

A stable (amino)(phosphino)carbene as bidentate ligand for palladium and nickel complexes: Synthesis, structure, and catalytic activity

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Abstract

Two original complexes featuring an (amino)(phosphino)carbene η^2 -bonded to the metal have been obtained in 60% and 80% yields, by addition of the corresponding stable carbene to $\text{PdCl}_2(\text{cod})$ and $\text{NiCl}_2(\text{PPh}_3)_2$, respectively. Both complexes have been fully characterized including X-ray diffraction studies. The catalytic activity of the palladium complex has been evaluated for aryl amination reactions.

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Keywords: Carbenes; Bidentate ligands; Palladium complexes; Nickel complexes; Aryl amination reaction

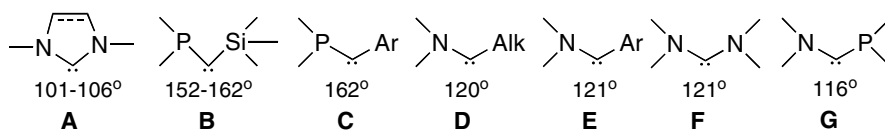
1. Introduction

Over the years, the success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behavior of a variety of metal-containing systems. Recently, spectacular achievements have been made in this area using *N*-heterocyclic carbenes (NHCs) **A** as strong σ -donor ligands for transition metals [1] (Scheme 1). In contrast, very little is known on the efficiency of stable non-heterocyclic carbenes [2] as ligands for transition metal catalysts. Despite their early discovery, direct complexation of (phosphino)(silyl)carbenes **B** [3] has not yet been reported, and all our attempts have failed. The-

oretical studies suggested that in contrast with NHCs **A**, carbenes **B** tend to adopt widened valence angles at the central carbon; as a consequence, conformational changes to a bent carbene structure are required to allow metal complexation, and this process is energetically too costly [4]. These conclusions have recently been corroborated by experimental observations. A considerable contraction of the bond angle about the carbene center of (phosphino)(aryl)carbenes **C** was observed for the $\text{RhCl}(\text{nbdc})(\text{C})$ complex (from 162° for the free carbene **C** to 119° for the complex) [5]. (Amino)(alkyl or aryl)carbenes **D** and **E** feature more acute bond angle (120 – 121°) than their phosphino counterparts **C**, and therefore easily undergo complexation with metals [6]. However, it is important to note that although complexes featuring carbenes **C**–**E** are thermally stable, they appear to be much more air sensitive than the corresponding NHC complexes, which partly precludes their

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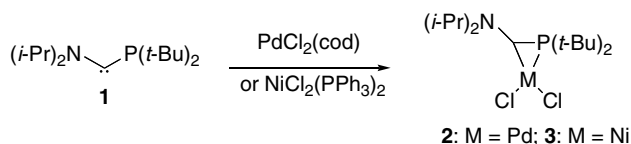
Scheme 1.

use in catalysis. Herrmann [8] has recently suggested that the poor coordination behavior of acyclic diamino carbenes **F** [7], compared to cyclic diamino carbenes **A** might be due to the larger N–C–N angle (121° compared to $101\text{--}106^\circ$). Interestingly, (amino)(phosphino)carbenes **G**, feature the most acute carbene bond angle of all the known stable acyclic carbenes: 116° [9]. Moreover, we have already shown that carbenes **G** reacts with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ to afford the cationic complex featuring two (amino)(phosphino)carbenes η^2 -bonded to the metal [10]. In other words, **G** can act as 4-electrons donors, with a strong σ -donor carbene next to a relatively labile phosphine. This very peculiar topology prompted us to study further the coordination behavior of carbenes **G**. Here we report the preparation of two original group 10 metal complexes of a stable carbene of type **G**, as well as preliminary results concerning the catalytic activity of the palladium complex in aryl amination reactions.

2. Results and discussion

The (amino)(phosphino)carbene **1** reacts at room temperature with one equivalent of $\text{PdCl}_2(\text{cod})$ complex. The reaction proceeds very cleanly, and complex **2** was isolated, after recrystallization from a CH_2Cl_2 solution at -30°C , as yellow crystals, in 60% yield. The analogous nickel complex **3** was prepared similarly by treatment of a THF solution of the (amino)(phosphino)carbene **1** with one equivalent of $\text{NiCl}_2(\text{PPh}_3)_2$. It was isolated as red crystals, in 80% yield, by slow recrystallisation from a CDCl_3 solution at -30°C (Scheme 2).

