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Synthesis, coordination and reactivity of 2-(trimethylsiloxymethyl)phenyl- and 2-(hydroxymethyl)phenyl isocyanides

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Abstract

2-(Trimethylsiloxymethyl)phenyl isocyanide, 2-(CH_2OSiMe_3)$C_6H_4N{\equiv}C$ (**2**) was prepared by reaction of 2-(trimethylsiloxymethyl)phenyl formamide, 2-(CH_2OSiMe_3)C_6H_4NHCHO (**1**) with trichloromethyl chloroformate. Reaction of **2** with F^- ions in MeOH leads to the formation of 2-(hydroxymethyl)phenyl isocyanide, 2-(CH_2OH)$C_6H_4N{\equiv}C$ (**3**), which is stable as free ligand and does not spontaneously undergo intramolecular cyclization to 4H-benzo[1,3]oxazine. The isocyanide **2** coordinates to Pt(II) and Pd(II) metal ions such as in the complexes *cis*-[$MCl_2(CNC_6H_4$–2-$CH_2OSiMe_3)_2$] and *cis*-[$PdCl_2(CNC_6H_4$-2-$CH_2OSiMe_3)(PPh_3)$], which are converted to the corresponding benzoxazin-2-ylidene derivatives [$MCl_2(CN(H)C_6H_4$–2-$CH_2O)_2$] and [$PdCl_2(CN(H)C_6H_4$–2-$CH_2O)(PPh_3)$], respectively, in the presence of a catalytic amount of F^- ions in MeOH. On the other hand, coordination of **2** to the {$M(CO)_5$} (M = W, Cr) fragments and subsequent reactions with of F^- ions in MeOH affords the corresponding 2-(hydroxymethyl)phenyl isocyanide complexes [$M(CO)_5(CNC_6H_4$–2-$CH_2OH)$], where the hydroxy function does not react with the coordinated isocyanide group.

Keywords: Functionalized isocyanide; Transition metal complexes; N-Heterocyclic carbene complexes

1. Introduction

The chemistry of several functionalized isocyanides has been recently reviewed [1,2]. In particular, it has been reported that the reactivity of these ligands towards transition metal complexes depends on several factors such as the nature of the function, the type of metal center and its oxidation state. An important class of these ligands is represented by hydroxy-functionalized compounds, which are reported in Chart A.

The hydroxyalkyl isocyanides of the type **I** reported by Fehlhammer et al. [3] are stable as free ligands and do not spontaneously undergo intramolecular cyclization to the corresponding oxazolidine ($n = 2$) or oxazine ($n = 3$). However, when coordinated to metal ions in higher oxidation states such as Pd^{2+} or Pt^{2+}, they spontaneously cyclize to *N*,*O*-heterocyclic carbenes [4–8]. On the other hand, the hydroxyaryl isocyanides of the type $\mathbf{II_a}$ [2,9,10] and $\mathbf{III_a}$ [2,11] reported by Hahn and coworkers could not be isolated cyclizing rapidly to benzoxazole and 4-hydroxybenzoxazole, respectively. They could be obtained as the silylated derivatives $\mathbf{II_b}$ and $\mathbf{III_b}$ by C–H deprotonation of the corresponding heterocyclic derivatives followed by reaction with trimethylchlorosilane [2]. It was also shown that coordination of $\mathbf{II_b}$ and $\mathbf{III_b}$ to suitable electron-poor metal centers followed by treatment with MeOH in the presence of F^- ions leads to the synthesis of benzoxazol-2-ylidene [2,12–14] and 4-hydroxybenzoxazol-2-ylidene [2,14] complexes, respectively.

Our interest in the chemistry of functionalized isocyanides of the type **IV** [15,16] (Chart B), prompted us to investigate the synthesis and coordination chemistry

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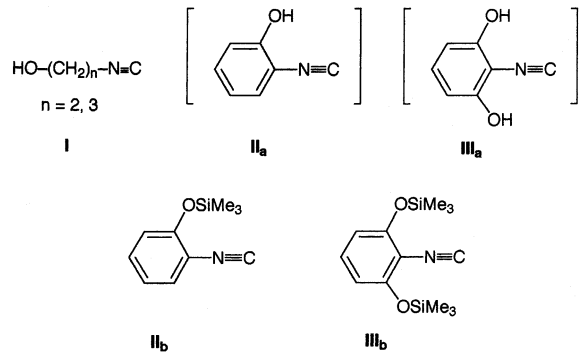


Chart A.

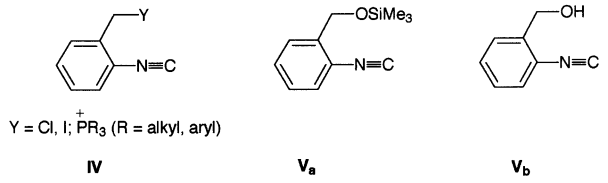


Chart B.

of another class of *O*-functionalized isocyanides such as 2-(trimethylsiloxymethyl)phenyl- (**V$_a$**) and 2-(hydroxymethyl)phenyl (**V$_b$**) isocyanides.

