

A nonenolizable imino-*N*-heterocyclic carbene ligand and corresponding silver (I) metal complex

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Abstract

The nonenolizable imino-*N*-heterocyclic carbene ligand precursor [1-*t*-butylimidazolium-3-{C(Ph)=N(Ph)}] chloride has been synthesised. The corresponding silver (I) complex Ag(C[^]imine)Cl; where C[^]imine = [1-*t*-butylimidazolium-2-ylidene-3-{C(Ph)=N(Ph)}], was prepared by reaction with Ag₂O. All of the compounds have been structurally characterized by single crystal X-ray diffraction.

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1. Introduction

Since their isolation [1], *N*-heterocyclic carbenes (NHCs) have attracted attention as new class of ligands in organo-transition metal chemistry [2–9]. The potential of NHC ligands for application in homogeneous catalysis [3,10] and their similarities with the more ubiquitous tertiary phosphines are well documented [4]. Metal complexes containing NHC ligands have demonstrated catalytic activity in hydrosilylation [11], ring opening and closing metathesis [12], cross-coupling [13–15], atom transfer radical polymerization [16] and carbon monoxide/ethylene copolymerisation reactions [17].

Our interests lie in the synthesis and reactivity of heteroditopic ligands that incorporate nitrogen or oxygen donor atoms along with strong donors such as tertiary phosphines [18,19] and carbenes [20,21]. Recently, we reported the synthesis of imino-*N*-hetero-

cyclic carbene ligands, of the type [1-(2,4,6-Me₃-C₆H₂)imidazol-2-ylidene-3-{CH₂C(*t*-Bu)=N(*i*-Pr)}], coordinated to silver (I) and ligand transfer to palladium (II) and rhodium (I). Interestingly, upon ligand transfer, tautomerisation of the imine moiety occurred and the corresponding enamine, [1-(2,4,6-Me₃-C₆H₂)imidazol-2-ylidene-3-{CH=C(*t*-Bu)NH(*i*-Pr)}], was observed to be coordinated to the metal centre, Fig. 1 [21]. Thus, herein we report the synthesis and reactivity of a new nonenolizable non-cyclic imino-*N*-heterocyclic carbene ligand precursor and the corresponding silver (I) metal complex.

2. Results and discussion

2.1. Synthesis and characterisation of the ligand precursor 3-(1-phenyliminophenylmethylene)-1-*tert*-butylimidazolium chloride (I)

The nonenolizable imine-imidazolium salt **1** was prepared by the reaction of the imidoyl chloride

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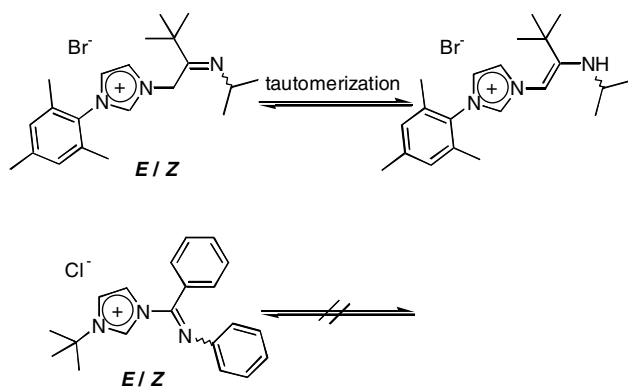
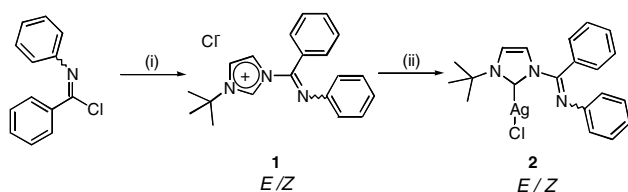


Fig. 1. Enolizable and nonenolizable bidentate imino-*N*-heterocyclic carbene ligand precursors.



Scheme 1. (i) *t*-butyl imidazole; (ii) Ag₂O.

