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Synthesis and structure of nickel(II) and palladium(II) carbene complexes containing the 1,3-diallylimidazolidin-2-ylidene ligand*

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Abstract

Trans-carbene complexes of nickel(II) and palladium(II) with 1,3-diallylimidazolidin-2-ylidene (L^{Allyl}) were prepared and characterized by i.r., n.m.r. and mass spectra. The structure of two complexes were determined by single crystal X-ray diffraction techniques.

Introduction

Investigations into the synthesis, reactivity, and structural characterization of metal carbene complexes have led to the development of a major area of organometallic research, due primarily to the numerous catalytic and stoichiometric reactions in which these species are often involved [1, 2]. A large number of transition metal carbene complexes derived from electron-rich olefins [3] are now known for the majority of transition metals including nickel(II) and palladium(II) [4, 5]. These carbene complexes can be prepared from an electron-rich olefin (L_2^R) and a suitable metallic complex [4, 5], however, the electron-rich alkene [L_2^{Allyl}] *(2)* is inaccessible for this synthetic approach. Instead, a regiospecific rearrangement was obtained to give the compound *(3)*, as result of a [3,3] sigmatropic amino-Claisen-type rearrangement [6] (Scheme 1). During our ongoing investigations into the imidazolidine carbene chemistry we have isolated and structurally characterized carbene complexes in which L^{Allyl} is the ligand derived from the specific aminal *(1)*, that was only accessible by a low yield *in situ* preparation [7, 8].

Experimental

All experiments were performed under Ar using freshly distilled dry solvents. The following starting materials were prepared and purified according to literature methods: $NiCl_2(PPh_3)_2$ [9], $C_3H_5\overline{NCH_2CH_2(C_3H_5)}NC(NMe_2)H$, *(1)* [10], and $PdCl_2(PEt_3)_2$ [11].

Measurements

I.r. spectra in the 4000–200 cm^{-1} range were obtained on a Nicolet Magna 750 FT-IR spectrophotometer as Nujol mulls. The ^1H-, ^{13}C- and ^{31}P-n.m.r. spectra were measured at room temperature on the Varian NOVA 300 or a Bruker DMX500 spectrometer in $CDCl_3$; TMS was used internal standard for ^1H (300.2 MHz) and the central peak of $CDCl_3$ at 76.90 was used for ^{13}C (75.5 MHz). Mass spectra were obtained on a Jeol JMS-SX102A at 70 eV. Melting points were recorded using an electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc. Knoxville, US.

Reaction of 1,3-diallyl-2-dimethylaminoimidazolidine, (1) with (a) dichlorobis(triethylphosphine)-palladium(II)

When a benzene solution of the aminal *(1)* (0.134 g, 0.69 mmol) was added, with vigorous stirring, to a yellow suspension of the palladium complex (0.25 g, 0.60 mmol) in benzene (25 cm^3), a light yellow solution formed. After 1.5 h, the solution was filtered and the filtrate was evaporated to dryness. The yellow residue was washed several times with cold hexane to yield *trans*-dichloro(1,3-diallylimidazolidin-2-ylidene)(triethylphosphine) palladium(II) *(4)*, (0.19 g, 71.0%). M.p. 183.0 °C(dec.). (Found: C, 40.7; H, 6.5; N, 6.4. $C_{15}H_{29}Cl_2N_2PPd$ Calcd.: C, 40.4; H, 6.5; N, 6.2%). $^{31}P\{^1H\}$-n.m.r. (δ p.p.m.): 20.2 (s, PEt_3). ^1H-n.m.r.

* Dedicated to Professor Hugo Torrens Miquel on the occasion of his 50th birthday

