Palladium(II)- and rhodium(I)-*N*-heterocyclic carbene complexes derived from menthol: synthesis and characterisation

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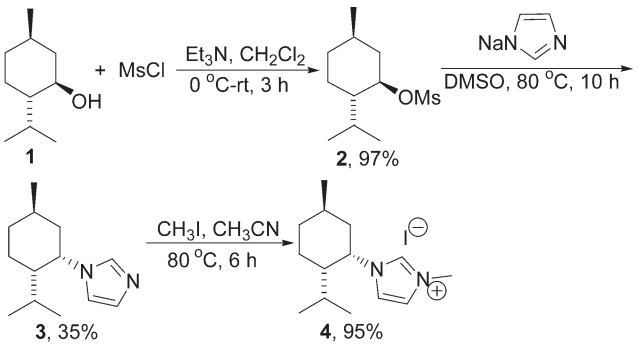
A carbene-Pd(II) complex and a carbene-Rh(I) complex, both derived from commercially available *L*-(–)-menthol, have been synthesised, characterised and their X-ray single-crystal structures determined.

Keywords: *N*-heterocyclic carbene, palladium complex, rhodium complex, menthol, X-ray structures

N-heterocyclic carbene (NHC) and their metal complexes have drawn increasing attention since the isolation of the first free carbene by Arduengo and co-workers in 1991.[1–9] Recently, we have become interested in synthesising metal–NHC complexes derived from naturally-occurring materials and investigating their applications toward carbon–carbon bond formation reactions. For instance, some novel Pd(II)– and Rh(I)–NHC complexes have been synthesised from *L*-proline and their coordination patterns have been unambiguously determined by X-ray single-crystal diffraction. In addition, some of them have been found to be versatile catalysts in the formation of carbon–carbon bonds.[10–15] These results prompted us to further synthesise metal–NHC complexes derived from other naturally-occurring materials and we considered the synthesis of Pd(II)– and Rh(I)–NHC complexes derived from menthol. As far as we know, this is the first example of metal–NHC complexes derived from menthol. We now report these results in detail.

The synthetic route for the menthol-based imidazolium salt **4** is shown in Scheme 1. First, treatment of commercially available *L*-(–)-menthol **1** with methanesulfonyl chloride (MsCl) using Et_3N as the base gave ester **2** in 97% yield.[16] Subsequently, ester **2**, by nucleophilic attack of imidazole sodium salt, was transformed to imidazole derivative **3** in 35% yield. The lower yield of this step may be due to the elimination reaction of ester **2** under identical conditions, which phenomenon was also confirmed by GC-MS. Finally, reaction of compound **3** with methyl iodide gave the target imidazolium salt **4** in 95% yield.

The Pd(II)-NHC complex **5** was obtained *via* the transmetallation route with Ag_2O.[17] Treatment of imidazolium salt **4** with Ag_2O under exclusion of light for 3 h at room temperature, followed by addition of [$PdCl_2$(COD)] (COD = 1,5-cyclooctadiene) to the solution of the *in situ* formed Ag(I)–NHC complex, gave the Pd(II)–NHC complex **5**, as a mixture of *cis*- and *trans*-isomers in the ratio of about 5:3, in 78% yield (Scheme 2).



Scheme 1 Synthesis of imidazolium salt **4**.

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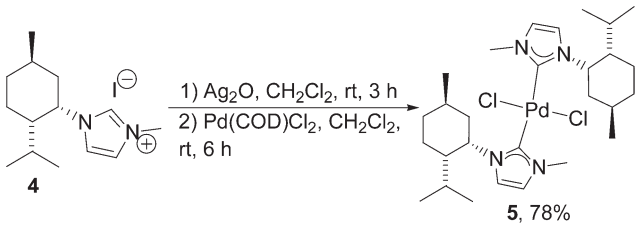
Complex **5** was fully characterised by ^{1}H NMR, ^{13}C NMR, IR, MS and elemental analysis. Furthermore, the structure of complex **5** was unambiguously determined by X-ray single-crystal diffraction (Fig. 1) and its CIF data are presented in CCDC with number 870690.

As can be seen from Fig. 1, the Pd(II) centre is coordinated by two carbene ligands, along with the two chlorine atoms to furnish the nearly square-planar coordination sphere. Representative data of bond distances and angles for this complex are also shown in Fig. 1.

Complex **6** was obtained in 86% yield using a similar procedure to that used for the synthesis of complex **5** (Scheme 3).

