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A route to new methylpalladium(II) carbene complexes

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Abstract

The nucleophilic carbene, 1,3-dimethylimidazolin-2-ylidene, reacts with PdClMe(cod) to produce the first methylpalladium(II) carbene complex, [PdMe(1,3-dimethylimidazolin-2-ylidene)(μ-Cl)]$_2$ **1**, from which the preparation of other methylpalladium carbene complexes may proceed, and the crystal structure of one such complex, [PdMe(1,3-dimethylimidazolin-2-ylidene)($NC_5H_4CO_2$-2)], is reported.

Keywords: Carbene complex; Palladium; 1,3-dimethylimidazolin-2-ylidene

In recent years the discovery of stable N-heterocyclic carbenes has provided exciting new possibilities for the chemistry of carbene complexes [1]. While some of these carbenes are isolable, less stable relatives may be generated and used in situ [2,3]. Therefore, the introduction of carbene ligands to metal complexes can now be performed under simpler and milder conditions than traditional methods which often required several steps or the use of strong bases or high temperatures [4]. This attractive feature permits the use of less stable precursors in the preparation of carbene complexes, a possibility not yet fully exploited. The rapidly expanding interest in *N*-heterocyclic carbenes is illustrated by the number of recent publications, predominantly from the group of Wolfgang Herrmann [5]. Surprisingly, there have been no reports of palladium carbene complexes containing simple alkyl groups. The very few examples of palladium complexes with both a carbene and an alkyl or aryl ligand have either perhalogenated hydrocarbyl ligands [6–8] or an intramolecularly coordinated alkyl or aryl ligand [6,9].

Several preliminary reports of catalytically active complexes having carbene ligands suggest that they play a similar role to phosphine ligands (parallels between nucleophilic carbenes and phosphines had been noted a number of years ago [10]), which are common in many established catalyst systems [11,12]. It is also likely that hydrocarbylpalladium carbene complexes play a pivotal role in the catalytic processes [11–13]. Thus, it was of interest to us to investigate the synthesis of simple alkylpalladium complexes containing carbene ligands. Our attempts to methylate Pd–carbene complexes with a variety of alkylating agents (including methyllithium) proved unsuccessful, therefore we investigated the alternative of introducing a free carbene ligand to a methylpalladium species.

The reaction of one equivalent of 1,3-dimethylimidazolin-2-ylidene (**iy**)[2] with PdClMe(cod) in THF at 0°C led to the immediate precipitation of the methylpalladium carbene chloro-bridged dimer, [PdMe(iy)(μ-Cl)]$_2$ **1** (Scheme 1). After filtration the crude product was recrystallised from DCM/THF. The ^{1}H-NMR spectrum of **1** shows three broad resonances at room temperature, but on cooling to −30°C, each resonance sharpens into two sharp singlets of approximately equal area. This indicates that isomerisation of the *cis* and *trans* isomers of **1** is slowed dramatically at lower temperatures. Such behaviour is known for the analogous

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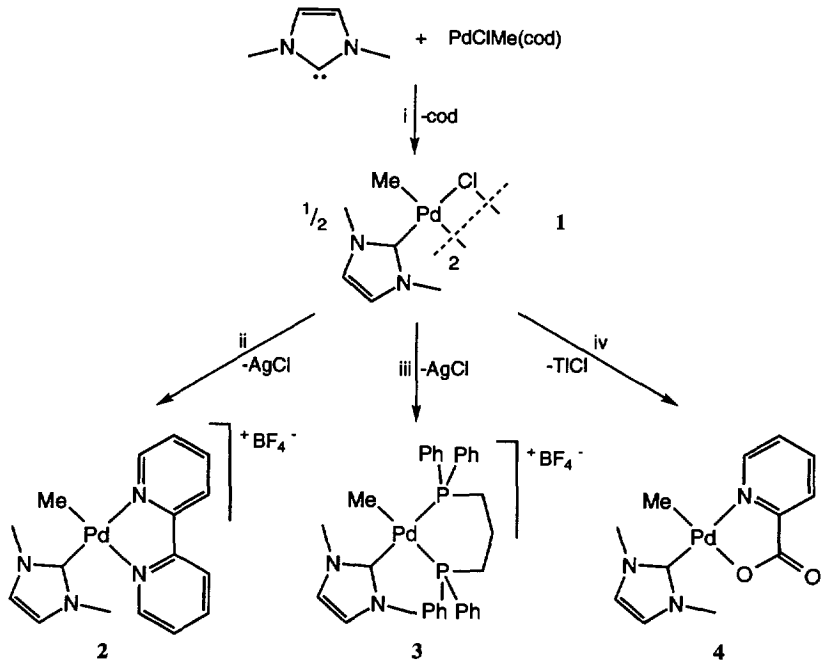