ClC(Ph)=N(Ph) with 1-*tert*-butylimidazole in THF, **Scheme 1**. The reaction was rapid with a white precipitate, compound **1**, formed upon heating to 60 °C. The imidazolium salt **1** was isolated, washed with THF, and characterized by ¹H and ¹³C{¹H} NMR spectroscopy, mass spectrometry (ES⁺ in MeCN), elemental analysis and single crystal X-ray diffraction. The ¹H NMR (CD₂Cl₂) spectrum showed the presence of two geometric isomers (*E/Z*) in a 1:8 ratio as evidenced by the presence of two *t*-butyl resonances at δ 1.58 and 1.83, respectively. Saturation transfer experiments indicated that the two isomers were exchanging in solution albeit slow on the NMR timescale precluding any detailed analysis. The *E/Z* exchange process was completely halted at –40 °C and NOE difference experiments, centred on the imidazolium proton (–NCHN–) resonance, recorded at this temperature suggested the *Z* isomer to be the major species in solution. The central imidazolium proton (NCHN) resonance is at δ 9.56 for the *Z* isomer and at δ 10.35 for the *E* isomer with the remainder heterocyclic ring protons (NCHCHN) at δ 7.56 and 8.35 for *Z* and δ 8.30 for the *E* isomer. In the ¹³C{¹H} NMR (CD₂Cl₂) the central imidazolium carbon resonance is at δ 134.2. Full ¹H and ¹³C NMR assignments are given in Section 3.

Crystals of **1** suitable for single-crystal X-ray diffraction were grown from a mixture dichloromethane and diethyl ether. An ORTEP view of the molecular structure is shown in **Fig. 2** and crystallographic data given in **Table 1**. Selected bond lengths and angles are listed in **Table 2**. In the solid state the imidazolium salt **1**

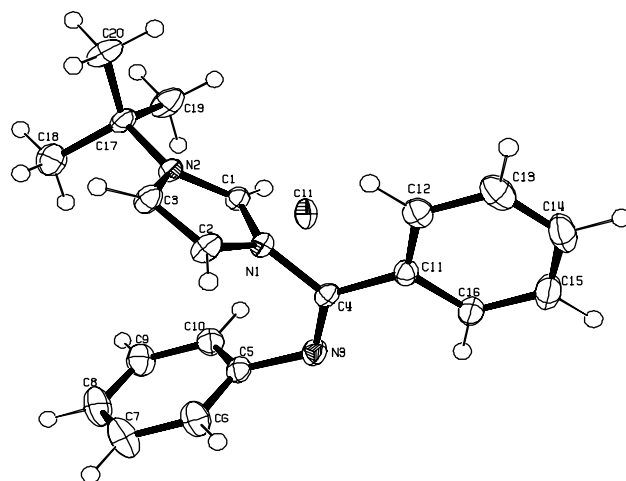


Fig. 2. ORTEP diagram of the molecular structure of **1**. Thermal displacement parameters are set at 40%.

adopts the *Z*-isomer configuration, the major isomer identified in solution. The C(4)–N(3) bond length of 1.261(2) Å is consistent with significant double bond character and is comparable to the C=N bond length in *N*-(diphenylmethylene)aniline, Ph₂C=NPh, and [1-(2,4,6-Me₃C₆H₂)imidazolium-3-{CH₂C(*t*-Bu)=N(*i*-Pr)}], of 1.287 Å [22] and 1.267(2) Å [21], respectively. Similarly, the bond angles at both C(4) and N(3) are indicative of sp² centres. The N(1)–C(1)–N(2) bond angle in the imidazolium ring is 108.08(13)° which is typical of an imidazolium salt [21–24]. The remainder of the bond lengths and angles are unexceptional and lie within the expected range.

2.2. Synthesis and characterization of the Ag(I) carbene complex **2**

Silver (I) NHC complexes are known to be effective reagents for the transfer of carbene ligands to palladium, gold and rhodium [25–31]. The use of transfer agents is particular important when the free NHC ligand cannot be generated cleanly by the deprotonation of the imidazolium salt with a strong base. This failure is often as a result of the presence of base sensitive functional groups. All attempts to deprotonate the ligand precursor **1** with strong bases failed to form the free carbene cleanly. Thus, to be able to prepare imino-NHC group 10 metal complexes containing imino-NHC ligands in the future, it was necessary to prepare the Ag(I) complex [AgCl(C_{limine})] (**2**), where C_{limine} = 3-(1-Phenylimino-phenylmethylene)-1-*tert*-butylimidazol-2-ylidene. Complex **2** was readily prepared by reaction of **1** with Ag₂O, **Scheme 1**. The silver complex [AgCl(C_{limine})] (**2**) was characterized by ¹H and ¹³C{¹H} NMR spectroscopy, elemental analysis and single crystal X-ray diffraction. ¹H NMR spectroscopy once again showed the