Complex **6** was also fully characterised by ^{1}H NMR, ^{13}C NMR, IR, MS and elemental analysis. Furthermore, the structure of complex **6** was also unambiguously determined by X-ray single-crystal diffraction (Fig. 2) and the crystal data of complex **6** has been deposited in CCDC with number 870676.

As can be seen from Fig. 2, a Rh(I)–NHC complex was obtained in this case. The Rh(I) centre is bound to one chlorine



Scheme 2 Synthesis of complex **5**.

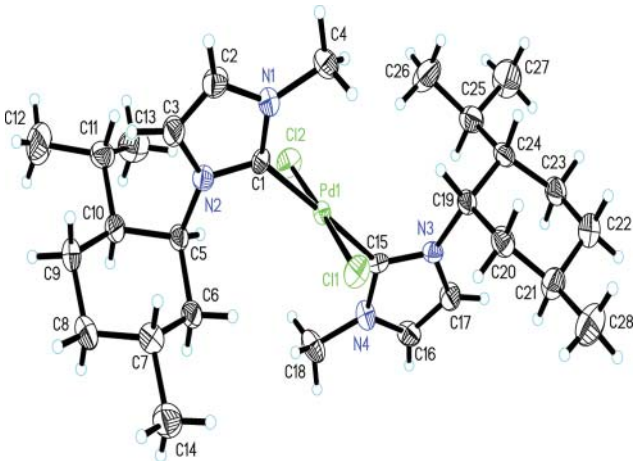
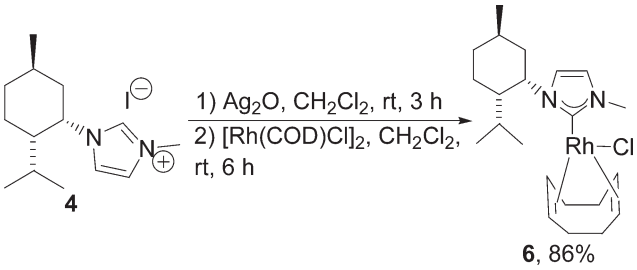


Fig. 1 ORTEP drawing of complex **5** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Pd_1–C_1 = 2.019(5), Pd_1–C_{15} = 2.023(5), Pd_1–Cl_2 = 2.3069(13), Pd_1–Cl_1 = 2.3121(14), C_1–Pd_1–C_{15} = 178.5(2), C_1–Pd_1–$C1_2$ = 91.18(15), C_{15}–Pd_1–Cl_2 = 88.34(15), C_1–Pd1–Cl_1 = 88.58(15), C_{15}–Pd_1–Cl_1 = 91.85(15), Cl_2–Pd_1–Cl_1 = 178.22(7).



Scheme 3 Synthesis of complex **6**.

atom and one carbene ligand and two alkene groups from COD in a pseudosquare-planar geometry with the average Rh–C (COD) bond distance of 2.141(10) Å and the Rh–Cl bond distance of 2.375(7) Å. The Rh–C (carbene) bond distance is 2.03(2) Å, which is typical for Rh–C σ-bonds with very little back-donation.[18] Representative data of bond distances and angles for this complex are also shown in Fig. 2.

Crystal data for complexes **5** and **6** were collected at 273(2) K and 298(2) K, respectively, on a Bruker APEX CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). Both of the structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL-97 program package.[19] All the H atoms were positioned geometrically and refined using a riding model. The final difference Fourier maps showed no peaks of chemical significance. Details of the crystal parameters, data collection and refinement are summarised in Table 1.

In conclusion, two new Pd(II)–NHC and Rh(I)–NHC complexes derived from commercially available *L*-(–)-menthol have been successfully synthesised. Both of them have been fully characterised by ^{1}H NMR, ^{13}C NMR, MS, IR, elemental analysis and X-ray single-crystal diffraction. Further investigations on the applications of these two complexes in organic synthesis are underway in this laboratory.

