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Nickel(II) Complexes of N-Heterocyclic Carbenes†

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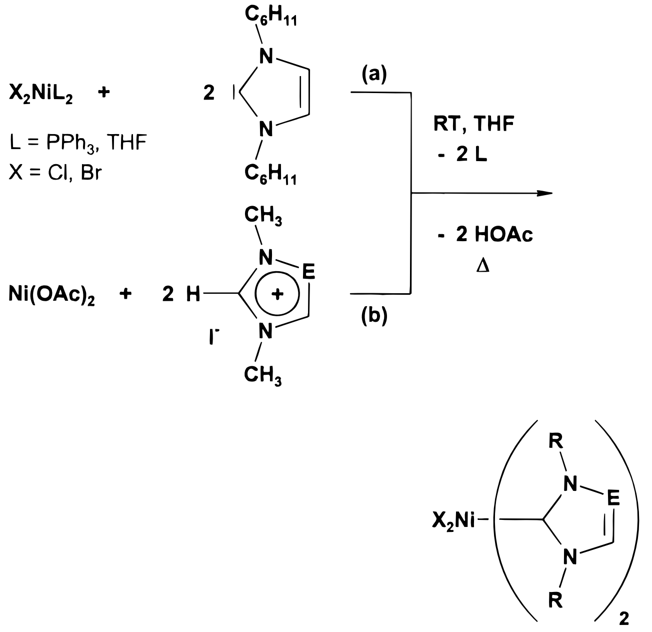
Summary: Nickel(II) complexes with N-heterocyclic carbenes are accessible through substitution of triphenylphosphine in $NiX_2(PPh_3)_2$ (X = Cl, Br) by the free carbenes or by in situ deprotonation of the corresponding azolium salts with $Ni(OAc)_2$ as the starting material. ^{1}H and ^{13}C NMR as well as X-ray crystallographic data are discussed.

Introduction

Over the last 5 years since the isolation of the first free imidazol-2-ylidenes,[1,2] these compounds have attained enormous attention not only as surprisingly stable, isolable reactants[3,4] but also as metal-attached ligands representing a new structure principle for homogeneous catalysts.[5] A large number of transition-metal complexes with this special type of N-heterocyclic carbene ligand have recently been synthesized,[2a,6] including nickel(0) derivatives, whereas nickel(II) complexes have not been reported.[7,8]

Our interest has been focused on stable nickel(II) carbene complexes as potential catalysts in CC-coupling reactions featuring a transmetalation step such as Grignard cross-coupling or Suzuki coupling.[9,10] These transformations have been extensively applied in organic syntheses.[11] The new carbene complexes were expected to perform better than traditional phosphine−nickel(II) or phosphine−palladium(II) catalyst systems in terms of solubility, long-term stability,[12] and activity.



1a : X = Cl, R = C_6H_{11}, E = CH
1b : X = Br, R = C_6H_{11}, E = CH
1c : X = I, R = CH_3, E = CH
2 : X = I, R = CH_3, E = N

Figure 1. Preparation of nickel(II) carbene complexes from nickel(II) precursors by reaction with free carbenes (a) or by *in situ* deprotonation of azolium salts (b).

Results and Discussion

Preparation and Spectroscopic Data of Complexes 1a−c and 2. According to Figure 1, nickel(II) carbene complexes could be prepared by two different synthetic approaches. In a THF suspension the free 1,3-disubstituted imidazol-2-ylidenes[4a,6b] easily replace other,

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(12) Earlier studies have shown practically no ligand dissociation in metal carbene complexes, and they have proved their extraordinary stability, for example, as catalysts in the Heck coupling.[5a]

(13) The imidazolium salt and the free carbene were prepared according to ref 4a; their ^{1}H NMR spectra were measured in $CDCl_3$ (360 MHz, 25 °C) and C_6D_6 (400 MHz, 25 °C), respectively.