Table 1
Summary of crystallographic data for compounds **1** and **2**

Compounds	1	2
Empirical formula	C ₂₀ H ₂₂ ClN ₃	C ₂₀ H ₂₁ AgClN ₃
<i>M_r</i>	339.87	446.73
<i>T</i> /K	150	150
λ /Å	0.71073	0.71073
Crystal system	Rhombohedral	Triclinic
Space group	<i>R</i> $\bar{3}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	21.4097(4)	9.7563(2)
<i>b</i> /Å	21.4097(4)	9.8967(2)
<i>c</i> /Å	20.9242(4)	10.6436(3)
α /°	90	101.1943(9)
β /°	90	98.6782(9)
γ /°	120	109.1389(12)
<i>V</i> /Å ³	8306.2	926.55
<i>Z</i>	18	2
<i>D_c</i> /Mg m ⁻³	1.223	1.601
μ /mm ⁻¹	0.212	1.239
<i>F</i> ₀₀₀	3242.724	450.138
Crystal size/mm	0.30 × 0.34 × 0.34	0.02 × 0.04 × 0.22
Description of crystal	Colourless block	Colourless needle
Absorption correction	Semi-empirical from equivalent reflections	Semi-empirical from equivalent reflections
Transmission coefficients (min., max.)	0.93, 0.94	0.76, 0.98
θ Range for data collection/°	5.0 ≤ θ ≤ 27.5	5.0 ≤ θ ≤ 27.5
Index ranges, <i>hkl</i>	−27 to 13, 0 to 27, 0 to 26	−12 to 12, −12 to 12, 0 to 13
Reflections measured	15419	13966
Unique reflections	4192	4206
<i>R</i> _{int}	0.029	0.038
Observed reflections (<i>I</i> > 3 σ (<i>I</i>))	2936	3384
Refinement method	Full-matrix least-squares on <i>F</i>	Full-matrix least-squares on <i>F</i>
Parameters refined	217	227
Weighting scheme	Chebyshev three-term polynomial	Chebyshev three-term polynomial
Goodness-of-fit	1.0547	1.0992
<i>R</i>	0.0393	0.0290
<i>wR</i>	0.0426	0.0314
Residual electron density (min., max.)/e Å ⁻³	−0.28, 0.28	−0.60, 0.54

presence of two species in solution in an approximate 3:1 ratio which are attributed to the *Z*- and *E*-isomers respectively. The ¹H NMR spectrum (CD₂Cl₂) of **2** is consistent with the coordination of the carbene carbon of the imino-NHC ligand to the Ag(I) metal centre with the disappearance of the central NCHN imidazolium proton resonance observed in **1**. Similarly, the remaining heterocyclic ring protons (NCHCHN) are now shifted to lower frequencies (δ 7.22 and 7.35 for the *Z*-isomer and δ 6.92 and 7.25 for the *E*-isomer) indicative of carbene formation and coordination. Unfortunately, as with the complex [Ag(1-(2,4,6-Me₃C₆H₂)imidazol-2-ylidene-3-{CH=C(*t*-Bu)NH(*i*-Pr)}₂)]AgBr₂ [21], the carbene resonance was not observed in the ¹³C{¹H} NMR spectrum. Full ¹H and ¹³C NMR assignments are given in Section 3.

The molecular structure of **2**, Fig. 3, determined by single crystal X-ray diffraction further supports the coordination of the ligand to the metal centre. Crystals of **2** suitable for diffraction were grown by slow diffusion of diethyl ether into a dichloromethane solution. A summary of crystallographic data are given in Table 1 and

selected bond lengths and angles are listed in Table 2. Silver (I) complexes with NHC ligands are known to adopt a variety of different coordination environments in the solid state including mononuclear complexes, with either one or two carbenes coordinated to the metal centre, binuclear complexes containing halide bridges and even polynuclear complexes [25–31]. Complex **2** was found to be a mononuclear complex with one imino-carbene ligand coordinated to the metal centre with the ligand adopting the *Z* conformation.

The C(4)–N(3) imine bond length is 1.268(4) Å (cf. 1.261(2) Å for the imidazolium salt **1**) and consistent with double bond character. The Ag(1)–C(1) bond distance (2.093(3) Å) is consistent with other reported silver–carbene complexes [26].