Interest in these ligands stems from the fact that the isocyanides of the type **V** have the isocyano function linked to an aryl group while the hydroxy group is bonded to an alkyl chain; thus, in principle, they might show an intermediate behavior between the previously described hydroxylakyl and hydroxyaryl isocyanides, which possess the two functions both ligated to an alkyl or an aryl moiety, respectively.

2. Experimental

2.1. General procedures and materials

All work was carried out under nitrogen atmosphere using standard Schlenck techniques. Solvents were distilled under dinitrogen prior to use; CH_2Cl_2 was distilled from CaH_2, Et_2O and THF were distilled from sodium benzophenone. IR spectra were taken on a Perkin–Elmer 983 (Nujol mulls, 4000–200 cm^{-1}), FT-IR AVATAR 320 (4000–400 cm^{-1}) or FT-IR Nexus (range 600–50 cm^{-1}) of the Nicolet Instrument Corporation (KBr or polyethylene (PE)) spectrophotometers; the wavenumbers ($\tilde{\nu}$) are given in cm^{-1}. ^{1}H-, ^{31}P{^{1}H}- and ^{13}C{^{1}H}-NMR spectra were run at 298 K, unless otherwise stated, on a Bruker 200 AC spectrometer operating at 200.13, 81.015 and 50.32 MHz, respectively. Peak positions are relative to Me_4Si and were calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). The elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of the University of Padova. The compounds 2-aminobenzyl alcohol, 2-$NH_2C_6H_4CH_2OH$, trimethylchlorosilane, $SiMe_3Cl$, trichloromethyl chloroformate, $ClCOCCl_3$, and tetra(*n*-butyl)ammonium fluoride (TBAF) were purchased from Aldrich and used as received, while 2-(hydroxymethyl)phenyl formamide, 2-$(CH_2OH)C_6H_4NHCHO$, was synthesized from 2-aminobenzyl alcohol using acetic formic anhydride (AFA) [17] according to a reported procedure [16]. The complexes $[PdCl_2(MeCN)_2]$ [16], $[PdCl(\mu\text{-}Cl)(PPh_3)]_2$ [16], $[PtCl_2(COD)]$ (COD = 1,5-cyclooctadiene) [18] and $[M(CO)_5I][NEt_4]$ (M = Cr, W) [19] were prepared as described in the literature.

2.2. Synthesis of the ligands

2.2.1. Synthesis of 2-(trimethysiloxymethyl)phenyl formamide (**1**)

A three-neck round-bottom flask of 500 ml, equipped with mechanical stirrer, dropping funnel and inlet–outlet for N_2, was charged with 2-(hydroxymethyl)phenyl formamide (19.94 g, 0.132 mol), THF (300 ml) and NEt_3 (22 ml, 15.96 g, 0.158 mol). A solution of $SiMe_3Cl$ (17 ml, $d = 0.857$ g ml^{-1}, 14.57 g, 0.134 mol) in THF (50 ml) was added dropwise under vigorous stirring at room temperature (r.t.) over a period of 2 h. After the addition was complete, the reaction mixture was stirred for an additional 30 min and then the solid $NHEt_3Cl$ formed was filtered off. The solution was taken to dryness to give a red oil. Yield: 20.7 g, 70.3%. IR ($\tilde{\nu}$, Nujol mull): 3300 (m, NH), 1696 (br, C=O). ^{1}H-NMR (δ, $CDCl_3$): 8.8–8.6 (N*H*, br); 8.5–8.1 (C*H*O, br); 4.72, 4.68 (CH_2, s); 0.16 (Si–CH_3, s). ^{13}C{^{1}H}-NMR (δ, $CDCl_3$): 162.8, 159.6 (*C*HO, s); 65.2, 64.5 (*C*H_2, s); 0.18 (Si–*C*H_3, s).

2.2.2. Synthesis of 2-(trimethysiloxymethyl)phenyl isocyanide (**2**)

A three-neck round-bottom flask of 500 ml, equipped with mechanical stirrer, dropping funnel and inlet–outlet for N_2, was charged with 2-(trimethylsiloxymethyl)phenyl formamide (**1**) (20.71 g, 0.093 mol), CH_2Cl_2 (100 ml), NEt_3 (26 ml, 0.187 mol) and the resultant mixture cooled to 0 °C with an ice-water bath. A solution of trichloromethyl chloroformate, $ClCOCCl_3$ (6.0 ml, $d = 1.64$ g ml^{-1}, 0.0497 mol) in CH_2Cl_2 (80 ml) was added dropwise under vigorous stirring over a period of ca. 2 h. After the addition was complete, the reaction mixture was stirred for an additional 30 min at r.t. and then Et_2O (100 ml) was added. The white precipitate of $NHEt_3Cl$ formed was filtered off and the solution was taken to dryness to give a thick red–brown oil. The latter was distilled at ca. 90 °C under reduced pressure (ca. 5×10^{-2} mmHg) to afford a pale yellow oil which was collected at −30 °C. Yield: 7.3 g, 38.2%. GC–MS: *m*/*z* 204 [M^+]. IR ($\tilde{\nu}$, CH_2Cl_2): 2122 (s, N≡C);

k(N≡C) 1715 N m^{-1}. ^{1}H-NMR (δ, $CDCl_3$): 7.60–7.26 (C_6H_4, m); 4.81 (CH_2, s); 0.20 (Si–CH_3, s). $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$): 167.5 (N≡C, s); 138.0–124.4 (C_6H_4, m); 61.4 (CH_2, s); 0.11 (Si–CH_3, s).

