}C{^{1}H} (100.53 MHz; d_6-DMSO; 25°C; ppm): δ 175.04 (COO); 154.81 ($C_{carbene}$); 123.37 (CH); 121.56 (CH); 62.23 (NCH_2N); 37.04 (CH_3); 24.45 (CH_3OO). MS (FAB, m/z (%)): 341 (100) $[M-OAc]^+$, 282 (39) $[M-2OAc]^+$. Anal. Found: C, 35.83; H, 4.64; N, 12.45%. Calc. for $C_{13}H_{18}N_4PdO_4$ + 2 H_2O (436.56): C, 35.77; H, 5.04; N, 12.83%.

2.4. Synthesis of bis{1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene}palladium(II) diiodide ***3a*** *{1,1′-dimethyl-3,3′-methylenediiimidazoline-2,2′-diylidene} {1″,1‴-dicyclohexyl-3″,3‴-methylenediimidazoline-2″,2‴-diylidene}palladium(II) diiodide* ***3b*** *and {1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene} {1″,1‴-dimethyl-3″,3‴-methyleneditriazoline-2″,2‴-diylidene}palladium(II) diiodide* ***3c***

2.4.1. Procedure A

A stirred DMSO solution (5 ml) of [{1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene}palladium (II) diiodide] (200 mg, 0.37 mmol), NaOAc (62 mg, 0.75 mmol) and 1,1′-dimethyl-3,3′-methylenediimidazolium diiodide (160 mg, 0.37 mmol), or 1,1′-dicyclohexyl-3,3′-

methylene-diimidazolium diiodide (210 mg, 0.37 mmol), or 1,1′-dimethyl-3,3′-methylene-ditriazolium diiodide (161 mg, 0.37 mmol) was heated at 60°C for 12 h and then at 130°C for a further 2 h. The remaining DMSO was then removed in vacuo at 70°C to give a white solid which was washed with cold MeOH. Recrystallisation from MeOH gave the products as white crystals. Yields: 240 mg (0.34 mmol, 91%), **3a**; 282 mg (0.33 mmol, 90%), **3b**; 243mg (0.34 mmol, 92%), **3c**.

2.4.2. Procedure B

A stirred DMSO solution (4 ml) of [{1,1′-dimethyl - 3,3′ - methylenediimidazoline - 2,2′ - diylidene}palladium(II) diacetate] **2** (180 mg, 0.45 mmol) and 1,1′-dimethyl-3,3′-methylenediimidazolium diiodide (194 mg, 0.45 mmol), or 1,1′-dicyclohexyl-3,3′-methylenediimidazolium diiodide (256 mg, 0.45 mmol), or 1,1′-dimethyl-3,3′-methylene-ditriazolium diiodide (148 mg, 0.45mmol) was heated at 60°C for 12 h and then at 130°C for a further 2 h. The remaining DMSO was removed in vacuo at 70°C to give a white solid. Recrystallisation from MeOH gave the products as white crystals. Yields: 295 mg (0.41 mmol, 92%), **3a**; 359 mg (0.42 mmol, 94%), **3b**; 292 mg (0.41 mmol, 91%), **3c**.

Compound **3a**. M.p. 227°C (decomp.); ^{1}H-NMR (400 MHz; d_6-DMSO; 25°C; ppm): δ 7.76 (d, $^3J(H,H) = 2$ Hz, 4H, CH); 7.43 (d, $^3J(H,H) = 2$ Hz, 4H, CH); 6.51, 6.85 (AB, $^2J(H,H) = 18$ Hz, 4H, NCH_2N); 3.38 (s, 12H, CH_3). $^{13}C\{^1H\}$-NMR (100.53 MHz; d_6-DMSO; 25°C; ppm): δ 170.15 ($C_{carbene}$); 123.51 (CH); 122.73 (CH); 63.15 (NCH_2N); 39.42 (CH_3). MS (FAB, m/z (%)): 585 (100) $[M-I]^+$, 457 (87) $[M-2I]^+$. Anal. Found: C, 30.21; H, 3.49; N, 14.55%. Calc. for $C_{18}H_{24}N_8I_2Pd + 1$ DMSO (790.80): C, 30.38; H, 3.82; N, 14.17%.