The high field ^{31}P NMR chemical shifts observed (**2**: -44.2 ppm; **3**: -82.1 ppm) suggested the formation of three-membered metallocycles. The η^2 -coordination mode was unambiguously established by X-ray diffraction studies (Figs. 1 and 2). In complexes **2** and **3**, the metal is in a distorted square-planar environment (sum of bond angles around Pd 360.37° and around Ni 361.17°). The carbene–palladium bond distance (2.019 Å) is in the typical range for C–Pd single bonds,



Scheme 2.

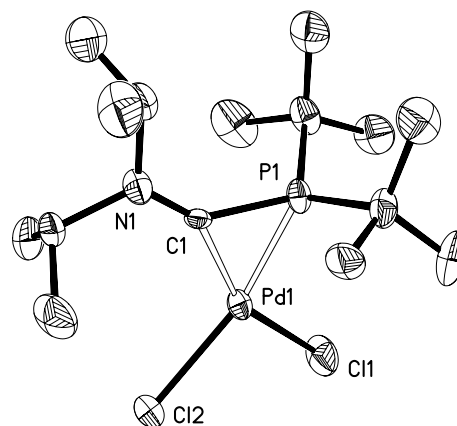


Fig. 1. X-ray crystal structure of complex **2** (ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: C(1)–Pd(1) 2.019(7); P(1)–Pd(1) 2.205(4); P(1)–C(1) 1.791(7); C(1)–N(1) 1.262(9) and P(1)–Pd(1)–C(1) 49.93(18); P(1)–Pd(1)–Cl(1) 106.15(9); Cl(1)–Pd(1)–Cl(2) 93.38(8); Cl(2)–Pd(1)–C(1) 110.91(19).

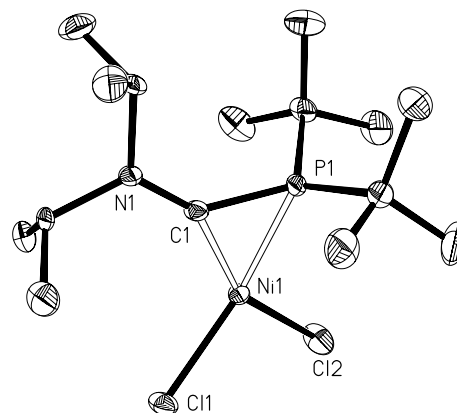


Fig. 2. X-ray crystal structure of complex **3** (ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: C(1)–Ni(1) 1.841(4); P(1)–Ni(1) 2.1068(13); P(1)–C(1) 1.755(4); C(1)–N(1) 1.300(5) and P(1)–Ni(1)–C(1) 52.25(14); P(1)–Ni(1)–Cl(2) 102.21(5); Cl(2)–Ni(1)–Cl(1) 96.00(5); Cl(1)–Ni(1)–C(1) 110.71(14).

and very similar to that observed for related *N*-heterocyclic carbene palladium complexes ($1.95\text{--}2.07$ Å) [11]. The nickel–carbene bond length of 1.841 Å is slightly shorter than observed for nickel(II) complexes bearing Cl and NHC ligands *cis* to one another [12]. The phosphorus–metal bond distances, 2.204 and 2.107 Å are in the typical range for P–Pd and P–Ni single bonds, respectively. In both complexes, the nitrogen atom

adopts a trigonal planar geometry with a short NC bond distance (**2**: 1.262 Å; **3**: 1.300 Å), which is very similar to that of free (amino)(phosphino)carbenes (1.30 Å). This indicates that, the carbene–metal interaction results from the donation of the carbene lone pair into an empty metal-based orbital; back-donation from the metal to the carbene center is almost negligible.

Three-membered metallocycles **2** and **3** are very stable toward air, moisture and heat. This is due to the fact that the phosphorus is not implicated in the stabilization of the carbene center, and thus has a lone pair fully available to complex the metal. We expected that this peculiar topology would confer original catalytic properties to complexes **2** and **3**. The first results of the catalytic study with complex **2** in aryl amination reactions [13] are summarized below.

Complex **2** was first tested for the catalytic aryl amination reaction using 4-bromotoluene and morpholine as coupling partners (Tables 1 and 2). The use of organic bases, such as *t*-BuONa, *t*-BuOK and *t*-AmONa, led, after 5 h at 110 °C, to the formation of the coupling product in 75%, 55% and 65% conversions, respectively; increasing the reaction time to 21 h gave 80%, 70% and 70% conversions, respectively (Table 1, entries 1–6). Under similar conditions, inorganic bases, such as Cs₂CO₃

Table 1

Influence of the base (1.4 equiv.) on the arylation of morpholine (1.0 equiv.) with 4-bromotoluene (1.0 equiv.) at 110 °C using 1 mol% of complex **2**, and dioxane as solvent