2.2.3. Synthesis of 2-(hydroxymethyl)phenyl isocyanide (3)

To a solution of **2** (1.09 g, 5.31 mmol) in MeOH (15 ml) at r.t. under dinitrogen atmosphere was added TBAF (four drops) and the reaction mixture was stirred for 24 h. After that time, the solvent was evaporated under reduced pressure to afford a pale green oil. Yield: 0.60 mg, 84.7%. IR ($\tilde{\nu}$, CH_2Cl_2): 3602 (m, OH), 2122 (s, N≡C); k(N≡C) 1717 N m^{-1}. ^{1}H-NMR (δ, $CDCl_3$): 7.54–7.23 (C_6H_4, m); 4.73 (CH_2, s); 3.47 (OH, s-br). $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$): 166.8 (N≡C, s); 138.0–124.7 (C_6H_4, m); 61.3 (CH_2, s).

2.3. Synthesis of the complexes

2.3.1. Synthesis of cis-[$PtCl_2$(CNC_6H_4–2-CH_2OSiMe_3)$_2$] (4)

To a solution of [(COD)$PtCl_2$] (0.51 g, 1.37 mmol) in CH_2Cl_2 (20 ml) at r.t. was added **2** (0.59 g, 2.87 mmol). The yellow–orange solution was stirred for 1 h. After this time, an IR spectrum showed the disappearance of the C≡N absorption of the free isocyanide, while two bands in the 2200–2230 cm^{-1} region were present. The solvent was removed under reduced pressure to half of the volume and then n-C_6H_{14} (10 ml) and Et_2O (20 ml) were added to give a pale yellow precipitate, which was filtered off, washed with n-C_6H_{14} (3 × 5 ml) and dried under vacuum. Yield: 0.53 g, 58%. Anal. Calc. for $C_{22}H_{30}Cl_2N_2O_2PtSi_2$: C, 39.05; H, 4.47; N, 4.14. Found: C, 39.48; H, 4.32; N, 4.14%. IR ($\tilde{\nu}$, CH_2Cl_2): 2229, 2196 (s, N≡C) (2233, 2203 (s), KBr); k(N≡C) 1893, 1837 N m^{-1} (from CH_2Cl_2 data); 346, 324 (m, PtCl, PE film). ^{1}H-NMR (δ, $CDCl_3$): 7.63–7.36 (C_6H_4, m); 4.90 (CH_2, s); 0.18 (Si–CH_3, s). ESI-MS: m/z 699 $[M+Na]^+$.

2.3.2. Synthesis of cis-[$PdCl_2$(CNC_6H_4–2-CH_2OSiMe_3)$_2$] (5)

This complex was prepared as described previously for **4** starting from [$PdCl_2(CH_3CN)_2$] (0.80 g, 3.09 mmol) in CH_2Cl_2 (30 ml) and **2** (1.33 g, 6.47 mmol). The yellow–orange solution was stirred for 20 min and then treated with n-C_6H_{14} (30 ml) to give a white precipitate, which was filtered off, washed with n-C_6H_{14} (3 × 5 ml) and dried under vacuum. Yield: 1.68 g, 93%. Anal. Calc. for $C_{22}H_{30}Cl_2N_2O_2PdSi_2$: C, 44.94; H, 5.14; N, 4.76. Found: C, 45.23; H, 5.14; N, 4.76%. IR ($\tilde{\nu}$, CH_2Cl_2): 2229, 2215 (s, N≡C) (2238, 2213 (s), KBr); k(N≡C) 1893, 1869 N m^{-1} (from CH_2Cl_2 data); 349, 319 (m, PtCl, PE film). ^{1}H-NMR (δ, $CDCl_3$): 7.64–7.38 (C_6H_4, m); 4.91 (CH_2, s); 0.19 (Si–CH_3, s). $^{13}C\{^1H\}$-NMR (δ, $CDCl_3$): 132.4–127.2 (C_6H_4, m); 61.4 (CH_2, s); 0.19 (Si–CH_3, s). ESI-MS: m/z 611 $[M+Na]^+$.