Compound **3b**. M.p. 235°C (decomp.); ^{1}H-NMR (400 MHz; d_6-DMSO; 25°C; ppm): δ 7.85 (s, 2H, CH); 7.81 (s, 2H, CH); 7.63 (s, 2H, CH); 7.49 (s, 2H, CH); 6.60, 6.95 (AB, $^2J(H,H) = 18$ Hz, 2H, NCH_2N); 6.35, 6.68 (AB, $^2J(H,H) = 17$ Hz, 2H, NCH_2N); 3.42 (s, 6H, CH_3); 0.78–1.90 (m, 22H, H_{cyc}). $^{13}C\{^1H\}$-NMR (100.53 MHz; d_6-DMSO; 25°C; ppm): δ 170.31 ($C_{carbene}$); 169.53 ($C_{carbene}$); 123.69 (CH); 123.35 (CH); 123.22 (CH); 119.34 (CH); 63.51 (NCH_2N); 60.91 (NCH_2N); 39.35 (CH_3); 36.85 (NCH); 32.44 (CH_2); 31.30 (CH_2); 26.63 (CH_2); 26.61 (CH_2); 25.40 (CH_2). MS (FAB, m/z (%)): 721 (100) $[M-I]^+$, 593 (48) $[M-2I]^+$. Anal. Found: C, 39.23; H, 5.36; N, 11.86%. Calc. for $C_{28}H_{40}N_8I_2Pd + 1$ DMSO (927.04): C, 38.87; H, 5.00; N, 12.09%.

Compound **3c**. M.p. 229°C (decomp.); ^{1}H-NMR (400MHz; d_6-DMSO; 25°C; ppm): δ 8.85 (s, 2H, CH); 7.82 (s, 2H, CH); 7.49 (s, 2H, CH); 6.51–7.10 (m, 4H, NCH_2N); 3.52 (s, 6H, CH_3); 3.44 (s, 6H, CH_3). $^{13}C\{^1H\}$-NMR (100.53 MHz; d_6-DMSO; 25°C; ppm): δ 174.12 ($C_{carbene}$); 173.25 ($C_{carbene}$); 123.66 (CH); 123.01 (CH); 122.71 (CH); 67.68 (NCH_2N); 61.29 (NCH_2N); 39.73 (CH_3); 39.44 (CH_3). MS (FAB, m/z (%)): 587 (55) $[M-I]^+$, 460 (50) $[M-2I]^+$. Anal. Found: C, 26.54; H, 4.12; N, 17.98%. Calc. for $C_{28}H_{40}N_8I_2Pd + 1$ DMSO (792.78): C, 27.27; H, 3.56; N, 17.67%.

*2.5. {1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene} {1″,1‴-dimethyl-3″,3‴-methylenedibenzimidazolin-2″,2‴-diylidene}palladium(II) diiodide **4***

A stirred DMSO solution (4 ml) of [{1,1′-dimethyl-3,3′ - methylenediimidazoline - 2,2′ - diylidene}palladium-(II) diacetate] **2** (180 mg, 0.45 mmol) and 1,1′-dimethyl-3,3′-methylenedibenzimidazolium diiodide (286 mg, 0.45 mmol) was heated at 50°C for 3 h. The remaining DMSO was then removed in vacuo at 70°C to give a white solid. Recrystallisation from MeOH gave the product as colorless rods. Yield: 376 mg (0.41 mmol, 90%). M.p. > 300°C; ^{1}H-NMR (400 MHz; d_6-DMSO; 25°C; ppm): δ 7.50–8.43 (m, 14H, sp^2-H, $N_{BI}CH_2N_{BI}$); 6.62, 6.94 (AB, $^2J(H,H) = 15$ Hz, 2H, NCH_2N); 3.43 (s, 6H, CH_3); 3.39 (s, 6H, CH_3). $^{13}C\{^1H\}$-NMR (100.53 MHz; d_6-DMSO; 25°C; ppm): δ 181.46 ($C_{BI\text{-}carbene}$); δ 168.76 ($C_{carbene}$); 134.33 ($C_{arom.}$); 133.53 ($C_{arom.}$); 125.13 ($C_{arom.}$); 124.77 ($C_{arom.}$); 123.76 ($C_{arom.}$); 123.06 ($C_{arom.}$); 112.82 ($C_{arom.}$); 111.66 ($C_{arom.}$); 67.48 (NCH_2N); 63.32 (NCH_2N); 38.58 (CH_3); 35.65 (CH_3). MS (FAB, m/z (%)): 685 (60) $[M-I]^+$, 558 (72) $[M-2I]^+$. Anal. Found: C, 37.98; H, 3.50; N, 14.16%. Calc. for $C_{26}H_{28}N_8I_2NPd$ (812.79): C, 38.42; H, 3.47; N, 13.79%.