Entry	Base	Time (h)	Conversion (%)
1	<i>t</i> -BuONa	5	75
2	<i>t</i> -BuONa	21	80
3	<i>t</i> -BuOK	5	55
4	<i>t</i> -BuOK	21	70
5	<i>t</i> -AmONa	5	65
6	<i>t</i> -AmONa	23	70
7	Cs ₂ CO ₃	5	10
8	Cs ₂ CO ₃	21	20
9	NaOH	5	8
10	NaOH	21	25

Table 2

Influence of the solvent on the arylation of morpholine (1.0 equiv.) with 4-bromotoluene (1.0 equiv.) at 110 °C using 0.5 mol% of complex **2**, and *t*-BuONa (1.4 equiv.)

Entry	Solvent	Time (h)	Conversion (%)
1	Anisole	2	30
2	Anisole	18	55
3	<i>t</i> -AmOH	2	55
4	<i>t</i> -AmOH	18	95
5	NMP	2	25
6	NMP	18	55
7	Xylene	2	90
8	Xylene	18	98
9	DME	2	40
10	DME	18	50

Table 3

Arylation of morpholine (1.0 equiv.) with diverse aryl halides (1.0 equiv.) at 140 °C using 0.5 mol% of complex **2**, *t*-BuONa (1.4 equiv.), and xylene as solvent

Entry	Solvent	Time (h)	Conversion (%)
1	4-Bromotoluene	1	90
2	4-Bromoanisole	20	80
3	3,5-Dibromotoluene	20	10 (mono), 60 (di)
4	1-Bromo-4-fluorobenzene	20	85
5	1-Bromo-4-chlorobenzene	20	90
6	4-Chlorotoluene	1	20

or NaOH, appeared to be inefficient; conversion of 4-bromotoluene does not exceed 25% after 21 h (Table 1, entries 7–10). Thus *t*-BuONa appears to be the most efficient base for this reaction. Then we examined the influence of the solvent. Xylene gave the best results, with a conversion reaching 90% in 2 h at 110 °C, and even 98% after 18 h (Table 2, entries 7 and 8). *t*-AmOH could be an alternative choice, since a 95% conversion was obtained in 18 h (Table 2, entry 4).

Using the optimized conditions (*t*-BuONa; xylene), the aryl amination reactions of a variety of aryl halides with morpholine were studied. As can be seen in Table 3, electron-rich and electron-poor aryl bromides afforded the corresponding coupling products in good yields (entries 1–5). Unfortunately, aryl chlorides are not efficiently coupled, since only 20% of conversion occurred when 4-chlorotoluene was used (entry 6); this explains the total selectivity (involving the bromide) observed entries 4 and 5.

3. Conclusion

Although the results of the catalytic tests are not impressive, they are extremely stimulating. Indeed, as mentioned in the introduction, cyclic carbenes are much more efficient as ligands for transition metal catalysts than their acyclic variants. Therefore, it is quite reasonable to believe that cyclic versions of (amino)(phosphino)carbenes will have very interesting ligand properties. The synthesis of such species is under current investigations.

4. Experimental

All experiments were carried out under dry argon using standard Schlenk or dry box techniques. THF and ether were distilled under argon from sodium/benzophenone. Pentane and CH₂Cl₂ were distilled under argon from P₂O₅ · PdCl₂(cod) and NiCl₂(PPh₃)₂ were used as supplied from Strem Chemicals. Compound **1** was prepared according to the reported procedure [9a]. Commercially available reagents were used without

further purification. ^{31}P NMR, ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AMX 250, AMX400 and AMX500 instruments. Chemical shifts are reported in ppm downfield from Me_4Si and were referenced to solvent peaks (^1H , ^{13}C) or external 85% H_3PO_4 (^{31}P). Coupling constants are given in Hz.