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Table 1. ^{1}H NMR Chemical Shifts in Nickel(II) Carbene Complexes 1a and 1b, in the Free Carbene, and in the Corresponding Azolium Salt

compound	δ(NC−H) (ppm)	δ(CH=CH) (ppm)
1,3-dicyclohexylimidazolium iodide[a]	4.50	7.36
1,3-dicyclohexylimidazol-2-ylidene[a]	4.15	6.68
1a	6.88	6.42
1b	6.75	6.42

[a] See ref 13.

weaker donor ligands such as triphenylphosphine and THF at ambient temperature (Figure 1a), thus forming the bis(carbene)nickel(II) complexes **1a**,**b** in good yields (76% and 87%, respectively). This clean, quantitative substitution of phosphine ligands is unprecedented and clearly reflects the extraordinarily strong σ-donor properties of the nucleophilic imidazol-2-ylidenes. Earlier spectroscopic studies had already shown that imidazole carbenes are even more basic than electron-rich phosphines such as PMe_3 ond P(cyclohexyl)$_3$ and therefore induce higher electron density at the metal center.[6c]

By deprotonation through nickel(II) acetate, the free carbenes are generated *in situ* from the corresponding azolium iodides (Figure 1b) and the bis(carbene) nickel(II) complexes **1c** and **2** are obtained in modest (30%, **1c**) to good yields (77%, **2**) in *one* step. The deprotonation of the imidazolium salt requires conditions more drastic (150 °C, vacuum, no solvent) than for the triazolium salt (60 °C, THF solution, ultrasound).

All bis(imidazol-2-ylidene)nickel(II) complexes **1a**−**c** and **2** were isolated as violet-red solids of which **1a**−**c** are stable to air and soluble in polar organic solvents such as chloroform or DMSO, scarcely soluble in THF and benzene/toluene, and insoluble in diethyl ether. **2**, however, dissolves well in THF and can be heated in substance above 240 °C without decomposition.

Compounds **1a**−**c** and **2** exhibit characteristic ^{13}C NMR carbon shifts of $\delta \sim 170$ ppm (**1a**,**b** in C_6D_6, **1c** in $CDCl_3$) and δ 187.1 ppm (**2** in C_6D_6) for the carbene carbon. This resembles a clear upfield shift compared to reported nickel(0) complexes of $\Delta\delta \sim 20$ ppm in the case of Arduengo's NiL_2 (L = 1,3-dimesitylimidazol-2-ylidene)[8] and of $\Delta\delta \sim 5$ ppm for nickel(0) complexes $Ni(CO)_3L$ and $Ni(CO)_2L_2$ (L = N-heterocyclic carbene). The latter are prepared from $Ni(CO)_4$ by substitution of one or two carbonyl ligands with the free carbene.[7]

A remarkable ^{1}H NMR downfield shift for the α-CH proton at the cyclohexyl ring in **1a**,**b** compared to that of the free carbene (cf. Table 1) indicates a strong electron donation toward the carbene−metal bond exerted by the nitrogen atoms, thus deshielding the adjacent proton, Table 1. This effect may also be explained by the anisotropy of the imidazole ring on coordination to the metal.

In first catalytic experiments, compounds **1a**,**b** proved their suitability as catalyst precursors for the Suzuki coupling of phenylboronic acid with *p*-chloroacetophenone.[14]

Table 2. Experimental Crystallographic Data for 1a

formula	$C_{30}H_{48}Cl_2N_4Ni$
mol wt	594.33
cryst dimens (mm)	0.43 × 0.13 × 0.13
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
temp (K)	193
a (pm)	1096.7(2)
b (pm)	1115.2(2)
c (pm)	1300.6(2)
α (deg)	84.29(1)
β (deg)	88.87(1)
γ (deg)	76.23(1)
V (10^6 pm^3)	1537.3(5)
Z	2
ρ (g cm^{-3})	1.284
μ (cm^{-1})	26.9
F_{000}	636
λ(Cu K$\bar{\alpha}$ radiation) (pm)	154.184
scan type	$\omega/2\theta$ scan
no. of rflns collected	5222
sector of measurement (deg)	$1.0° < \theta < 68.0°$
no. of indep rflns	5006
no. of obsd rflns, $I > 2\sigma(I)$	4391
no. of params	383
final R1[a]	0.0377
final wR2[b]	0.0994
residual electron density (e/Å^{-3})	−0.59/0.24

[a] $R1 = \Sigma(||F_o| - F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(||F_o{}^2| - |F_c{}^2||)^2/\Sigma w|F_o{}^2|^2]^{1/2}$.