*2.6. X-ray structure determination of compound **1a***

$C_{18}H_{24}N_8NiI_2$, $M = 664.94$, trigonal, space group R-3 (no. 148), $a = 20.4886(6)$, $b = 20.4886(6)$, $c = 17.9945(5)$ Å, $V = 6541.8(3)$ Å^3, $Z = 9$, $D_{calc.} = 1.519$ g cm^{-3}, $F(000) = 2898$. Monochromated Mo–K_α radiation, $\lambda = 0.71073$ Å, $\mu = 28.8$ cm^{-1}.

A crystal of **1a**, $0.17 \times 0.15 \times 0.08$ mm, suitable for X-ray structure determination was grown by vapour diffusion of methanol into a concentrated dimethylsulfoxide solution and mounted in a glass capillary. Data were collected on a Nonius KappaCCD detection system at 193 K ($\theta_{min} - \theta_{max} = 4.34–26.4°$). A total of 19 437 reflections were measured and 2971 unique reflections ($R_{int} = 0.0437$) were used in the full matrix least squares refinement. Preliminary positions of heavy atoms were found by direct methods [10], and the positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with initial isotropic least squares refinement [11]. Anisotropic thermal parameters were refined for all non-hydrogen atoms in the structure determination. The hydrogen atoms were refined with individual isotropic thermal parameters. A highly disordered solvent molecule, possibly DMSO, was dealed with by the 'calc

squeeze' option included in the program PLATON [12]. The final residuals were $R_1 = 0.0225$ and $wR_2 = 0.0565$ for 181 parameters, $s = 1.072$, and a final difference map had extreme values of 0.76 and -0.64 e Å^{-3}. Non-hydrogen atom coordinates and isotropic thermal parameters are presented in Table 1, and selected structural parameters are given in Table 2. Further details of the crystal structure determination can be obtained from the Cambridge Crystallographic Data Centre.

3. Results and discussion

3.1. Preparation and spectroscopic data of complexes *1a–d*, *3*, *3a–c* and *4*

According to Fig. 1, homoleptic nickel(II) carbene complexes with two chelating di(carbene) ligands could be prepared by the reaction of anhydrous $Ni(OAc)_2$ with an equimolar amount of the corresponding diazolium diiodide in excellent yields. The free carbenes are generated in situ by deprotonation by the acetate anions, so that the formation of one homoleptic nickel complex requires four acetates. Therefore, NiI_2 is observed as a byproduct in these reactions.

This is the first report of homoleptic carbene species using the so called salt method, firstly described by Öfele and co-workers [13]. Using the same reaction conditions in the analogous $Pd(OAc)_2$ case, the corresponding neutral di(carbene) *cis*-dihalide complexes (Fig. 1), versatile catalyst precursors for various coupling reactions [1], are formed in almost quantitative yields. The reaction of $Ni(OAc)_2$ with two equivalents of monodentate azolium iodides resulted in the formation of dihalide complexes exhibiting *trans*-configuration [14].

Even in the case where sterically more demanding *N*-substituents are present (**1b**, **1c**), the formation of neutral *cis*-dihalide complexes was never observed. No reaction occurred with *N*-'Bu-substituted diimidazolium analogues. Furthermore carbene intermediates, bearing pendant azolium halide side groups, that have been isolated in reactions with $Pd(OAc)_2$ [5], could never be seen by in situ ^{1}H-NMR experiments. Such species [(azolium halide–carbene)$_2$NiX$_2$], could account for the exclusive formation of the dicationic tetra(carbene) nickel(II) complexes. Even when the stoichiometry of the reaction was diazolium dihalide:Ni(OAc)$_2$ = 2:1, a mixture of **1a–d** and diazolium dihalide was obtained.

Palladium analogues (R = Me, Et; E = CH; X = I$^-$, BF_4^-) of **1a–c** have already been described by Fehlhammer et al. [6]. They were synthesized in very low yields by the free carbene route as prerequisites for the construction of macrocyclic systems with *C*-encapsulated metal atoms.

In course of our studies, we developed two different improved approaches for the preparation of homoleptic tetra(carbene) palladium complexes, which are now accessible in excellent yields (Fig. 2). Furthermore, it is now possible to put two different chelating ligands on the palladium centre. The general utility of these approaches was demonstrated by the synthesis of **3b–c** and **4**.