Table 1 Details of the crystal parameters, data collection and refinement for complexes **5** and **6**

Crystal data	**5**	**6**
Empirical formula	$C_{28}H_{48}Cl_2N_4Pd$	$C_{22}H_{36}ClN_2Rh$
Formula weight	618.00	466.89
T (K)	273(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	P2(1)2(1)2(1)	P21
Unit cell dimensions		
a (Å)	7.5385(4)	9.6529(14)
b (Å)	14.7417(9)	10.8200(16)
c (Å)	28.0534(16)	11.1327(16)
α (°)	90	90
β (°)	90	105.369(2)
γ (°)	90	90
V (Å^3)	3117.6(3)	1121.2(3)
Z	4	2
Calculated density (Mg m^{-3})	1.317	1.383
Absorpation coefficient (mm^{-1})	0.789	0.889
F(000)	1296	488
Crystal size (mm^3)	0.35×0.26×0.20	0.30×0.19×0.13
θ-Range for data collection (°)	1.45 to 26.00	1.90 to 25.20
Limiting indices	$-9\le h\le 9$ $-12\le k\le 18$ $-33\le l\le 34$	$-11\le h\le 11$ $-9\le k\le 12$ $-12\le l\le 13$
Reflections collected	17695	4712
Independent reflections (R_{int})	6122 (0.0248)	2676 (0.0482)
Absorption correction	Empirical	Semi-empirical
Max. and min. transmission	1.00 and 0.70	0.8932 and 0.7764
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6122/0/325	2676/148/236
Goodness-of-fit on F^2	1.302	1.248
Final R indices [I>2σ(I)]	R^1 = 0.0532, wR^2 = 0.1255	R^1 = 0.1282, wR^2 = 0.2852
R indices (all data)	R^1 = 0.0557, wR^2 = 0.1305	R^1 = 0.1328, wR^2 = 0.2872
Absolute structure parameter	0.01 (5)	0.1(2)
Largest diff. peak and hole	0.912 and −1.201 e·Å^{-3}	1.201 and −973 e·Å^{-3}

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-III 500 MHz spectrometer for solutions in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J*-values are in Hz. Mass spectra were recorded with a Thermo Finnigan LCQ Advantage instrument (ESI). Satisfactory CHN microanalyses were obtained *via* a Carlo-Erba 1106 analyser. X-ray diffraction analysis was performed on a Bruker Smart APEX CCD X-ray diffraction meter. Et_3N, CH_3CN, DMSO and CH_2Cl_2 were distilled from CaH_2 under a nitrogen (N_2) atmosphere. Commercially obtained reagents were used without further purification. Flash column chromatography was carried out using Huanghai 300-400 mesh silica gel at increased pressure.

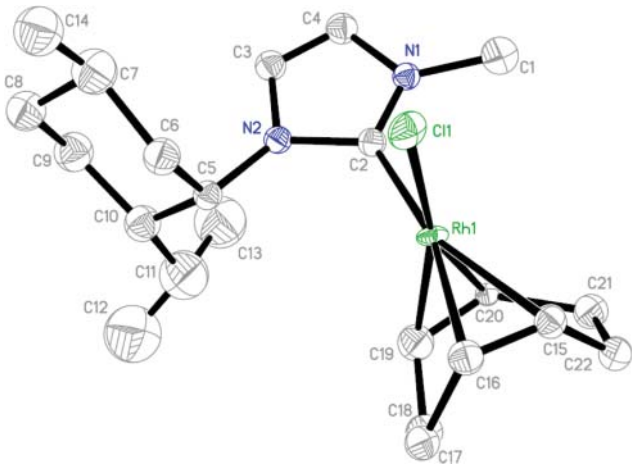


Fig. 2 ORTEP drawing of complex **6** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): Rh_1–C_2 = 2.03(2), Rh_1–C_{20} = 2.064(17), Rh_1–C_{19} = 2.12(3), Rh_1–C_{16} = 2.17(3), Rh_1–C_{15} = 2.209(19), Rh_1–Cl_1 = 2.375(7), C_2–Rh_1–C_{20} = 91.4(9), C_2–Rh_1–C_{19} = 96.5(11), C_2–Rh_1–C_{16} = 165.3(10), C_{20}–Rh_1–C_{16} = 95.5(9), C_{19}–Rh_1–C_{16} = 81.4(11), C_2–Rh_1–C_{15} = 160.0(13), C_{20}–Rh_1–C_{15} = 80.4(7), C_{19}–Rh_1–C_{15} = 87.8(12), C_2–Rh_1–Cl_1 = 88.8(7), C_{20}–Rh_1–Cl_1 = 162.5(6), C_{19}–Rh_1–Cl_1 = 160.0(6), C_{16}–Rh_1–Cl_1 = 88.5(8), C_{15}–Rh_1–Cl_1 = 93.7(7).