X-ray Crystal Structure of 1a. Crystals of **1a** were obtained by slow evaporation from a concentrated benzene solution. Crystallographic data are given in Table 2. There are two independent molecules in the asymmetric unit. Except for a disordered cyclohexyl ring, both independent molecules show essentially the same structural parameters. Each molecule is located on a center of inversion, and therefore, half of the molecule depicted in Figure 2 is symmetry-generated. The carbene ligands are situated *trans* to each other, and the imidazole rings are twisted against the square-planar coordination sphere by 75.64(65) and 77.98(13)°, respectively, which is a common structural feature of imidazol-2-ylidene metal complexes.[5b,6b,7a,16] Slightly shorter Ni−Cl distances ($\Delta d \approx 2$ pm) compared to the educt phosphine complex $NiCl_2(PPh_3)_2$[17] confirm the poor π-acceptor and the marked σ-donor qualities of the N-heterocyclic carbene ligands. Also, the Ni1−C1 bond length of $d = 191.1(2)$ pm fits well in this picture: nickel(0) carbene carbonyl complexes exhibit longer Ni−C bonds[7a,d] and nickel(II) complexes with imidazolidine-2-ylidenes[18] or with Fischer-type and related carbenes[19] contain shorter Ni−C bonds than **1a**.

1b could be crystallized from benzene as well and shows identical structural characteristics.[20] In com-

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(20) Crystal data for compounds **1b** and **2** are included in the Supporting Information.

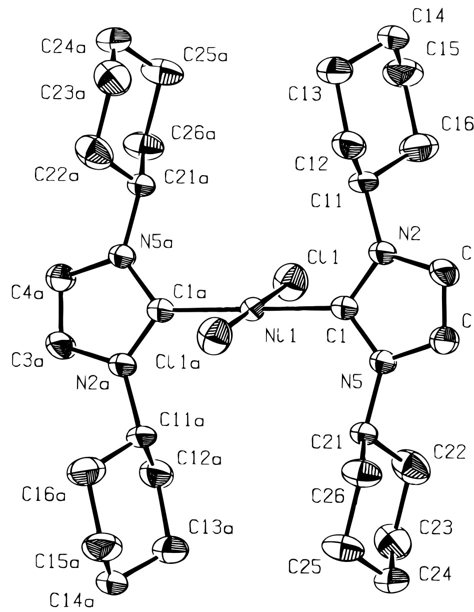

Figure 2. PLATON[15] plot of **1a** with thermal ellipsoids (50% probability). For greater clarity, only one of the two independent molecules is presented, and all hydrogen atoms are omitted. Selected bond lengths (pm) and angles (deg): Ni1−Cl1, 218.18(8); Ni1−C1, 191.1(2); C1−N2, 135.4(3); N2−C3, 139.0(3); C3−C4, 133.3(5); C4−N5, 138.7(4); N5−C1, 135.7(3); Cl1−Ni1−C1, 90.75(7); Cl1−Ni1−C1a, 89.25(7); Ni1−C1−N2, 127.81(17); Ni1−C1−N5, 127.56(18); N2−C1−N5, 104.5(2).

pound **2**, however, no distinction between the isoelectronic fragments N2 and CH could be achieved by means of single-crystal structure analysis.[20]

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry argon using Schlenk techniques. The solvents were dried by standard methods. $NiCl_2(PPh_3)_2$ was purchased from Merck and used without further purification. Free 1,3-dicyclohexylimidazol-2-ylidene[4a,6b] was prepared according to the literature procedure, as was $NiBr_2(PPh_3)_2$.[21]

Dichlorobis(1,3-dicyclohexylimidazol-2-ylidene)nickel(II) (1a) and Dibromobis(1,3-dicyclohexylimidazol-2-ylidene)nickel(II) (1b). A 465 mg (2.00 mmol) amount of 1,3-dicyclohexylimidazol-2-ylidene dissolved in 3 mL of THF is slowly added to a suspension of 654 mg (1.00 mmol) of $NiCl_2(PPh_3)_2$ or 743 mg (1.00 mmol) of $NiBr_2(PPh_3)_2$, respectively, in 10 mL of THF. As an alternative to $NiBr_2(PPh_3)_2$, 362 mg (1.00 mmol) of $NiBr_2{\cdot}2THF$ can be used to obtain a product of greater purity. After 10 min of stirring at room temperature, the violet-red solid is filtered, washed twice with 3 mL of diethyl ether, and dried *in vacuo*. Yields: 452 mg (0.76 mmol, 76%), **1a**; 594 mg (0.87 mmol, 87%), **1b**.