Table 1
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms of **1a**

Atom	*x*	*y*	*z*	U_{iso} (Å^2)
Ni	1/6	1/3	1/3	0.0265(1)
N(2)	0.14245(9)	0.40897(10)	0.21188(11)	0.0310(5)
N(5)	0.19576(10)	0.48982(10)	0.29841(11)	0.0319(5)
N(8)	0.16702(10)	0.31328(10)	0.17609(10)	0.0321(5)
N(10)	0.24814(10)	0.28840(10)	0.22277(11)	0.0347(5)
C(1)	0.17011(11)	0.41651(12)	0.28198(12)	0.0290(6)
C(3)	0.15048(13)	0.47599(13)	0.18512(14)	0.0370(7)
C(4)	0.18385(13)	0.52627(13)	0.24013(14)	0.0388(7)
C(6)	0.23228(16)	0.52802(15)	0.36726(16)	0.0403(7)
C(7)	0.11251(13)	0.33839(13)	0.17140(12)	0.0337(6)
C(9)	0.19724(11)	0.30944(11)	0.24191(12)	0.0290(6)
C(11)	0.24839(15)	0.27949(14)	0.14634(15)	0.0444(8)
C(12)	0.19834(15)	0.29505(15)	0.11713(14)	0.0426(7)
C(13)	0.29599(15)	0.27569(15)	0.27411(18)	0.0434(8)
I	0.24805(1)	0.05475(1)	0.30169(1)	0.0388(1)

Table 2
Selected bond distances (Å) and angles (°) of **1a**

Bond distances (Å)			
Ni–C(1)	1.909(2)	C(3)–C(4)	1.343(3)
Ni–C(9)	1.909(2)	C(11)–C(12)	1.325(5)
N(2)–C(1)	1.360(3)	N(2)–C(3)	1.385(3)
N(2)–C(7)	1.453(3)	N(5)–C(1)	1.353(3)
N(5)–C(4)	1.378(3)	N(5)–C(6)	1.457(3)
N(8)–C(7)	1.447(4)	N(8)–C(9)	1.357(3)
N(8)–C(12)	1.384(4)	N(10)–C(9)	1.357(3)
N(10)–C(11)	1.388(3)		
Bond angles (°)			
C(1)–Ni–C(9)	86.64(9)	N(10)–C(11)–C(12)	107.9(3)
C(1)–Ni–C(1)a	180.00	N(8)–C(12)–C(11)	106.2(2)
C(1)–Ni–C(9)a	93.36(9)	C(9)–Ni–C(9)a	180.00
C(1)–N(2)–C(3)	111.95(19)	C(1)–N(2)–C(7)	121.52(19)
C(3)–N(2)–C(7)	126.5(2)	C(1)–N(5)–C(4)	111.08(19)
C(1)–N(5)–C(6)	126.3(2)	C(4)–N(5)–C(6)	122.6(2)
C(7)–N(8)–C(9)	121.82(19)	C(7)–N(8)–C(12)	126.5(2)
C(9)–N(8)–C(12)	111.5(2)	C(9)–N(10)–C(11)	110.3(2)
C(9)–N(10)–C(13)	125.9(2)	C(11)–N(10)–C(13)	123.8(2)
Ni–C(1)–N(2)	121.37(15)	Ni–C(1)–N(5)	134.90(17)
N(2)–C(1)–N(5)	103.73(19)	N(2)–C(3)–C(4)	105.5(2)
N(5)–C(4)–C(3)	107.8(2)	N(2)–C(7)–N(8)	107.9(2)
Ni–C(9)–N(8)	121.30(18)	Ni–C(9)–N(10)	134.66(17)
N(8)–C(9)–N(10)	104.02(19)		

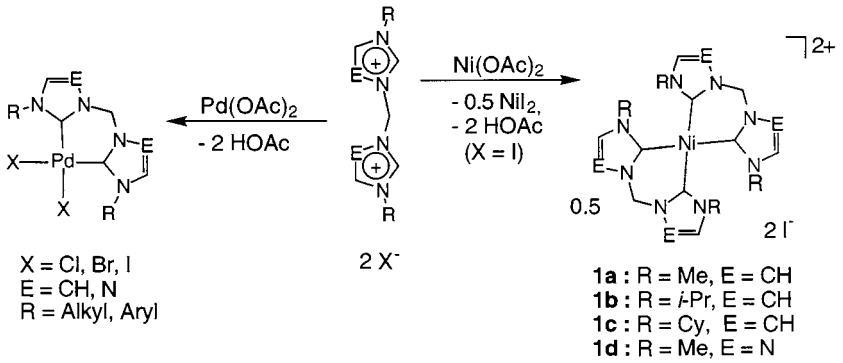

Fig. 1. Preparation of homoleptic nickel(II) carbene complexes with two chelating di(carbene) ligands can be prepared by the reaction of anhydrous $Ni(OAc)_2$ with diazolium diiodide.