In summary, a new nonenolizable imino-*N*-heterocyclic carbene ligand precursor has been prepared along with the corresponding silver (I) carbene complex and both structurally characterised. Further studies are now underway to use the silver (I) metal complex as a carbene transfer agent to prepare group 9 and 10 metal carbene complexes

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

Compound 1	
C(1)–N(1)	1.338(2)
C(1)–N(2)	1.328(2)
N(1)–C(2)	1.387(2)
N(1)–C(4)	1.4611(19)
C(2)–C(3)	1.348(2)
C(3)–N(2)	1.392(2)
N(2)–C(17)	1.5034(19)
C(4)–N(3)	1.261(2)
N(1)–C(1)–N(2)	108.08(13)
C(1)–N(1)–C(2)	109.21(13)
C(1)–N(1)–C(4)	123.11(13)
N(1)–C(2)–C(3)	106.56(14)
C(2)–C(3)–N(2)	107.33(14)
C(1)–N(2)–C(3)	108.79(13)
N(1)–C(4)–N(3)	120.23(14)
N(1)–C(4)–C(11)	116.28(13)
C(4)–N(3)–C(5)	119.95(13)
Compound 2	
Ag(1)–Cl(1)	2.3314(8)
Ag(1)–C(1)	2.093(3)
C(1)–N(2)	1.346(4)
C(1)–N(1)	1.364(4)
N(2)–C(3)	1.390(4)
N(2)–C(17)	1.516(4)
C(2)–C(3)	1.347(4)
C(2)–N(1)	1.388(4)
N(1)–C(4)	1.445(4)
C(4)–N(3)	1.268(4)
Cl(1)–Ag(1)–C(1)	175.73(8)
Ag(1)–C(1)–N(2)	133.2(2)
Ag(1)–C(1)–N(1)	121.9(2)
N(1)–C(1)–N(2)	104.5(2)
C(1)–N(2)–C(3)	111.1(2)
C(1)–N(2)–C(17)	124.8(2)
N(2)–C(3)–C(2)	107.0(3)
C(3)–C(2)–N(1)	106.4(3)
C(1)–N(2)–C(3)	111.0(2)
C(1)–N(1)–C(4)	124.6(2)
N(1)–C(4)–N(3)	123.7(3)

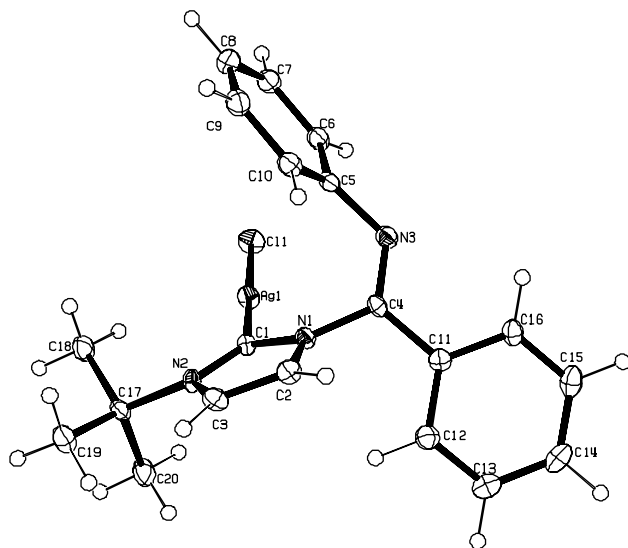


Fig. 3. ORTEP diagram of the molecular structure of **2**. Thermal displacement parameters are set at 40%.

3. Experimental

3.1. General procedures

All manipulations were performed under dinitrogen using standard Schlenk techniques or in an inert atmosphere glove box. All solvents were dried by passage through an alumina column under a positive pressure of dinitrogen and deoxygenated by bubbling dry dinitrogen through the dried solvents for twenty minutes before use. NMR spectra were recorded on either a Varian Unity Plus 500 (^1H at 500 MHz, ^{13}C at 125.7 MHz) or on a Varian Mercury 300 (^1H at 300 MHz, ^{13}C at 75.5 MHz) spectrometer and are at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio-solvent (^1H) and solvent (^{13}C) resonances and chemical shifts were reported with respect to $\delta = 0$ for tetramethylsilane. Electrospray mass spectra were recorded in acetonitrile on a Micromass LC TOF spectrometer. Microanalyses were performed by the microanalytical laboratory of the Inorganic Chemistry Laboratory, University of Oxford.