Scheme 1. Reagents and conditions: (i) THF, 0°C, 2 min; (ii) bpy, $AgBF_4$, CH_2Cl_2, 0°C, 25 min; (iii) dppp, $AgBF_4$, CH_2Cl_2, 0°C, 25 min; (iv) Tl–$NC_5H_4CO_2$-2, CH_2Cl_2, −20°C → 5°C, 20 h.

methylpalladium phosphine dimers [14]. The ^{13}C-NMR spectrum of **1** at −34°C also shows two distinct Pd–Me resonances, although the NMe and alkene signals for the two isomers are coincident.

The complex, $[PdMe(iy)(\mu\text{-}Cl)]_2$ **1**, is a valuable precursor for the preparation of an extensive range of other methylpalladium complexes, both neutral and cationic. For example, complexes **2**–**4** were obtained in quantitative yields by the addition of exact equimolar amounts of **1** and the appropriate bidentate ligand (and $AgBF_4$ in the case of the cationic complexes **2** and **3**) (Scheme 1). The complexes have been characterised by ^{1}H, ^{13}C and ^{31}P-NMR, IR, MS(LSIMS) and microanalysis. Complexes **1**–**3** are moisture and temperature sensitive in solution and as solids, but can be stored successfully under a nitrogen atmosphere below 5°C, whereas **4** is stable in air at room temperature even in solution.

At room temperature in CH_2Cl_2 solution, complex **4** exists as two isomers in a ratio of ca. 3:1. The X-ray structure (Structure Determination—$C_{12}H_{15}N_3O_2Pd$, $M = 339.7$, Triclinic, $P\bar{1}$, $a = 11.459(3)$, $b = 8.187(3)$, $c = 7.306(4)$ Å, $\alpha = 74.88(4)$, $\beta = 82.06(3)$, $\gamma = 88.32(2)°$, $Z = 2$. Conventional R on $|F| = 0.033$ (R_w (statistical weights) = 0.043) for 3681 'observed' ($I > 2\sigma(I)$) out of 3813 independent four-circle diffractometer reflections, absorption corrected. Anisotropic thermal parameter refinement for non-H atoms; $(x, y, z, U_{iso})_H$ refined. Monochromatic Mo–K_α radiation; $T \approx 295$ K; $2\theta_{max} = 60°$) of **4** has been determined (only one isomer was present in the crystal selected for X-ray diffraction, the existence of only one isomer in the solid state is also supported by Raman spectroscopy of single crystals of **4**) (Fig. 1). The carbene ligand is strictly planar and the plane of the ligand is inclined by 68.7(1)° to the Pd coordination plane. The $Pd-C_{carbene}$ bond length (1.971(2) Å) is significantly shorter in **4** than for other palladium complexes with similar carbene ligands (1.990(3)–2.137(5) Å) [10,15–17]. The extent to which this may reflect the different *trans* influences of the *trans* ligands is uncertain

Reaction of complexes **1**–**4** with CO was attempted at a variety of temperatures and pressures. Under atmospheric pressures of CO, complexes **1** and **2** decomposed quickly to Pd(0) and organic products, while the more stable complexes **3** and **4** did not react. Significant decomposition of **3** and **4** occurred after treatment with CO at 20 bar overnight at 30°C, with no identifiable products obtained. It has been shown that the new methylpalladium carbene dimer, $[PdMe(iy)(\mu\text{-}Cl)]_2$, can be successfully used as a precursor in the preparation of neutral and cationic methylpalladium carbene complexes. It is expected that this method will be widely applicable in the synthesis of other methylpalladium carbene complexes.