The reaction of [*cis*-$CH_2\{\overline{N(H)C{=}C(H)N(Me)C}\}_2$-$PdI_2$] with one diazolium dihalide salt precursor and two equivalents of sodium acetate in DMSO gave the dicationic complexes **3a**–**c** in over 90% yield (Fig. 2, path a).

The reaction of [*cis*-$CH_2\{\overline{N(H)C{=}C(H)N(Me)C}\}_2$-$PdBr_2$] with two equivalents of Ag(OAc) in acetonitrile resulted in the formation of the neutral diacetate complex **2** in quantitative yield. This is in contrast to our previous studies with weakly coordinating anions (BF_4^-, PF_6^-), in which solvent stabilized dicationic complexes could be obtained.

Starting from **2**, the complexes **3a**–**c** and **4** could be prepared by the salt method using the corresponding diazolium salts in excellent yields. In any case the presence of the basic and weakly coordinating acetate anion is necessary for the formation of the dicationic tetra(carbene) complexes.

All described homoleptic and heteroleptic complexes have excellent solubility in DMSO, good solubility in hot MeOH, are sparingly soluble in DCM and THF and have no solubility in diethyl ether and hydrocarbon solvents. The complexes are indefinitely stable in air and water and display high thermal stability, decomposing only at temperatures in excess of 225°C in the solid and are stable in refluxing DMSO for varying periods. Furthermore, the use of technical grade solvents did not result in a decrease in yield in any case.

The ^{1}H-NMR spectra of **1a**–**c** and **3a** show two singlets in the range of $\delta = 7$–8 for the imidazoline-2-ylidene ring protons and two doublets at about $\delta = 6$–7 for the methylene protons. The resonances of **1d** of both the imidazoline-2-ylidene ring proton and the methylene bridge are shifted to lower fields ($\delta = 8.81$ and 7–8, respectively). As expected, complexes with two different chelating ligands (**3b**–**c**, **4**) show four doublets at $\delta = 6$–8 in the ^{1}H-NMR for the methylene protons and two signals in the ^{13}C-NMR for the two inequivalent carbene carbons. Six signals in the ^{13}C-NMR for the cyclohexyl carbons in **1c** and **3b** suggest a hindered rotation around the N–CH bond.

The appearance of inequivalent methylene proton resonances for the complexes **1a**–**d**, **3a**–**c** and **4** even at 150°C indicate the retention of conformationally restrained boat shaped six-membered chelate rings for the complexes as was determined in the X-ray crystal structure of the methyl-substituted nickel complex **1a**. Related *cis*-di(carbene)PdX_2 complexes show fluxional exchange of these protons at varying temperatures in