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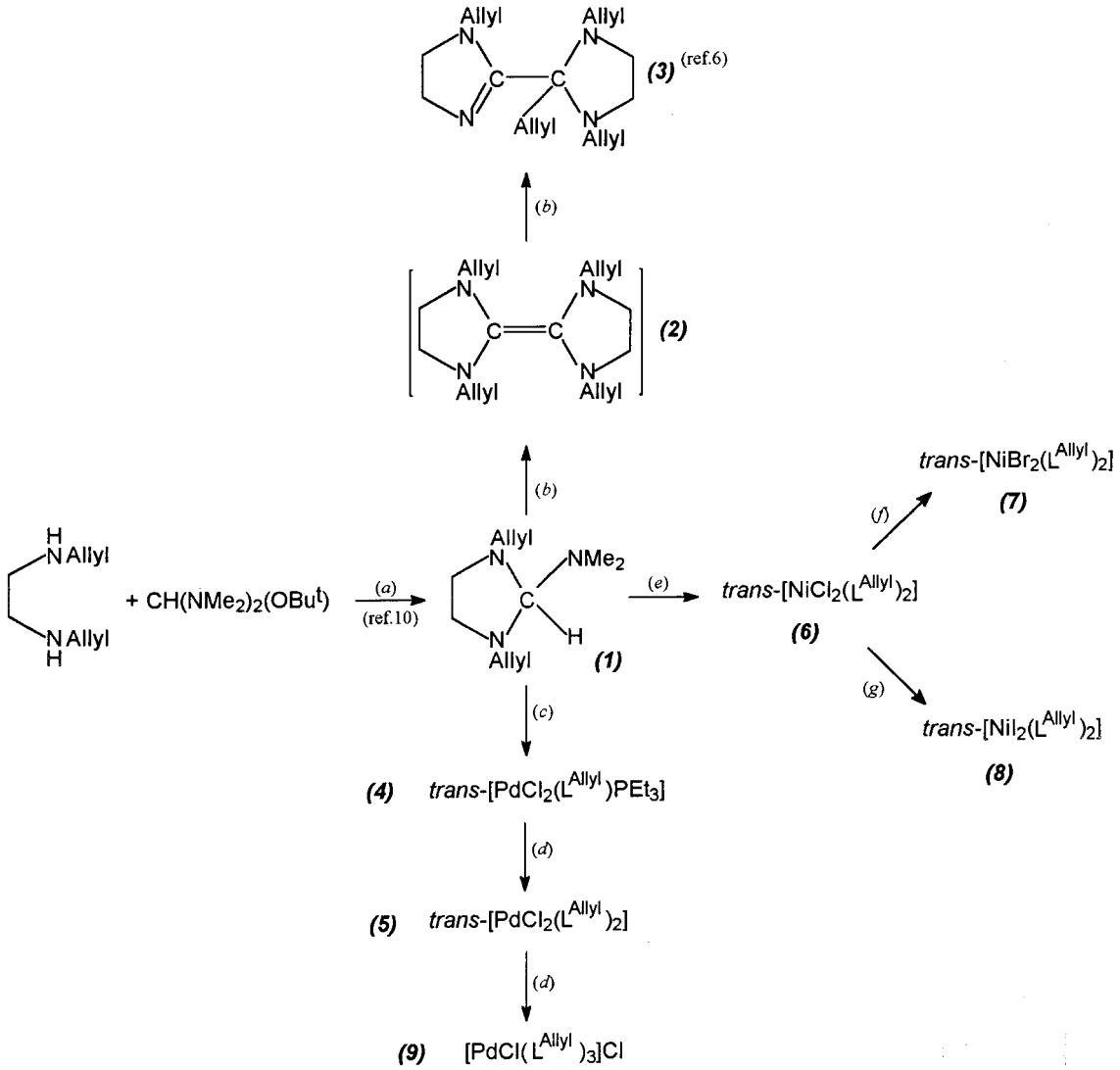

Scheme. Routes to mono-, bis- and *tris*-carbene metal(II) complexes. All reactions at room temperature: (a) ref. 10, (b) ref. 6, (c) $PdCl_2(PEt_3)_2$, benzene, (d) aminal *(1)*, benzene, (e) $NiCl_2(PPh_3)_2$, THF, (f) LiBr, Me_2CO, (g) NaI, Me_2CO.

(δ p.p.m.): 5.5 (m, =CH), 5.1 (m, CH_2=), 4.2 (d, RCH_2N), 3.6 [s, $(CH_2)_2$], 0.9 (q, CH_3), 1.6 (m, CH_2). $^{13}C\{^1H\}$-n.m.r. (δ p.p.m.): 191.0 (s, $C_{carbene}$), 129.7 (s, =CH), 120.9 (s, CH_2=), 52.9 (s, RCH_2N), 48.1 [s, $(CH_2)_2$], 7.8 (s, CH_3), 14.7 (t, CH_2). I.r: 1652.2 $\nu(CH_2$=CH), 1518.7 $\nu(CN_2)$, 333.1 ν(Pd—Cl) cm^{-1}. MS (*m*/*z*): 410 (M^+—Cl), 375 (M^+—2Cl).