Full experimental and spectroscopic data for complexes **1**–**4**: all manipulations were carried out using standard Schlenk techniques under a dry nitrogen atmosphere. All solvents were dried and purified by standard methods and freshly distilled under nitrogen before use.

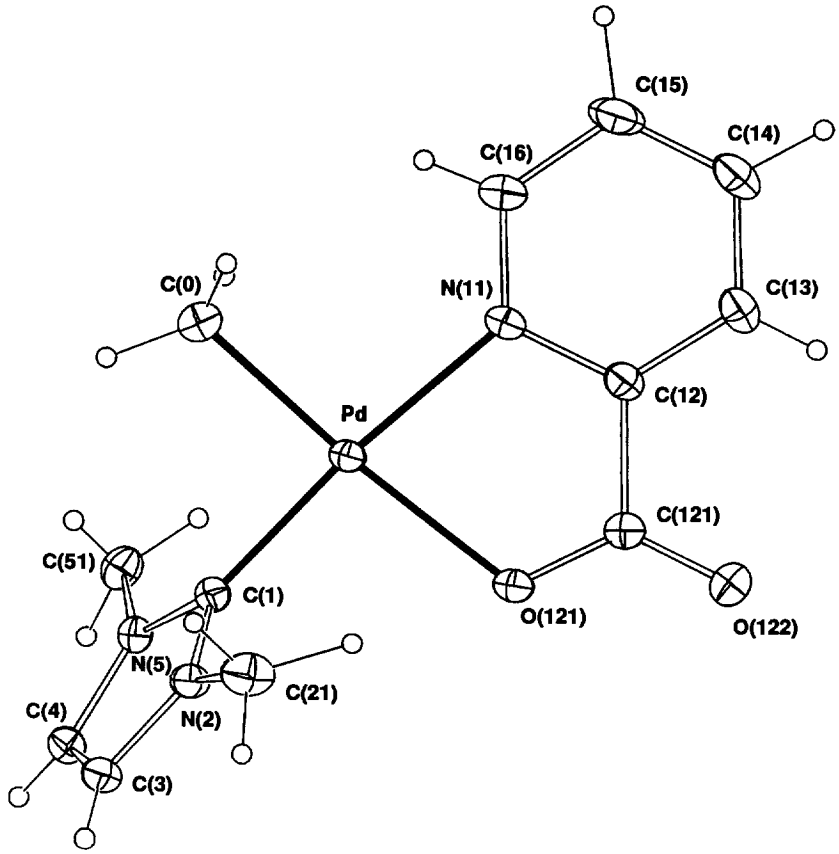

Fig. 1. Crystal structure of **4**; 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having an arbitrary radius of 0.1 Å. Selected bond lengths (Å) and angles (°); Pd–C(0) 2.019(4), Pd–N(11) 2.092(2), Pd–O(121) 2.140(2), Pd–C(1) 1.971(2), C(121)–O(121) 1.268(3), C(121)–O(122) 1.223(3); C(0)–Pd–N(11) 97.4(1), C(0)–Pd–O(121) 174.5(1), C(0)–Pd–C(1) 88.3(1), N(11)–Pd–O(121) 78.67(8), N(11)–Pd–C(1) 174.21(8), O(121)–Pd–C(1) 95.61(8), N(2)–C(1)–N(5) 104.6(2).