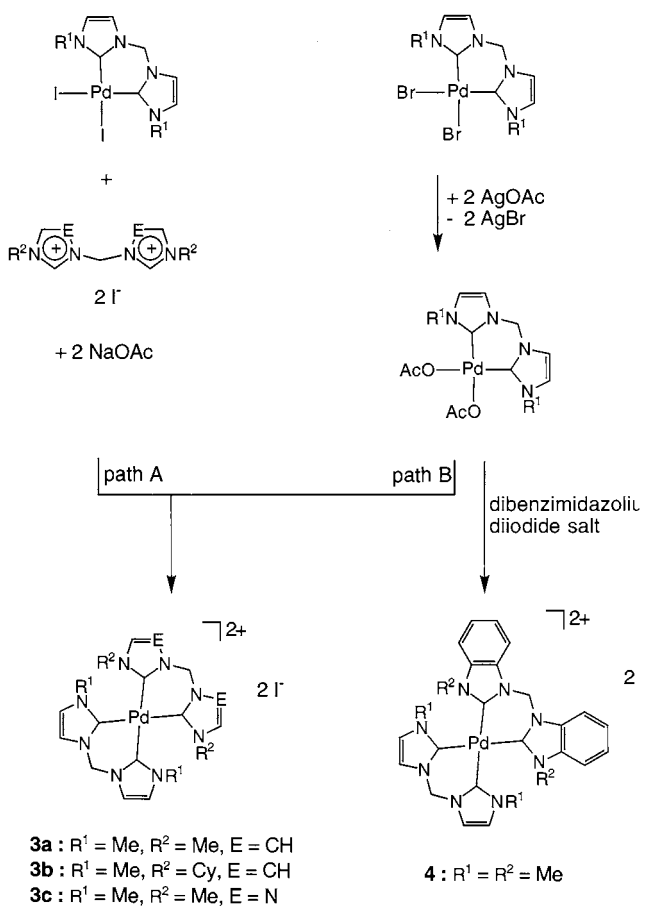

Fig. 2. Approaches for the preparation of homoleptic tetra(carbene) palladium complexes.

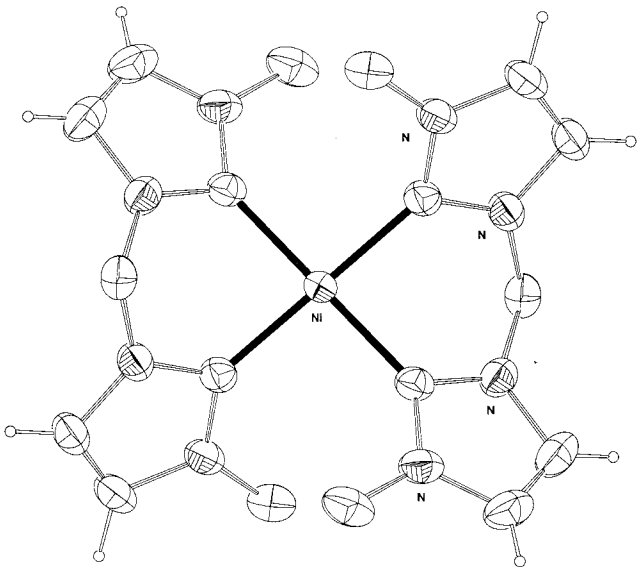

Fig. 3. Molecular structure of the dication of bis{1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene}nickel(II) diiodide **1a**, showing the atom labelling scheme [9]. Thermal ellipsoids are drawn at the 50% probability level. For clarity the hydrogens are omitted.

DMSO [15]. The observation of the conformationally locked tetra(carbene) species here is consistent with the expected steric hindrance between the chelating di(carbene) ligands in the transition structures.

The NCH_2N-protons in **2** display a singlet at room temperature, i.e. the structure is fluxional with respect to an equilibration of the geminal protons by quickly passing through a planar arrangement as was observed in the case of [*cis*-{tetracarbonyl(1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidene}chromium [16].

3.2. X-ray crystal structure of *1a*

Crystals of complex **1a** suitable for X-ray crystal analysis were grown by vapour diffusion of MeOH into a saturated DMSO solution of **1a**. The crystal structure determination has shown the compound to be monomeric with two di(carbene) ligands chelating the Ni(II) centre. The asymmetric unit contains one half of the centrosymmetric dication, one iodide and a highly disordered solvent molecule. The two I^- anions are noncoordinating. Selected bond distances and angles are given in Table 2 and Fig. 3.

The Ni–C bond distances (1.909(2) ppm) are within the expected range and compare to those in *trans*-dichlorobis(1,3-dicyclohexylimidazoline-2-ylidene) nickel(II) (191.1(2) ppm) [11]. The formation of the six-membered chelate ring of the dicarbene distorts the coordination geometry of the nickel only slightly, with the C–Ni–C bite angle being reduced to 86.64(9)°. A further effect of the chelating structure is evident in the angles of the imidazolin-2-ylidene based ring systems to the coordination plane of the nickel centre, 39.64(9) and 40.85(8)°, which are much smaller compared to those in nickel(II)-complexes with monodentate imidazoline-2-ylidene ligands (75.64(65) and 77.98(13)°) and are similar compared to related palladium analogues (42 and 43°) [6]. The C–C and C–N bond distances within the imidazline-2-ylidene based ring systems and the Ni–C bond distances are consistent with both contributions from σ- and π-donation to the metal centre and π-stabilisation of the carbene onto the adjacent nitrogens.

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