Reaction of (1) with (b) the trans-dichloro (4) complex

The same procedure as for (a) was employed. The *trans*-palladium complex *(4)* (0.2 g, 0.44 mmol) and aminal (0.109 g, 0.56 mmol) gave yellow crystals of the *trans*-dichloro-bis-(1,3-diallylimidazolidin-2-ylidene)palladium(II) *(5)*, (0.19 g, 88.7%). M.p. 188.4 °C(dec.). ^1H-n.m.r. (δ p.p.m.): 6.0 (m, =CH), 5.1 (m, CH_2=), 4.5 (m, RCH_2N), 3.4 [s, $(CH_2)_2$]. $^{13}C\{^1H\}$-n.m.r. (δ p.p.m.): 199.0 (s, $C_{carbene}$), 133.7 (s, =CH), 118.8 [s, CH_2=], 52.7 (s, RCH_2N), 48.0 [s, $(CH_2)_2$]. I.r: 1643.3 $\nu(CH_2$=CH), 1519.8 $\nu(CN_2)$, 352.5 ν(Pd—Cl) cm^{-1}. MS (*m*/*z*): 442 (M^+—Cl), 407 (M^+—2Cl).

Reaction of (1) with (c) dichlorobis(triphenylphosphine) nickel(II)

To a suspension of $NiCl_2(PPh_3)_2$ (1.2 g, 1.85 mmol) in THF (20 cm^3) was added a small quantity of aminal (0.85 g, 4.4 mmol) with vigorous stirring at room temperature. After 2.0 h, the mixture was filtered and hexane was added to the dark orange filtrate to give orange crystals of *(6)*, (460 mg, 59%). M.p. 186.0 °C(dec.). ^1H-n.m.r. (500 MHz, δ p.p.m.): 6.19 (m, =CH), 5.38 (m, CH_2=), 5.16 (m, RCH_2N), 3.37 [s, $(CH_2)_2$]. $^{13}C\{^1H\}$-n.m.r: (125.7 MHz, δ p.p.m.): 200.07 (s, $C_{carbene}$), 133.80 (s, =CH), 118.76 (s, CH_2=), 52.61 (s, RCH_2N), 47.75 [s, $(CH_2)_2$]. I.r.: 1643.3 $\nu(CH_2$=CH), 1508.5 $\nu(CN_2)$, 391.2 ν(Ni—Cl) cm^{-1}. MS (*m*/*z*): 430 (M^+), 395 (M^+—Cl), 360 (M^+—2Cl).

Chloride replacement. (a) Reaction with LiBr

The *trans*-bis-carbenedichloride *(6)* (60 mg, 0.14 mmol) was treated with LiBr (*ca.* 20-fold excess) in Me_2CO at room temp. for 24 h. The solvent was removed *in vacuo*

and the residue was washed with H_2O (3×5 cm^3) and then recrystallised from $CHCl_3$ to give orange crystals of the *trans*-dibromo-bis-(1,3-diallylimidazolidin-2-ylidene)nickel(II) *(7)*, (51 mg, 60%). M.p. 160.0 °C(dec.). ^{1}H-n.m.r. (δ p.p.m.): 6.1 (m, =CH), 5.2 (m, CH_2=), 5.0 (m, RCH_2N), 3.3 [s, $(CH_2)_2$]. $^{13}C\{^1H\}$-n.m.r. (δ p.p.m.): 193.8 (s, $C_{carbene}$), 133.1 (s, =CH), 118.7 (s, CH_2=), 53.5 (s, RCH_2N), 48.1 [s, $(CH_2)_2$]. I.r: 1643.1 ν(CH_2=CH), 1503.1 ν(CN_2), 387.7 ν(Ni—Br) cm^{-1}. MS (*m*/*z*): 518 (M^+), 438 (M^+—Br), 358 (M^+—2Br).

(b) Reaction with NaI

The same procedure as for (a) was employed. Red crystals of the *trans*-diiodo-bis-(1,3-diallylimidazolidin-2-ylidene)nickel(II) *(8)*, (57.6 mg, 67.0%). M.p. 245.0 °C(dec.), were prepared from NaI. ^{1}H-n.m.r. (δ p.p.m.): 6.17 (m, =CH), 5.3 (m, CH_2=), 4.8 (d, RCH_2N), 3.37 [s, $(CH_2)_2$]. $^{13}C\{^1H\}$-n.m.r. (δ p.p.m.): 207.9 (s, $C_{carbene}$), 133.1 (s, =CH), 118.9 (s, CH_2=), 53.3 (s, RCH_2N), 48.3 [s, $(CH_2)_2$]. I.r: 1647.2 ν(CH_2=CH), 1508.4 ν(CN_2) cm^{-1}. MS (*m*/*z*): 612 (M^+), 485 (M^+—I), 358 (M^+—2I).