Synthesis of **2**: Triethylamine (5.39 mL, 38.76 mmol) was added to a solution of *L*-(–)-menthol **1** (5.0 g, 32.00 mmol) in CH_2Cl_2 (25.0 mL) at 0 °C, then freshly distilled methanesulfonyl chloride (3.0 mL, 38.76 mmol) was added dropwise. An off-white slurry was formed during the addition. The reaction mixture was stirred for an additional 3 h at room temperature and was quenched by the addition of saturated brine over 5 min with vigorous stirring. The organic layers were separated, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford compound **2** as a pale yellow oil (7.28 g, 97%). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 4.55 (dt, *J* = 15.5, 5.0 Hz, 1H), 3.01 (s, 3H), 2.28–2.24 (m, 1H), 2.10–2.04 (m, 1H), 1.75–1.67 (m, 2H), 1.53–1.39 (m, 2H), 1.31–1.24 (m, 2H), 1.10–1.05 (m, 1H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 83.2, 47.3, 42.1, 39.0, 33.7, 31.5, 25.7, 23.0, 21.7, 20.7, 15.6.

Synthesis of **3**: Imidazole sodium salt (Na^+Im^-, 5.46 g, 60.63 mmol) was added to the solution of compound **2** (7.10 g, 30.29 mmol) in anhydrous DMSO (20.0 mL). The mixture was heated to 80 °C for 10 h and then cooled to room temperature. The resulted mixture was washed with saturated brine (30 mL), then extracted with ethyl acetate (20 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash

chromatography on silica gel to give the desired product **3** as a pale yellow solid (2.19 g, 35% yield). M.p. 66–67 °C. ^{1}H NMR (500 MHz, $CDCl_3$,TMS) δ 7.60 (s, 1H), 7.07 (s, 1H), 7.03 (s, 1H), 4.54 (d, *J* = 2.5 Hz, 1H), 1.96–1.88 (m, 2H), 1.79–1.70 (m, 2H), 1.50–1.38 (m, 2H), 1.35–1.29 (m, 1H), 1.24–1.17 (m, 1H), 1.08–0.99 (m, 1H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.84 (d, *J* = 6.5 Hz, 3H), 0.78 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 128.4, 120.2, 55.6, 46.5, 41.7, 34.3, 29.1, 26.7, 25.4, 22.3, 21.2, 20.3. HRMS (ESI): Calcd for $C_{13}H_{23}N_2$ $[M+H]^+$ requires 207.1857; found: 207.1858. IR (neat) ν 2954, 2926, 2875, 1489, 1452, 1261, 1222, 1110, 1079, 909, 806, 744, 734, 670 cm^{-1}.

Synthesis of **4**: CH_3I (0.80 mL, 12.84 mmol) was added to a CH_3CN (20 mL) solution containing compound **3** (1.32 g, 6.40 mmol) at room temperature. The solution was kept at 80 °C for 6 h. The solvent was then removed under vacuum to give a yellow solid, which was washed with Et_2O (15 mL) to afford compound **4** as a pale-yellow solid (2.11g, 95%). M.p. 169–171 °C (decomposed). ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 10.31 (s, 1H), 7.40 (s, 2H), 4.98 (s, 1H), 4.23 (s, 3H), 2.07–1.98 (m, 3H), 1.75 (br, 1H), 1.59–1.44 (m, 3H), 1.27–1.20 (m, 1H), 1.09–1.02 (m, 1H), 0.93 (d, *J* = 5.5 Hz, 3H), 0.91 (d, *J* = 5.5 Hz, 3H), 0.86 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 123.2, 123.0, 60.1, 45.7, 40.5, 37.2, 33.6, 29.0, 26.0, 24.8, 22.0, 21.5, 20.5. HRMS (ESI): Calcd for $C_{14}H_{25}N_2$ $[M-I]^+$ requires 221.2012; found: 221.2013. IR (neat) ν 3067, 2948, 2915, 2862, 1503, 1454, 1265, 1198, 1152, 1136, 867, 745, 735 cm^{-1}.