Compound 1a. ^{1}H-NMR (400 MHz, C_6D_6, 25 °C; ppm): δ 6.88 (tt, $^3J(H_{ax},H_{ax}) = 12.0$ Hz, $^3J(H_{ax},H_{eq}) = 4.0$ Hz, 4 H, NCH), 6.42 (s, 4 H, CH=CH), 2.68 (d, $^3J(H_{ax},H_{eq}) = 12.0$ Hz, 8 H, $NCHCH_{ax}$), 1.81−1.13 (m, 32 H, remaining cyclohexyl −CH and $-CH_2$). $^{13}C\{^1H\}$NMR (100.5 MHz, C_6D_6, 25 °C; ppm): δ 169.3 ($C_{carbene}$), 116.7 (CH=CH), 59.7 (NCH), 34.2 (2 CH_2), 26.5 (2 CH_2), 25.9 (CH_2). IR (KBr; cm^{-1}): $\tilde{\nu} = 3166$ w, 3127 w, 3095 w, 2932 vs, 2853 vs, 2659 w, 1644 m, 1550 s, 1502 m, 1446 vs, 1427 vs, 1411 s, 1384 s, 1348 m, 1292 m, 1280 m, 1266 s, 1238 s, 1199 vs, 1160 m, 1142 m, 1112 w, 1094 w, 1054 w, 1030 w, 998 m, 996 m, 895 s, 820 s, 756 s, 728 m, 697 vs, 654 m, 564 m, 542 w, 509 w, 454 w, 413 w. MS (CI; *m/z* (%)): 594 (9) [M$^+$], 559 (15) [M$^+$ - Cl], 277 (22), 267 (100), 262 (63), 233 (15) [(carbene ligand)$^+$ + H]. Anal. Calcd for $C_{30}H_{48}N_4Cl_2Ni$ (594.34): C, 60.63; H, 8.14; N, 9.43. Found: C, 58.41; H, 8.02; N, 8.40.

Compound 1b. ^{1}H NMR (400 MHz, C_6D_6, 25 °C; ppm): δ 6.75 (tt, $^3J(H_{ax},H_{ax}) = 12.0$ Hz, $^3J(H_{ax},H_{eq}) = 4.0$ Hz, 4 H, NCH), 6.42 (s, 4 H, CH=CH), 2.70 (d, $^3J(H_{ax},H_{eq}) = 12.0$ Hz, 8 H, $NCHCH_{ax}H_{eq}$), 1.86−1.13 (m, 32 H, remaining cyclohexyl −CH and $-CH_2$). $^{13}C\{^1H\}$NMR (100.5 MHz, C_6D_6, 25 °C; ppm): δ 170.6 ($C_{carbene}$), 117.2 (CH=CH), 59.9 (NCH), 33.8 (2 CH_2), 26.4 (2 CH_2), 25.8 (CH_2). IR (Nujol; cm^{-1}): $\tilde{\nu} = 3161$ w, 3131 w, 3092 w, 2923 vs, 2853 vs, 2661 w, 2361 w, 2000 w, 1640 w, 1548 w, 1445 vs , 1427 vs, 1408 m, 1383 m, 1348 w, 1292 w, 1280 w, 1265 w, 1237 s, 1197 s, 1160 w, 1141 w, 1109 w, 1094 w, 1073 w, 1053 w, 1030 w, 998 m, 935 m, 894 s, 820 m, 756 m, 725 w, 695 vs, 563 w, 541 w, 509 w, 476 w, 462 w, 454 w, 430 w. MS (CI; *m/z* (%)): 684 (28) [MH$^+$], 682 (38) [M$^+$ − 2H], 603 (33) [M$^+$ − Cl], 313 (97), 311 (100), 233 (75) [(carbene ligand)$^+$ + H]. Anal. Calcd for $C_{30}H_{48}N_4Br_2Ni$ (683.24): C, 52.74; H, 7.08; N, 8.20. Found: C, 51.64; H, 6.72; N, 7.78.