All reagents were purchased from Aldrich and used as received unless otherwise stated. The reagent 1-*tert*-butylimidazolidazole [32] was prepared using published procedures. The Imidoyl chloride was prepared by heating the starting amide and phosphorous pentachloride under vacuum in the absence of solvent [33,34].

3.2. Preparations

3.2.1. 3-(1-Phenyliminophenylmethylene)-1-*tert*-butylimidazolium chloride (**1**)

tert-Butylimidazole (5.25 g, 42 mmol) was added to an empty Schlenk in a nitrogen glove box. Subsequently, 40.0 mL of dry THF was added to the Schlenk followed by the phenyl imidoyl chloride (9.1 g, 42 mmol). The reaction mixture was stirred under nitrogen at 60 °C for 2 h, during which time the product was formed as a white precipitate. The precipitate was filtered, washed with dry THF (3×10.0 mL) and dried under vacuum. Yield: 12.4 g (86%) Elemental Analysis (%): Found (Calc.) C, 69.93 (70.68); H, 6.55 (6.52); N, 12.34 (12.36). MS (ES+) (CH_3CN): $m/z = 304.1$ [M^+] (100%). Crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether through a dichloromethane solution. The ^1H NMR showed the presence of two geometric isomers (*E/Z*) in a roughly 1:8 ratio.

3.2.2. ^1H NMR (*Z*-isomer (major)) (500 MHz, 293 K, CD_2Cl_2)

1.83 (s, 9H, *t*-butyl), 6.86 (d, $J = 7.5$ Hz, 2H, *N*-phenyl $\text{H}_{2,6}$), 7.08 (t, $J = 7.5$ Hz, 1H, *N*-phenyl H_4), 7.22 (t, $J = 7.7$ Hz, 2H, *N*-phenyl $\text{H}_{3,5}$), 7.43 (t, $J = 7.6$ Hz, 2H, *C*-phenyl $\text{H}_{3,5}$), 7.51 (t, $J = 7.6$ Hz, 1H, *C*-phenyl H_4),

7.54 (dd, $^3J_{\text{HH}} = 7.5$ Hz, $^4J_{\text{HH}} = 1.4$ Hz, 2H, C-phenyl H_{2,6}), 7.56 (t, $J = 1.7$ Hz, 1H, –NCHCHN–), 8.35 (t, $J = 1.9$ Hz, 1H, –NCHCHN–), 9.56 (t, $J = 1.4$ Hz, 1H, –NCHN–).

3.2.3. ^1H NMR (*E*-isomer (minor)) (500 MHz, 293 K, CD₂Cl₂)

1.58 (s, 9H, *t*-butyl), 6.97 (d, $J = 7.7$ Hz, 2H, *N*-phenyl H_{2,6}), 7.22 (t, $J = 7.6$ Hz, 2H, *N*-phenyl H_{3,5}), 7.62 (t, $J = 7.4$ Hz, 1H, C-phenyl H₄), 7.86 (d, $J = 7.7$ Hz, 2H, C-phenyl H_{2,6}), 8.30 (s + br, 2H, –NCHCHN–), 10.35 (s + br, 1H, –NCHN–).

3.2.4. $^{13}\text{C}\{^1\text{H}\}$ NMR (*Z*-isomer (major)) (75.5 MHz, 293 K, CD₂Cl₂)

29.9 (s, *t*-butyl), 62.1 (s, *t*-butyl-C), 121.0 (s, –NCHCHN–), 12.9 (s, –NCHCHN–), 121.6 (s, *N*-phenyl-C_{2,6}), 125.8 (s, *N*-phenyl-C₄), 127.4 (s, C=N), 129.2 (s, *N*-phenyl-C_{3,5}), 129.6 (s, C-phenyl-C_{3,5}), 130.3 (s, C-phenyl-C_{2,6}), 132.3 (s, C-phenyl-C₄), 134.2 (s, NCHN), 145.5 (s, C-phenyl-C₁), 149.4 (s, *N*-phenyl-C₁).

3.2.5. 3-(1-phenyliminophenylmethylene)-1-*tert*-butylimidazol-2-ylidene silver (*I*) chloride (**2**)

The phenyl imidazolium salt (1.0 g, 2.9 mmol) was dissolved in ca. 20.0 mL of dry dichloromethane and the solution added, under nitrogen, to a Schlenk containing activated powdered 4A molecular sieves. Silver (*I*) oxide (0.54 g, 2.3 mmol) was then added and the reaction mixture stirred in the absence of light for 12 h. The reaction mixture was then filtered in the dark and the volume of the solution reduced to 3.0 mL. Pentane (10.0 mL) was added to afford the product as an off-white light sensitive solid. ^1H NMR showed the presence of two geometric isomers (*E/Z*) in a roughly 1:3 ratio. Yield: 0.98 g (76%) Elemental Analysis (%) Found (Calc.): C, 53.28 (53.77); H, 4.79 (4.73); N 9.27 (9.41). Crystals suitable for X-ray analyses were grown by slow diffusion of diethyl ether through a dichloromethane solution.