2.3.3. Synthesis of cis-[$PtCl_2${$CN(H)C_6H_4$–2-CH_2O}$_2$] (6)

To a suspension of **4** (0.30 g, 4.44 mmol) in MeOH (20 ml) at r.t. was added TBAF (8 mg, 0.03 mmol). The reaction mixture was stirred for 2 h to afford a white solid, which was filterd off, washed with Et_2O (3 × 5 ml) and n-C_6H_{14} (3 × 5 ml) and then dried under vacuum. Yield: 0.18 g, 75%. Anal. Calc. for $C_{16}H_{14}Cl_2N_2O_2Pt$: C, 36.10; H, 2.65; N, 5.26. Found: C, 36.07; H, 2.45; N, 4.97%. IR ($\tilde{\nu}$, KBr): 3452 (br, NH), 1543 (s, $\tilde{\nu}_{asym}$N⋯C⋯O) 332, 300 (m, PtCl, PE film). ^{1}H-NMR (δ, Me_2SO-d_6): 12.42 (NH, s), 7.42–7.17 (C_6H_4, m); 5.41 (CH_2, s). $^{13}C\{^1H\}$-NMR (δ, Me_2SO-d_6): 181.3 ($C_{carbene}$, s, $^1J_{PtC}$ 1590 Hz); 131.1–115.5 (C_6H_4, m); 67.68 (CH_2, s). ESI-MS: m/z 531 $[M-H]^+$.

2.3.4. Synthesis of cis-[$PdCl_2${$CN(H)C_6H_4$–2-CH_2O}$_2$] (7)

To a yellow solution of **5** (0.59 g, 1.00 mmol) in MeOH (20 ml) at r.t. was added NaF (6 mg, 0.14 mmol). The reaction mixture was stirred for 24 h to afford a cream–yellow precipitate, which was filterd off, washed with Et_2O (3 × 10 ml) and n-C_6H_{14} (3 × 10 ml) and then dried under vacuum. Yield: 0.32 g, 72%. Anal. Calc. for $C_{16}H_{14}Cl_2N_2O_2Pd$: C, 43.32; H, 3.18; N, 6.31. Found: C, 43.66; H, 3.06; N, 6.14%. IR ($\tilde{\nu}$, KBr): 3477 (m, NH), 1548 (s, $\tilde{\nu}_{asym}$N⋯C⋯O), 312, 283 (m, PdCl, PE film). ^{1}H-NMR (δ, Me_2SO-d_6): 12.94 (NH, s), 7.43–7.14 (C_6H_4, m), 5.45 (CH_2, s). $^{13}C\{^1H\}$-NMR (δ, Me_2SO-d_6): 200.9 ($C_{carbene}$, s), δ 129.5–115.5 (C_6H_4, m), 67.9 (CH_2, s).

2.3.5. Synthesis of cis-cis-[$PdCl_2${$CN(H)C_6H_4$–2-CH_2O}(PPh_3)] (8)

This complex was prepared by reaction of [PdCl(μ-Cl)(PPh_3)]$_2$ (0.40 g, 0.45 mmol) with **2** (0.19 g, 0.93 mmol) in MeOH (15 ml) and CH_2Cl_2 (5 ml) in the presence of TBAF (three drops). The reaction mixture was stirred for 2 h. Then the yellow precipitate was filtered off, washed with Et_2O (3 × 10 ml) and dried under vacuum. Yield: 0.32 g, 72%. Anal. Calc. for $C_{26}H_{22}Cl_2NOPPd$: C, 54.52; H, 3.84; N, 2.45. Found: C, 54.27; H, 3.79; N, 2.14%. IR ($\tilde{\nu}$, KBr): 3416 (m, NH), 1536 (s, $\tilde{\nu}_{asym}$N⋯C⋯O), 314, 276 (m, PdCl, PE film). ^{1}H-NMR (δ, Me_2SO-d_6): 13.18 (NH, s), 7.75–7.40 (C_6H_4, m), 4.94 (CH_2, s). $^{13}C\{^1H\}$-NMR (δ, Me_2SO-d_6): 200.8 ($C_{carbene}$, s, $^2J_{CP}$ 5.3 Hz), 134.4–115.1 (C_6H_4, m), 68.9 (CH_2, s). $^{31}P\{^1H\}$-NMR (δ, Me_2SO-d_6): 25.4 (PPh_3, s).

2.3.6. Synthesis of [W(CO)$_5$(CNC$_6$H$_4$–2-CH$_2$OSiMe$_3$)] (9)

To a suspension of [W(CO)$_5$I][NEt$_4$] (2.32 g, 3.99 mmol) in acetone (40 ml) at 0 °C was added a solution of $AgBF_4$ (0.80 g, 4.11 mmol) in C_3H_6O (20 ml) dropwise over a period of 20 min. After the addition was complete, the mixture was quickly filtered and the dark orange solution was treated dropwise with a solution of **2** (0.86 g, 4.20 mmol) in acetone (20 ml). After being stirred for an additional 20 min, the yellow–orange solution was allowed to reach r.t. and concentrated to ca. 20 ml under reduced pressure. Et_2O (100 ml) was added and the reaction mixture stirred for 30 min. It was then filtered off and the dark orange solution was evaporated to dryness. It was taken up with Et_2O (30 ml) and *n*-C_6H_{14} (30 ml) and left stirring for 1 h. The solution was concentrated under reduced pressure to give a small amount of a whitish solid (0.08 g) which was filtered off and revealed to be the hydroxyisocyanide drivative **11**. The solution was taken to dryness to afford a red oil of compound **9**. IR ($\tilde{\nu}$, CH_2Cl_2): 2134 (s, N≡C); k(N≡C) 1735 N m^{-1}; 2055, 1934 (s, C≡O). ^{1}H-NMR (δ, $CDCl_3$): 7.60–7.30 (C_6H_4, m), 4.80 (CH_2, s), 0.20 (Si–CH_3, s). ^{13}C{^{1}H}-NMR (δ, $CDCl_3$): 196.6 (*trans* CO, s), 194.5 (*cis* CO, s, ^1J(^{183}W–*cis* CO) 125.3 Hz), 155.6 (N≡*C*, s), 138.8–125.6 (C_6H_4, m), 61.5 (CH_2, s), 0.04 (Si–CH_3, s).