(c) Reaction with aminal (1)

A benzene solution of the aminal (19 mg, 0.10 mmol) was added with vigorous stirring to a yellow suspension of the palladium complex *(5)* (42.0 mg, 0.087 mmol) in benzene (25 cm^3). The colour gradually faded and a white precipitate formed after agitating the mixture for 5 h at room temperature. The solid was filtered off, washed with cold benzene, evaporated to dryness and then recrystallised from $CDCl_3$ to give white crystals of the chloro*tris*-(1,3-diallylimidazolidin-2-ylidene)palladium(II), *(9)*, (45.0 mg 82.3%). M.p. 180.0 °C(dec.). Spectroscopic data (assigned to two *trans* L^{Allyl} ligands/assigned to a *cis* L^{Allyl} ligand): ^{1}H-n.m.r. (δ p.p.m.): 6.0/5.8 (m, =CH), 5.2–5.3 (m, CH_2=), 4.5 (m, RCH_2N), 3.5 [d, $(CH_2)_2$]. $^{13}C\{^1H\}$-n.m.r. (δ p.p.m.): 199.0/190.4 (d, $C_{carbene}$), 133.6/132.6 (d, =CH), 118.8/119.4 (d, CH_2=), 52.7/53.6 (d, RCH_2N), 48.0/47.8 [d, $(CH_2)_2$]. I.r: 1645.0 ν(CH_2=CH), 1514.3 ν(CN_2) cm^{-1}. MS (*m*/*z*): 628 (M^+).

X-ray data collection and structure determination for (6) and (9)

The crystallographic data and data collection parameters for *(6)* and *(9)* are summarized in Table 1. The X-ray data of both complexes were collected on a Siemens P4/PC diffractometer using MoK_α radiation (λ = 0.71073 Å). Three standard reflections were monitored after every 97 data measurements. The crystal structures were solved by direct methods and successive Fourier syntheses using the SHELXTL 5.03 and SHELX97 systems [12, 13], and refined by full-matrix least-squares with anisotropic thermal parameters for all the non-hydrogen atoms. Atomic coordinates and other crystallographic data have been deposited in to Cambridge crystallographic data centre as supporting information. The CCDC deposition codes are 114490 (6) and 114491 (9).

Results and discussion

Aminal *(1)* has been used to provide an alternative route to carbene compounds when rearrangements

Table 1. Experimental crystallographic data for *(6)* and *(9)*

	(6)	*(9)*
Formula	$C_{18}H_{28}Cl_2N_4Ni$	$C_{27}H_{42}Cl_2N_6Pd$
Colour and habit	Orange, regular	Colourless, irregular
Crystal size (mm)	$0.4 \times 0.2 \times 0.1$	$0.4 \times 0.2 \times 0.2$
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a (Å)	8.2912(9)	8.7918(10)
b (Å)	8.2332(9)	12.731(2)
c (Å)	15.6529(14)	14.533(2)
α (°)		84.307(12)
β (°)	97.898(8)	79.944(11)
γ (°)		85.725(12)
V (Å^3)	1058.38(19)	1591.1(4)
Z	2	2
Temperature (K)	298	298
Radiation (Å)	MoK_α (λ = 0.71073)	MoK_α (λ = 0.71073)
Monochromator	Graphite	Graphite
Scan mode	$\theta/2\theta$	ω
2θ range (°)	3.0–50.0	3.0–55.0
Number of data collected	2599	6273
Unique data (R_{int})	1852 (2.48%)	4082 (5.45%)
Number of data ($Fo > 4.0\sigma(Fo)$)	1453	3317
Completeness	92.9% to 2θ = 50°	55.7% to 2θ = 55°
Absorption correction	Ψ-scans (0.410–0.485)	not applied
Goodness-of-fit	1.022	1.035
R (observed data)	0.0358	0.0637
wR (all data)	0.0931	0.1910