4.1. Synthesis of the (amino)(phosphino)carbene palladium complex 2

A slight excess of freshly prepared (amino)(phosphino)carbene **1** in THF (3 mL) was added to a CH_2Cl_2 solution (10 mL) of $\text{PdCl}_2(\text{cod})$ complex (1.4 mmol, 0.40 g). After the solution mixture was stirred at room temperature for 3 h, ^{31}P NMR spectroscopy indicated the quantitative formation of complex **2**. Cooling the solution to 0 °C gave a yellow precipitate, which was filtered, washed with diethyl ether (2×20 mL), and dried under reduced pressure. After recrystallization from a CH_2Cl_2 solution at –30 °C, complex **2** was isolated as yellow crystals (0.36 g, 60%). ^{31}P NMR (CD_2Cl_2): –44.2 ppm. ^1H NMR (CD_2Cl_2): 1.55 (d, $^3J_{\text{P-H}} = 19.4$ Hz, 18H, PCCH_3), 1.57 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 6H, NCHCH_3), 1.91 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 6H, NCHCH_3), 4.02 (sept, $^3J_{\text{H-H}} = 6.7$ Hz, 1H, NCHCH_3), 4.35 (broad sept, 1H, NCHCH_3). ^{13}C NMR (CD_2Cl_2): 20.7 (NCHCH_3), 21.7 (NCHCH_3), 30.6 (d, $J_{\text{P-C}} = 2.9$ Hz, PCCH_3), 39.4 (d, $J_{\text{P-C}} = 10.0$ Hz, PCCH_3), 57.5 (NCHCH_3), 80.4 (d, $J_{\text{P-C}} = 5.0$ Hz, N CHCH_3), 202.0 (PdC).

4.2. Synthesis of the (amino)(phosphino)carbene nickel complex 3

A slight excess of freshly prepared (amino)(phosphino)carbene **1** in THF (3 mL) was added to a CH_2Cl_2 solution (10 mL) of $\text{NiCl}_2(\text{PPh}_3)_2$ (1.4 mmol, 0.92 g). The solution was stirred for 3 h at room temperature. After filtration, 10 mL of pentane was added and a precipitate was formed. After filtration, the solid was washed with a THF/pentane mixture (3×10 mL) and dried under reduced pressure. After recrystallization from a CDCl_3 solution at –30 °C, complex **3** was obtained as red crystals (0.43 g, 80%). ^{31}P NMR (CDCl_3): –82.06 ppm. ^1H NMR (CDCl_3): 1.44 (d, $^3J_{\text{H-H}} = 6.5$, 6H, NCHCH_3), 1.65 (d, $^3J_{\text{P-H}} = 18.5$, 18H, PCCH_3), 2.02 (d, $^3J_{\text{H-H}} = 6.5$, 6H, NCHCH_3), 3.78 (sept, $^3J_{\text{H-H}} = 6.5$, 1H, NCHCH_3), 4.28 (broad sept, 1H, NCHCH_3). ^{13}C NMR{ ^1H } (CDCl_3): 20.3 (NCHCH_3), 21.7 (NCHCH_3), 30.5 (PCCH_3), 38.3 (PCCH_3), 55.9 (NCHCH_3), 78.0 (NCHCH_3), 189.5 (PdC).

4.3. Crystallographic data for complexes 2 and 3

Data for both structures were collected at low temperature $T = 193(2)$ K (for **2**) and $T = 133(2)$ K (for **3**) using

an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) [14] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2 [15]. Crystal data for **2**: $\text{C}_{16}\text{H}_{34}\text{Cl}_4\text{NPPd}$, $M = 519.61$, triclinic, space group $P\bar{1}$ with $a = 9.78(2)$ Å, $b = 10.07(2)$ Å, $c = 12.21(2)$ Å, $\alpha = 91.11(3)^\circ$, $\beta = 90.68(3)^\circ$, $\gamma = 97.50(3)^\circ$, $V = 1192(3)$ Å³, $Z = 2$. 5111 reflections (3325 independent, $R_{\text{int}} = 0.0894$), largest electron density residue: $0.954 \text{ e } \text{Å}^{-3}$, $R_1 = 0.0539$ (for $I > 2\sigma(I)$) and $wR_2 = 0.1409$ (all data). Crystal data for **3**: $\text{C}_{16}\text{H}_{33}\text{Cl}_5\text{NNiP}$, $M = 506.36$, orthorhombic, space group $P2_12_12_1$ with $a = 9.710(1)$ Å, $b = 12.037(1)$ Å, $c = 20.624(2)$ Å, $V = 2410.6(4)$ Å³, $Z = 4$. 11972 reflections (4065 independent, $R_{\text{int}} = 0.0596$), largest electron density residue: $0.843 \text{ e } \text{Å}^{-3}$, $R_1 = 0.0454$ (for $I > 2\sigma(I)$) and $wR_2 = 0.0890$ (all data).

4.4. Typical reaction procedure for aryl amination reactions

To a solution (6 mL) of aryl halide (6 mmol), amine (6 mmol) and base (8.4 mmol) was added complex **2**. The reaction mixture was stirred at 110 °C for the time mentioned in Tables 1–3 and monitored by GC analysis.

5. Supplementary material

CCDC – 270980 (**2**), 270981 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ UK, fax: +44 1223 336 033, email: deposit@ccdc.cam.ac.uk or at www.ccdc.cam.ac.uk/conts/retrieving.html.

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