3.2.6. ^1H NMR (*Z*-isomer (major)) (500 MHz, 293 K, CD₂Cl₂)

1.71 (s, 9H, *t*-butyl), 6.74 (d, $J = 7.9$ Hz, 2H, C-phenyl H_{2,6}), 7.02 (tt, $^3J_{\text{HH}} = 7.5$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 1H, C-phenyl H₄), 7.17 (td, $^3J_{\text{HH}} = 8.1$ Hz, $^4J_{\text{HH}} = 1.8$ Hz, 2H, C-phenyl H_{3,5}), 7.19 (dd, $^3J_{\text{HH}} = 7.8$ Hz, $^4J_{\text{HH}} = 1.6$ Hz, 2H, *N*-phenyl H_{2,6}), 7.22 (d, $J = 1.8$ Hz, 1H, –NCHCHN–), 7.35 (d, $J = 1.8$ Hz, 1H, –NCHCHN–), 7.38 (t, $J = 7.9$ Hz, 2H, *N*-phenyl H_{3,5}), 7.46 (t, $J = 7.6$ Hz, 2H, *N*-phenyl H₄).

3.2.7. ^1H NMR (*E*-isomer (minor)) (500 MHz, 293 K, CD₂Cl₂)

1.59 (s, 9H, *t*-butyl), 6.76 (d + br, 2H, C-phenyl H_{2,6}), 6.96 (d, $J = 1.9$ Hz, 1H, –NCHCHN–), 7.07 (tt,

$^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 1H, C-phenyl H₄), 7.22 (br, 2H, C-phenyl H_{3,5}), 7.25 (d, $J = 1.9$ Hz, 1H, –NCHCHN–), 7.51 (t, $J = 7.6$ Hz, 2H, *N*-phenyl H_{3,5}), 7.63 (tt, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, 1H, *N*-phenyl H₄), 7.74 (dd, $^3J_{\text{HH}} = 7.4$ Hz, $^4J_{\text{HH}} = 1.3$ Hz, 2H, *N*-phenyl H_{2,6}).

3.2.8. $^{13}\text{C}\{^1\text{H}\}$ NMR (*Z*-isomer (major)) (75.5 MHz, 293 K, CD₂Cl₂)

31.9 (s, *t*-butyl-CH₃), 60.0 (s, *t*-butyl-C), 119.4 (s, –NCHCHN–), 120.8 (s, –NCHCHN–), 121.3 (s, C-phenyl-C_{2,6}), 124.8 (s, C-phenyl-C₄), 129.1 (s, *N*-phenyl-C_{3,5}), 129.4 (s, C-phenyl-C₁), 129.5 (s, *N*-phenyl-C_{2,6}), 129.9 (s, C-phenyl-C_{3,5}), 131.8 (s, *N*-phenyl-C₄), 146.8 (s, *N*-phenyl-C₁), 154.2 (s, C=N).

4. X-ray crystallography

Crystals were isolated under an atmosphere of dinitrogen, covered with perfluoropolyether oil, and mounted on the end of a glass fibre. Crystal data are summarised in Table 1.

Data were collected at 150 K on Enraf-Nonius KapkaCCD diffractometer (graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å) as summarised in Table 1. Intensity data were processed using the DENZO-SMN package [35]. The crystal structures were solved using direct-methods program SIR92 [36], which located all non-hydrogen atoms. Subsequent full-matrix least-squares refinement was carried out using the CRYSTALS [37] program suite. Coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were positioned geometrically after each cycle of refinement. A three-term Chebychev polynomial weighting scheme was applied. Crystal structure diagrams were produced using the CRYSTALS program suite.

For the silver complex **2** initial attempts to index the diffraction pattern were unsuccessful, however, careful analysis of the data showed that the crystal was a twin. The two components of the twin were found to be related by a 180° rotation about the crystallographic *a*-axis.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 272970 for compound **1** and 272971 for complex **2**.

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