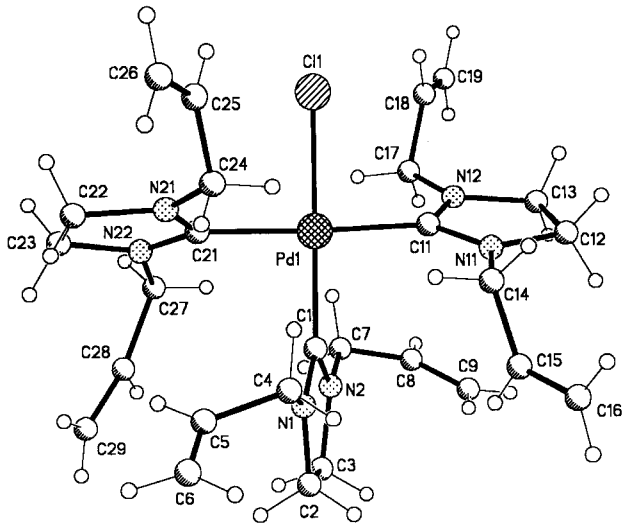

Fig. 1. Molecular structure and atom labelling for complex *(9)*.

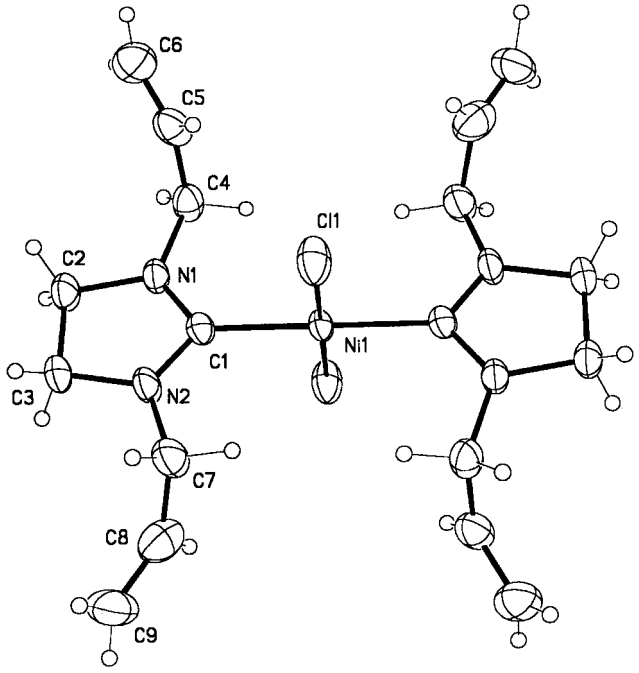

Fig. 2. Molecular structure and atom labelling for complex *(6)*.

are possible. The yields are higher than *in situ* reactions [8].

The i.r. spectra exhibit strong bands in the metal halogen region and characteristic absorptions due to the ligand L^{Allyl}. The mass spectra of the complexes are in agreement with their formulation as metal di-halogen derivatives, showing consecutive peaks corresponding to m/z = $[M^+—X]$, $[M^+—2X]$. The proton and carbon resonances are very similar for the all *trans*-complexes. The imidazolidine ring protons was observed as a singlet resonance, all the protons are equivalent. Compound *(4)* show the characteristic signals of the CH_3 and CH_2 protons in the phosphine ligand. The most characteristic spectroscopic feature in the ^{13}C-n.m.r. spectrum is the signals for the carbene carbon atoms which fall in the range expected for other nickel(II) and palladium(II) carbene complexes [5]. The ^{1}H- and ^{13}C-signals for the complex *(9)* are more complicated (*e.g.*, two signals for carbene carbon atoms) and a crystal structure determination was therefore undertaken in order to clarify its assignment.

X-ray structure of (6) and (9)

The molecular structures and the numbering schemes are given in Figures 1 and 2. Selected bond distances and bond angles are listed in Table 2 and 3. Conclusive evidence for the existence of the *tris*-carbene complex is finally produced by an X-ray analysis of *(9)*. In spite of the poor quality of the data [14] the overall geometry of a central palladium atom surrounded by one chloride atom and three five-membered rings approximately orthogonal to the square plane of the complex is reliably defined (Figure 1). The average values of the ring dimensions compare favorably with those determined for the *trans*-$[PdCl_2(L^{Allyl})_2]$ [15], complex *(5)* (configuration confirmed by X-ray analysis) [16]. In both cases, the metal-to-carbene distances [C(11)—Pd—C(21), mean 2.04 Å] are only slightly shorter than the estimated M—Csp^2 single-bond lengths [Pd—C, 2.05 Å], precluding any possibility of π interaction between the metal and the carbene ligands. In this connection the length of the Pd—Cl bond