Diiodobis(1,3-dimethylimidazol-2-ylidene)nickel(II) (1c). A 354 mg (2.00 mmol) amount of anhydrous nickel(II) acetate and 896 mg (4.00 mmol) of 1,3-dimethylimidazolium iodide are suspended in 20 mL of nitromethane, and the mixture is thoroughly stirred. This mixture is heated at 150 °C *in vacuo* for 1 h. After the temperature is lowered, the red product is extracted several times with warm THF, washed twice with 3 mL of diethyl ether, and dried *in vacuo*. Yield: 464 mg (0.61 mmol, 30%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C; ppm): δ 6.73 (s, 4 H, CH=CH), 4.22 (s, 12 H, CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 25 °C; ppm): δ 173.9 ($C_{carbene}$), 122.9 (CH=CH), 37.7 (CH_3). IR (KBr; cm^{-1}): $\tilde{\nu} = 3147$ s, 3116 vs, 2955 s, 2924 m, 2855 m, 2455 w, 2362 w, 2009 w, 1624 s, 1575 s, 1462 s, 1400 s, 1222 vs, 1173 vs, 1076 m, 1016 w, 844 m, 747 vs, 697 vs, 619 vs, 470 w. MS (CI; *m/z* (%)): 506 (24) [MH$^+$], 504 (60) [M$^+$ − 2H], 379 (25) [M$^+$ − I], 377 (68) [M$^+$ − I − 2H], 250 (100). Anal. Calcd for $C_{10}H_{16}N_4I_2Ni$ (504.76): C, 23.80; H, 3.19; N, 11.10. Found: C, 23.90; H, 3.36; N, 10.94.

Diiodobis(1,4-dimethyl-1,2,4-triazol-2-ylidene)nickel(II) (2). A 177 mg (1.00 mmol) amount of anhydrous nickel(II) acetate is suspended in 30 mL of THF and heated at 60 °C with 473 mg (2.00 mmol) of 1,4-dimethyl-1,2,4-triazolium iodide for 3 h in an ultrasound bath. Then the solvent is evaporated and the red product is washed twice with 3 mL of diethyl ether and dried *in vacuo*. Yield: 390 mg (0.77 mmol, 77%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C; ppm): δ 6.41 (br s, 2 H, CH), 3.96 and 3.95 (two s, each 3 H, CH_3), 3.32 and 3.31 (two s, each 3 H, CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6, 25 °C; ppm): δ 187.1 ($C_{carbene}$), 143.1 (CH), 34.3 (CH_3). IR (KBr; cm^{-1}): $\tilde{\nu}$ 3117 s, 2938 s, 2355 m, 2334 m, 1700 w, 1652 w, 1589 w, 1540 s, 1472 s, 1437 m, 1417 w, 1370 m, 1349 vs, 1261 m, 1211 vs, 1200 m, 1113 s, 1098 m, 1049 s, 1019 m, 963 s, 855 m, 801 m, 770 vs, 700 vs, 643 vs, 473 w, 453 w, 400 w. MS (CI; *m/z* (%)): 506 (46) [MH$^+$], 379 (36) [M$^+$ − I], 252 (100) [M$^+$ − 2I]. Anal. Calcd for $C_8H_{14}N_6I_2Ni$ (506.74): C, 18.96; H, 2.79; N, 16.59; I, 50.09. Found: C, 18.97; H, 2.89; N, 16.38; I, 49.00.

X-ray Crystallography: Crystal Data for 1a. The data were collected on an Enraf-Nonius CAD4 diffractometer at 193 K using graphite-monochromated Cu Kα radiation ($\lambda = 1.541\ 84$ Å).[22] The structure was solved by direct methods[23] and refinedby full-matrix least-squares fitting based on F^2. All

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non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated in ideal positions.[24] Crystal data and details of the refinement can be found in Table 2.

Acknowledgment. We are indebted to Christian Köcher and Lukas Goossen for practical help and advice.

Supporting Information Available: Tables of atomic coordinates, atomic displacement parameters, and bond distances and angles and figures giving additional views for compounds **1a,b** and **2** (24 pages). Ordering information is given on any current masthead page.

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