2.3.7. Synthesis of [Cr(CO)$_5$(CNC$_6$H$_4$–2-CH$_2$OSiMe$_3$)] (10)

This compound was prepared by a procedure similar to that used for complex **9** starting from [Cr(CO)$_5$I][NEt$_4$] (1.35 g, 3.01 mmol), $AgBF_4$ (0.61 g, 3.13 mmol) and the isocyanide **2** (0.66 g, 3.22 mmol). The final compound resulted to be a pale green oil. IR ($\tilde{\nu}$, CH_2Cl_2): 2134 (s, N≡C); k(N≡C) 1735 N m^{-1}; 2054, 1950 (s, C≡O). ^{1}H-NMR (δ, $CDCl_3$): 7.56–7.30 (C_6H_4, m), 4.81 (CH_2, s), 0.20 (Si–CH_3, s). ^{13}C{^{1}H}-NMR (δ, $CDCl_3$): 217.0 (*trans* CO, s), 215.0 (*cis* CO, s), 175.4 (N≡*C*, s), 138.5–124.6 (C_6H_4, m), 61.4 (CH_2, s), 0.01 (Si–CH_3, s).

2.3.8. Synthesis of [W(CO)$_5$(CNC$_6$H$_4$–2-CH$_2$OH)] (11)

To a solution of **9** in MeOH (15 ml) at r.t. was added TBAF (three drops). The reaction mixture was stirred for 24 h and then the solution evaporated to dryness. Et_2O (50 ml) and *n*-C_6H_{14} (50 ml) were added and the reaction mixture stirred for 1 h at ambient temperature. It was filtered off and the solution concentrated under reduced pressure to give a pale yellow solid, which was filtered off, washed with *n*-C_6H_{14} (2 × 5 ml) and dried under vacuum. Anal. Calc. for $C_{13}H_7NO_6W$: C, 34.16; H, 1.54; N, 3.06. Found: C, 34.88; H, 1.37; N, 3.14%. IR ($\tilde{\nu}$, CH_2Cl_2): 3603 (w, OH), 2138 (s, N≡C); k(N≡C) 1741 N m^{-1}; 2059, 1955 (s, C≡O). ^{1}H-NMR (δ, $CDCl_3$): 7.59–7.24 (C_6H_4, m), 4.85 (CH_2, s), 1.89 (O*H*, br). ^{13}C{^{1}H}-NMR (δ, $CDCl_3$): 189.1 (*trans* CO, s, ^1J(^{183}W–*trans* CO) 133 Hz), 188.2 (*cis* CO, s, ^1J(^{183}W–*cis* CO) 126 Hz), 148.5 (N≡*C*, s-br), 130.6–117.8 (C_6H_4, m), 54.5 (CH_2, s).

2.3.9. Synthesis of [Cr(CO)$_5$(CNC$_6$H$_4$–2-CH$_2$OH)] (12)

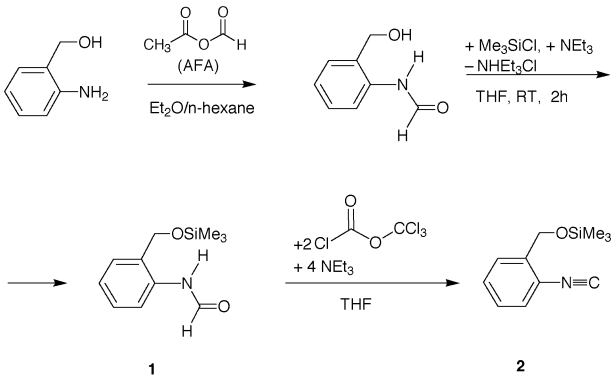
This compound was prepared by a procedure similar to that used for complex **11** starting from **10**, TBAF (three drops) and MeOH (10 ml). Work up of the reaction mixture as for **11** gave a pale yellow solid, which was filtered off, washed with *n*-C_6H_{14} (2 × 3 ml) and dried under vacuum. Anal. Calc. for $C_{13}H_7CrNO_6$: C, 48.00; H, 2.17; N, 4.31. Found: C, 47.58; H, 2.11; N, 4.12%. IR ($\tilde{\nu}$, CH_2Cl_2): 3603 (w, OH), 2134 (s, N≡C); k(N≡C) 1735 N m^{-1}; 2059, 1955 (s, C≡O). ^{1}H-NMR (δ, $CDCl_3$): 7.58–7.33 (C_6H_4, m), 4.85 (CH_2, s), 2.18 (O*H*, br). ^{13}C{^{1}H}-NMR (δ, $CDCl_3$): 217.0 (*trans* CO, s), 215.1 (*cis* CO, s), 175.8 (N≡*C*, s-br), 137.8–126.5 (C_6H_4, m), 62.0 (CH_2, s).