[PdMe(1,3-dimethylimidazolin-2-ylidene)(μ-Cl)]$_2$ 1: A solution of 1,3-dimethylimidazolin-2-ylidene in 35 ml THF was prepared by the procedure of Arduengo et al. [J. Am. Chem. Soc., **114**, 1992, 5530] using 1.21 g 1,3-dimethylimidazolium chloride, 0.38 g NaH (oil free), 0.05 g potassium *tert*-butoxide. The reaction mixture was filtered (to remove NaCl, unreacted NaH and 1,3-dimethylimidazolium chloride) into a suspension of 0.94 g PdClMe(cod) in 10ml THF at 0°C. After addition of the carbene, the solvent was removed in vacuo. The crude product was dissolved in DCM and filtered through Celite to remove Pd(0). The remaining yellow solid was washed with a 1:2 solution of DCM/THF to leave a white chalky solid (yield 56%). Found: C, 28.56; H, 4.23; N, 10.73. Calc. for $C_{12}H_{22}N_4Pd_2Cl_2 \cdot 0.2CH_2Cl_2$: C, 28.01; H, 4.32; N, 10.71%. 1H-NMR (300 MHz, CD_2Cl_2): (22°C) δ 6.89 (br s, 2H, CH), 4.00 (br s, 6H, NCH_3), 0.28 (br s, 3H, $PdCH_3$). (-30°C two isomers in approx. 1:1 ratio) δ 6.96, 6.93 (s, 2H, CH), 4.02, 3.98 (s, 6H, NCH_3), 0.29, 0.26 (s, 3H, $PdCH_3$). ^{13}C-NMR (75 MHz, CD_2Cl_2): (-34°C) δ 170.87 (NCN), 121.74 (CH), 37.93 (NCH_3), -9.11, -9.74 ($PdCH_3$).

[PdMe(1,3-dimethylimidazolin-2-ylidene)(bipy)]BF$_4$ 2: At 0°C, **1** (0.080 g, 0.32 mmol) was partly dissolved in 10 ml DCM and added to a solution of bipy (0.049 g, 0.32 mmol) in 3 ml DCM. After 10 min, the clear yellow solution was added to a suspension of $AgBF_4$ (0.063 g, 0.32 mmol) in 5 ml DCM at 0°C. The resulting mixture was filtered through Celite after 15 min. A light yellow foam was obtained after removing the DCM in vacuo (yield: quantative). Found: C, 40.57; H, 4.29; N, 11.72. Calc. for $C_{16}H_{19}N_4PdBF_{40}$. $1CH_2Cl_2$: C, 41.22 H, 4.10; N, 11.95%. MS(LSIMS) *m/z*: 373 (100%, $[M]^+$), 358 (13%, $[PdL(bipy)]^+$), 262 (13%, $[Pd(bipy)]^+$), 202 (14%, $[PdL]^+$). 1H-NMR (300 MHz, CD_2Cl_2): δ 8.66 (m, 1H, pyrH), 8.35 (m, 2H, pyrH), 8.22 (m, 1H, pyrH), 8.15 (m, 1H, pyrH), 7.75 (m, 1H, pyrH), 7.70 (m, 1H, pyrH), 7.52 (m, 1H, pyrH), 7.21 (s, 2H, CH), 3.91 (s, 6H, NCH_3), 0.45 (s, 3H, $PdCH_3$). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ 171.79 (NCN), 156.48, 154.27 (pyrC2, pyrC2'), 149.96, 148.03, 140.58, 140.18, 127.73, 127.02 (6 pyrC), 123.51, 123.44, 123.27 (2 pyrC + CH), 38.16 (NCH_3), -6.49 ($PdCH_3$).

[PdMe(1,3-dimethylimidazolin-2-ylidene)(dppp)]BF$_4$ 3: Prepared in a similar manner to **2**. Recrystallised from

DCM/ether to remove dppp impurity. White solid (yield: quantative-based on **1**). Found: C, 55.04; H, 5.12; N, 3.93. Calc. for $C_{33}H_{37}N_2P_2PdBF_4$: C, 55.29 H, 5.20; N, 3.91%. MS(LSIMS) *m/z*: 629 (100%, $[M]^+$), 614 (25%, $[PdL(dppp)]^+$), 518 (20%, $[Pd(dppp)]^+$), 441 (10%, $[Pd(dppp)\text{-}(C_6H_5)]^+$). 1H-NMR (300 MHz, CD_2Cl_2): δ 7.63–7.12 (m, 20H, aromH), 6.76 (s, 2H, CH), 3.39 (s, 6H, NCH_3), 2.59 (m, 4H, PCH_2), 1.91 (m, 2H, $CH_2CH_2CH_2$), 0.11 (t, 3H, $J_{HP} = 6.7$ Hz, $PdCH_3$). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ 179.50 (dd, $J_{CP} = 134$, $J_{CP} = 16$ Hz, NCN), 133.86–128.97 (aromC), 123.07 (CH), 37.58 (NCH_3), 26.54 (m, PCH_2), 18.53 ($CH_2CH_2CH_2$), 0.71 (d, $J_{CP} = 91$ Hz, $PdCH_3$). ^{31}P-NMR (121.5 MHz, CD_2Cl_2): δ 58.3 (d, $J_{PP} = 49$ Hz), 45.7 (d, $J_{PP} = 49$ Hz).