Synthesis of **5**: Compound **4** (348.1 mg, 1.0 mmol), Ag_2O (118.2 mg, 0.51 mmol) and CH_2Cl_2 (5.0 mL) were added under an N_2 atmosphere into a 50 mL flask. Then the flask was covered with aluminum foil and stirred at room temperature for 3 h. The resulting mixture was filtered quickly, and the filtrate was transferred to a second 50 mL round-bottom flask, which was also covered with aluminum foil. After adding [$PdCl_2$ (COD)] (143.9 mg, 0.50 mmol) and CH_2Cl_2 (10.0 mL), the mixture was stirred for an additional 6 h at room temperature and then was filtered through Celite. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (CH_2Cl_2) to give the Pd(II)-NHC complex **5** as a pale yellow solid (243.0 mg, 78%). The single crystal for X-ray diffraction was obtained by recrystallisation from acetone and ethyl acetate (5:1). M.p. 248–250 °C (decomposed). (*trans*- or *cis*-isomer) ^{1}H NMR (500 MHz, $CDCl_3$,TMS) δ 7.16 (d, *J* = 3.0 Hz, 2H), 6.79 (d, *J* = 1.5 Hz, 2H), 5.87 (d, *J* = 2.0 Hz, 2H), 4.18 (s, 6H), 2.52 (d, *J* = 14.0 Hz, 2H), 1.94–1.90 (m, 4H), 1.68–1.63 (m, 4H), 1.55–1.50 (m, 4H), 1.44–1.36 (m, 2H), 1.17 (d, *J* = 5.5 Hz, 6H), 1.15–1.04 (m, 2H), 0.87 (d, *J* = 6.0 Hz, 6H), 0.79 (d, *J* = 6.5 Hz, 6H). (*cis*- or *trans*-isomer) ^{1}H NMR (500 MHz, $CDCl_3$,TMS) δ 7.16 (d, *J* = 2.0 Hz, 2H), 6.78 (d, *J* = 2.0 Hz, 2H), 5.83 (d, *J* = 2.5 Hz, 2H), 4.14 (s, 6H), 2.68 (d, *J* = 16.5 Hz, 2H), 1.94–1.90 (m, 4H), 1.68–1.63 (m, 4H), 1.55–1.50 (m, 4H), 1.44–1.36 (m, 2H), 1.16 (d, *J* = 6.5 Hz, 6H), 1.15–1.04 (m, 2H), 0.87 (d, *J* = 6.0 Hz, 6H), 0.81 (d, *J* = 5.5 Hz, 6H). (*trans*- or *cis*-isomer) ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 121.2, 120.8, 58.2, 46.7, 41.7, 37.7, 34.5, 29.0, 26.5, 25.2, 22.7, 22.4, 20.3. (*cis*- or *trans*-isomer) ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 121.0, 120.9, 58.0, 46.5, 42.0, 37.8, 34.5, 29.0, 26.4, 25.3, 22.7, 22.4, 20.5. MS (ESI) *m*/*z* 655 $[M+K]^+$. IR (neat) ν 2947, 2924, 2870, 2359, 1454, 1396, 1262, 1228, 1195, 730, 697 cm^{-1}. Anal. Calcd for $C_{28}H_{48}Cl_2N_4Pd$: C, 54.41; H, 7.83; N, 9.07. Found: C, 54.42; H, 7.89, N, 9.01%.

Synthesis of **6**: Compound **4** (348.5 mg, 1.0 mmol), Ag_2O (116.9 mg, 0.50 mmol) and CH_2Cl_2 (5.0 mL) were added under an N_2 atmosphere into a 50 mL flask. The flask was covered with aluminum foil and stirred at room temperature for 3 h. The resulting mixture was filtered quickly, and the filtrate was transferred to a second 50-mL round-bottom flask, which was also covered with aluminum foil. After adding [{RhCl(COD)}$_2$] (246.5 mg, 0.50 mmol) and CH_2Cl_2 (10.0 mL), the mixture was stirred for an additional 6 h at room temperature and then was filtered through Celite. The solvent was removed under reduced pressure and the residue was purified by a flash chromatography on silica gel (CH_2Cl_2) to give the Rh(I)-NHC complex **6** as a yellow solid (401.7 mg, 86%). The single crystal for X-ray diffraction was obtained by recrystallisation from CH_2Cl_2 and ethyl acetate (4:1). M.p. 174–176 °C (decomposed). MS (ESI) *m*/*z* 431 $[M-Cl]^+$. IR (neat) ν 2924, 2870, 1454, 1440, 1389, 1262, 1228, 1194, 750, 737, 704 cm^{-1}. Anal. Calcd for $C_{22}H_{36}ClN_2Rh$: C, 56.59; H, 7.77, N, 6.00. Found: C, 56.72; H, 7.93, N, 5.92%.

Financial support from the National Natural Science Foundation of China (No. 21002072) and the Opening Foundation of Zhejiang Provincial Top Key Discipline (No. 1000612001) is greatly appreciated.

Received 16 April 2012; accepted 22 August 2012
Paper 1201266 doi: 10.3184/174751912X13467827890747
Published online: 12 November 2012

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