3. Results and discussion

3.1. Synthesis of the ligands

The reactions sequence leading to the synthesis of 2-(trimethylsiloxymethyl)phenyl isocyanide **2** is reported in Scheme 1.

The first stage involves the conversion of the amino group of the commercially available 2-aminobenzyl alcohol to the corresponding formamide using AFA as previously reported [16]. Subsequent reaction with a stoichiometric amount of Me_3SiCl in the presence of a slight excess of NEt_3 in THF affords the *O*-silylated formamide **1** in good yield. Compound **1** has been characterized by IR, ^{1}H- and ^{13}C{^{1}H}-NMR (see Section 2). In particular, the ^{13}C{^{1}H}-NMR spectrum shows two C=O resonances at 162.8 and 159.6 ppm suggesting the presence of the two conformers **1a** and **1b**



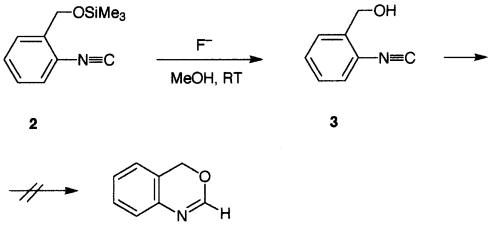
Scheme 1.

Chart C.

as illustrated in Chart C. This experimental evidence is also supported by the observation for the methylene moiety of **1** of two resonances in the ^{1}H (4.72 and 4.68 ppm) as well as in the $^{13}C\{^{1}H\}$ (65.2 and 64.5 ppm) NMR spectra.

The formamide is then dehydrated with trichloromethyl chloroformate in the presence of NEt_3 in CH_2Cl_2 at 0 °C [20] to give the isocyanide **2**, albeit in low yield (ca. 38% after distillation), as a pale yellow oil. The isonitrile **2** was characterized by IR, ^{1}H- and $^{13}C\{^{1}H\}$-NMR (see Section 2). The IR spectrum (CH_2Cl_2 solution) shows the $\tilde{\nu}$(N≡C) at 2122 cm^{-1} (with a force costant [21] k(N≡C) of 1715 N m^{-1}). This value may be compared with that reported for other functionalized isocyanides such as 2-$(CH_2X)C_6H_4N{\equiv}C$ (CH_2Cl_2 solution, X = Cl, $\tilde{\nu}$(N≡C) 2124 cm^{-1} [15], k(N≡C) 1718 N m^{-1}; X = PPh_3^+, $\tilde{\nu}$(N≡C) 2120 cm^{-1} [16], k(N≡C) 1712 N m^{-1}) and as 2-$(OSiMe_3)C_6H_4N{\equiv}C$ ($\tilde{\nu}$(N≡C) 2120 cm^{-1} (neat), k(N≡C) 1712 [22]). Similarly, the $^{13}C\{^{1}H\}$-NMR ($CDCl_3$) spectrum shows the isocyanide carbon at 167.5 ppm which matches the corresponding resonance found at 168 ppm for the aforementioned isocyanides 2-$(CH_2X)C_6H_4N{\equiv}C$.

The isocyanide **2** is stable in $CDCl_3$ solution. However, it can be readily converted to the corresponding 2-(hydroxymethyl)phenyl isocyanide (**3**) in the presence of a catalytic amount of F^- ions in MeOH at room temperature. The isocyanide **3**, which is isolated as a pale green oil, is also stable as free ligand and shows no tendency to undergo intramolecular cyclization to 4H-benzo[1,3]oxazine (Eq. (1)) as can be inferred by monitoring the ^{1}H-NMR spectrum of a $CDCl_3$ solution for 2 days at room temperature.



(1)

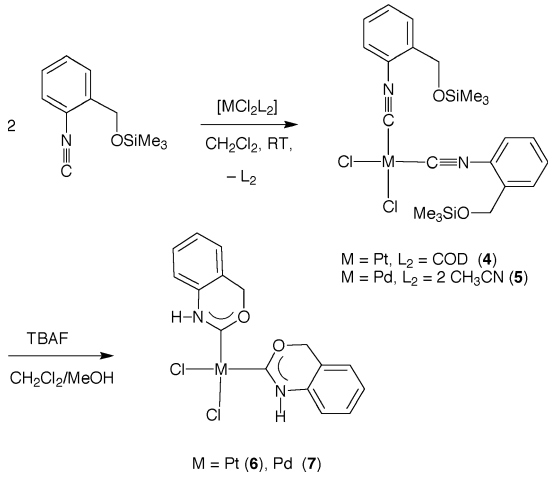
The isocyanide **3** was characterized by IR, ^{1}H- and $^{13}C\{^{1}H\}$-NMR (see Section 2). The spectroscopic data are quite similar to those found for the isocyanide precursor **2**; in particular, diagnostic spectral features are the $\tilde{\nu}$(N≡C) at 2123 cm^{-1} (CH_2Cl_2) (k(N≡C) 1717 N m^{-1}), the OH resonance at 3.47 ppm in the ^{1}H-NMR spectrum and the isocyanide carbon resonance in the $^{13}C\{^{1}H\}$-NMR spectrum at 166.8 ppm.