Table 2. Selected bond lengths (Å) and angles (°) for *(9)*

Bond lengths			
Pd(1)—C(1)	2.002(11)	Pd(1) —C(11)	2.029(6)
Pd(1)—C(21)	2.053(6)	Pd(1)—Cl(1)	2.357(3)
C(1)—N(2)	1.332(11)	C(1)—N(1)	1.351(10)
C(11)—N(12)	1.328(8)	C(11)—N(11)	1.345(10)
C(21)—N(22)	1.305(8)	C(21)—N(21)	1.328(10)
Bond angles			
C(1)—Pd(1)—C(11)	91.6(4)	C(1)—Pd(1)—C(21)	91.4(4)
C(11)—Pd(1)—C(21)	176.7(3)	C(1)—Pd(1)—Cl(1)	179.07(19)
C(11)—Pd(1)—Cl(1)	88.5(3)	C(21)—Pd(1)—Cl(1)	88.5(3)
N(2)—C(1)—N(1)	107.0(9)	N(2)—C(1)—Pd(1)	126.0(6)
N(1)—C(1)—Pd(1)	127.0(7)	N(12)—C(11)—N(11)	108.7(5)
N(12)—C(11)—Pd(1)	126.7(6)	N(11)—C(11)—Pd(1)	124.5(5)
N(22)—C(21)—N(21)	110.3(6)	N(22)—C(21)—Pd(1)	125.5(6)
N(21)—C(21)—Pd(1)	124.1(5)		

Table 3. Selected bond lengths (Å) and angles (°) for *(6)*

Bond lengths			
Ni(1)—Cl(1)	2.1751(9)	Ni(1)—C(1)	1.917(3)
C(1)—N(1)	1.330(4)	C(1)—N(2)	1.324(4)
N(1)—C(2)	1.460(4)	N(1)—C(4)	1.444(4)
C(2)—C(3)	1.519(4)	C(3)—N(2)	1.467(3)
N(2)—C(7)	1.460(4)	C(4)—C(5)	1.487(5)
C(5)—C(6)	1.290(5)	C(7)—C(8)	1.440(5)
C(8)—C(9)	1.318(6)		
Bond angles			
Cl(1)—Ni(1)—C(1)	90.61(9)	Cl(1)—Ni(1)—Cl(1)#1	180.0
C(1)—Ni(1)—C(1)#1	89.39(9)	Cl(1)—Ni(1)—C(1)#1	89.39(9)
C(1)—Ni(1)—C(1)#1	180.0	Cl(1)#1—Ni(1)—C(1)#1	90.61(9)
Ni(1)—C(1)—N(1)	125.7(2)	Ni(1)—C(1)—N(2)	126.0(2)
N(1)—C(1)—N(2)	108.3(2)		

[2.357(3) Å] is greater than that of the *trans*-[$PdCl_2$-(L^{Allyl})$_2$] complex [2.306(1) Å], reflecting the high *trans* influence of the carbene ligand. On the other hand, Figure 2 clearly shows that coordination around the metallic center is square-planar, in agreement with the observed diamagnetism of complex *(6)*. The observed Ni—C(1) bond length [1.917(3) Å] is appropriate for a Ni—carbene bond [17–21]. Bond angles around the carbene carbon atom, N(1)—C(1)—N(2) [108.3(2)], N(1)—C(1)—Ni(1) [125.7(2)] and N(2)—C(1)Ni(1) [126.0(2)°] suggest, as previously found [22], sp^2 hybridization for this atom. Slightly shorter Ni—Cl bond lengths [2.175(9) Å], compared to that reported [23] for the phosphine complex $NiCl_2(PPh_3)_2$ [2.2075(2) Å], denote the poor π-acceptor and the marked σ-donor qualities of the L^{Allyl} ligand. Both equivalent five-membered rings for the L^{Allyl} ligands given a planar conformation for which a dihedral angle of 0° is observed. All bond distances and angles in the L^{Allyl} moiety fall in the expected range and are similar, for example, to those observed for *trans*-[$PdCl_2$(L^{Allyl})$_2$] [16]. Nevertheless, distances C(1)—N(1, 2) [1.330(4), 1.324(4) Å] are slightly shortened in comparison with the free acetanilide [1.35(3) Å] [24]. This difference can be interpreted as being due to incipient π character for the $C_{carbene}$—N bond in the complex.

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Supporting information available

For *(6)* and *(9)*, Tables giving details of the crystallographic data collection, full sets of bond lengths and angles, anisotropic displacement coefficients, H-atom coordinates, and displacements coefficients (32 pages) are available. Ordering information is given on any current masthead page.

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