3.2. Synthesis of the complexes

The coordinating ability of the isocyanide ligand **2** has been tested in a series of reactions with some transition metal complexes which have been appropriately chosen in order to investigate more deeply the subsequent reaction chemistry of these metal–ligand systems. Thus, we have initially reacted **2** with some Pt(II) and Pd(II) complexes as illustrated in Scheme 2.

Complexes **4** and **5** were easily obtained in good yield from the precursors $[MCl_2L_2]$ (M = Pt, L_2 = 1,5-cyclooctadiene; M = Pd, $L_2 = 2CH_3CN$) by reaction with two equivalents of **2** in CH_2Cl_2 at room temperature. These complexes display the $\tilde{\nu}$(N≡C) absorption in the range at 2200–2230 cm^{-1} (k(N≡C) ca. 1830–1890 N m^{-1}), with a $\Delta\tilde{\nu} = \tilde{\nu}(N{\equiv}C)_{coord} - \tilde{\nu}(N{\equiv}C)_{free}$ [1] of ca. 80–110 cm^{-1}, as expected for isocyanides coordinated to Pt^{2+} and Pd^{2+} metal ions [1]. As also previously observed a high positive shift indicates the susceptibility of the isocyanide carbon to nucleophilic attack. Thus, complexes **4** and **5** are converted in MeOH in the presence of a catalytic amount of F^- ions to the corresponding benzo[1,3]oxazin-2-ylidene derivatives **6** and **7**, respectively.

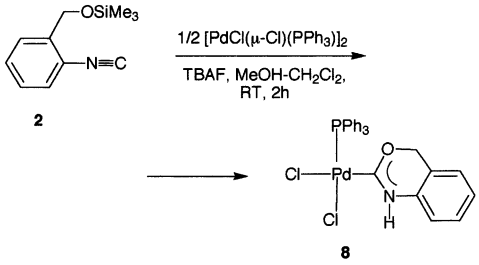
The dicarbene complexes were isolated as pale yellow or white solids, insoluble in chlorinated solvents, but soluble in DMSO. They were characterized by elemental analysis, IR, ^{1}H- and $^{13}C\{^{1}H\}$-NMR (see also Section 2). The IR spectra (KBr) show a strong absorption in the range 1536–1548 cm^{-1} typical of the $\tilde{\nu}_{asym}$(N⋯C⋯O) stretching [6,23] and the N–H absorption around 3400 cm^{-1}; two absorptions at 332 and 300 cm^{-1} (M = Pt) and 312 and 283 cm^{-1} (M = Pd) are observed in the IR spectra (PE films) and are characterstic of the *cis* stereochemistry of the complexes [16,24]. The ^{1}H-NMR



Scheme 2.

spectra (DMSO-d_6) show the N–H resonance of the heterocyclic carbene in the range 12.4–12.9 ppm as a sharp singlet. The $-CH_2-$ resonance shows up also as a singlet at ca. 5.40 ppm. Significantly, the $^{13}C\{^1H\}$-NMR (DMSO-d_6) spectra of **6** and **7** display the carbene carbon at 181.3 and 200.9 ppm, respectively, which are values that are also found for the chemical shifts of other aminooxy- or diaminocarbene complexes of Pt(II) and Pd(II) [25–28]. Complex **6** shows also coupling of the carbene carbon with ^{195}Pt of 1590 Hz and the magnitude of this coupling constant is in agreement with those reported for Pt(II)–carbene complexes ranging between ca. 1300 and 1500 Hz for carbenes *trans* to a halide [26–28]. It is also interesting to observe that the ^1H- and $^{13}C\{^1H\}$-NMR chemical shifts of the methylene group of the heterocyclic carbenes in compounds **6** and **7** are close to those found for the heterocyclic compound 4*H*-benzo[1,3]oxazin-2-one which are found at 5.31 and 68.62 ppm, respectively [29].

Isocyanide **2** reacts also with the dimeric Pd(II) complex $[PdCl(\mu\text{-}Cl)(PPh_3)]_2$ in a solution of CH_2Cl_2–MeOH in the presence of TBAF to afford the carbene complex **8**. This latter was characterized by IR, ^1H- and $^{13}C\{^1H\}$-NMR (see also Section 2).

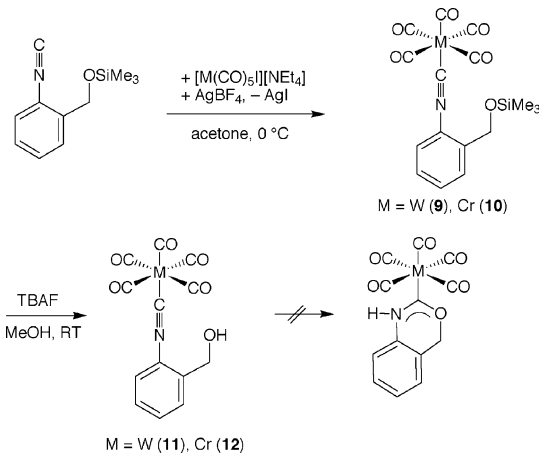


(2)

The ^1H-NMR spectrum (DMSO-d_6) shows the N–H and the $-CH_2-$ resonances of the heterocyclic carbene at 13.1 and 4.94 ppm, respectively, as singlets, while the $^{13}C\{^1H\}$-NMR spectrum displays the carbene carbon resonance at 200.8 ppm as a doublet by coupling with the *cis* phosphorus atom ($^2J_{CP}$ 5.3 Hz) [27–29].

In order to explore the chemical behavior of the isocyanide **2** also in comparison with that shown by other functional *O*-isocyanides (see Section 1), we have prepared the carbonyl complexes $[M(CO)_5(C{\equiv}NC_6H_4\text{-}2\text{-}CH_2OSiMe_3)]$ (M = W, **9**; Cr, **10**) (Scheme 3).

The N≡C IR absorption is observed at $\tilde{\nu}$ = 2134 cm^{-1} (k(N≡C) = 1734 N m^{-1}) with a $\Delta\tilde{\nu}$ of 12 cm^{-1}, thus reflecting a much lower electrophilicity of the carbene carbon compared to the Pt(II) and Pd(II) complexes previously described. In fact, upon treatment with F^- ions in MeOH compounds **9** and **10** are converted to the corresponding derivatives **11** and **12**, respectively, having the coordinated 2-(hydroxymethyl)phenyl isocyanide ligand. Again, the observed N≡C IR absorption ($\tilde{\nu}$ = 2134 – 2138 cm^{-1}; k(N≡C) = 1734–1741 N m^{-1}) is almost the same to that displayed



Scheme 3.

by the silylated derivatives and this would account (see also further on) for the lack of reactivity in the ylidene formation.

4. Concluding remarks

In this work, we have reported the synthesis, the coordination properties and the reactivity toward the formation of the heterocyclic carbene benzo[1,3]oxazin-2-ylidene of the new *O*-functionalized isocyanides 2-(trimethylsiloxymethyl)phenyl isocyanide (**2**) and 2-(hydroxymethyl)phenyl isocyanide (**3**). This latter is stable as free ligand and shows no tendency to spontaneously cyclize to benzo[1,3]oxazine: in this respect, it parallels the chemical behavior of the hydroxyalkyl isocyanides $HO-(CH_2)_n-NC$ (n = 2, 3) rather than that of the hydroxyaryl ligand 2-$(OH)C_6H_4NC$, which is unstable and can be isolated only as the silylated derivative (see Section 1). On the other hand, coordination of **2** to Pt^{2+} and Pd^{2+} and subsequent treatment with F^- ions leads to the formation of the heterocyclic carbene by intramolecular attack of the in situ generated OH function on the electrophilic isocyanide carbon (Chart D).

Although the 2-(hydroxymethyl)phenyl isocyanide metal complex intermediate could not be isolated in the case of Pt(II) and Pd(II) metal centers, complexes containing the isocyanide **3** could be prepared with $\{M(CO)_5\}$ (M = W, Cr) metal fragments. In this latter

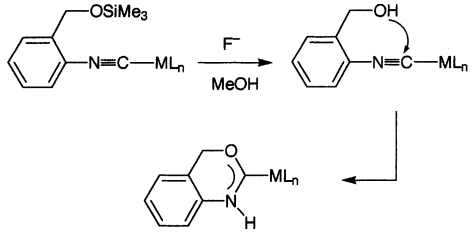


Chart D.

case, the coordinated isocyanide **3** is stable, giving no evidence for ylidene formation. Thus, once again, its chemical behavior resembles that of the hydroxyalkyl isocyanides HO–$(CH_2)_n$–NC rather than that of the hydroxyaryl isocyanide 2-$(OH)C_6H_4NC$. This latter, in fact, when coordinated to $\{M(CO)_5\}$ is partially converted to the corresponding carbene 1,2-dihydrobenzoxazol-2-ylidene, although it can be stabilized, without cyclization, when coordinated to sufficiently electron rich transition metal centers [14,30]. It is finally to point out, as previously suggested [2], that the greater tendency of intramolecular cyclization of 2-hydroxyphenyl isocyanide compared to the aliphatic isocyanides HO–$(CH_2)_n$–NC and **3** could be ascribed to the aromaticity of the resulting heterocyclic carbene products.

Acknowledgements

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