[PdMe(1,3-dimethylimidazolin-2-ylidene)($NC_5H_4CO_2$-2)] 4: At −20°C, **1** (0.171 g, 0.68 mmol) was partly dissolved in 80 ml DCM. Thallium 2-pyridinecarboxylate (0.221 g, 0.68 mmol) was rinsed in with 16 ml DCM and the suspension was left to stir overnight (20 h) at −10–5°C. After filtration through Celite and removal of the solvent, an off-white solid remained (yield 100%). Crystals suitable for X-ray diffraction were grown by ether diffusion into a DCM solution at 5°C. Found: C, 42.32; H, 4.53; N, 12.38. Calc. for $C_{12}H_{15}N_3O_2Pd$: C, 42.43 H, 4.45; N, 12.37%. MS(LSIMS) *m/z*: 340 (71%, $[MH]^+$), 324 (16%, $[PdL(N-O)]^+$), 217 (36%, $[PdMeL]^+$), 202 (51%, $[PdL]^+$), 174 (100%, organic fragment). IR (KBr): ν(C(O) 1653 (min), 1634 (maj) cm^{-1}. 1H-NMR (300 MHz, CD_2Cl_2): (two isomers in approx. 3:1 ratio) δ 8.39 (m, $1H_{maj}$, $pyrH_6$), 8.14 (ddd, $1H_{maj}$, $^3J = 7.5$, $^4J = 1.5$, $^4J = 0.8$ Hz, $pyrH_3$) + (m, $1H_{min}$, $pyrH_3$ or 6), 7.97 (dt, $1H_{maj}$, $^3J = 7.5$, $^4J = 1.5$ Hz, $pyrH_4$), 7.90 (dt, $1H_{min}$, $^3J = 7.5$, $^4J = 1.5$ Hz, pyrH4), 7.52 (ddd, $1H_{maj}$, $^3J = 7.5$, $^3J = 5.4$, $^4J = 1.5$ Hz, pyrH5) + (m, $1H_{min}$, $pyrH_{3\text{ or }6}$), 7.32 (ddd, $1H_{min}$, $^3J = 7.5$, $^3J = 5.4$, $^4J = 1.5$ Hz, $pyrH_5$), 7.05 (s, $2H_{min}$, CH), 6.97 (s, $2H_{maj}$, CH), 3.93 (s, $6H_{maj} + 6H_{min}$, NCH_3), 0.34 (s, $3H_{maj}$, $PdCH_3$), 0.28 (s, $3H_{min}$, $PdCH_3$). ^{13}C-NMR (75 MHz, CD_2Cl_2): δ 173.30 (min, NCN or C(O), 172.21 (maj, NCN or C(O), 171.95 (min, NCN or C(O), 170.91 (maj, NCN or C(O), 154.61 (maj, $NCCO_2$), 153.51 (min, $NCCO_2$), 147.66 (min, pyrC), 145.27 (maj, pyrC), 139.00 (maj, pyrC), 138.65 (min, pyrC), 126.87 (min, pyrC), 126.71 (maj, pyrC), 126.55 (maj, pyrC), (remaining minor peak likely to be coincident), 122.54 (min, CH), 122.42 (maj, CH), 38.19 (min, NCH_3), 37.99 (maj, NCH_3), −10.77 (maj, $PdCH_3$), −12.93 (min, $PdCH_3$).

Tables 1–3 show some atomic positional and isotropic displacement parameters, interatomic distances and interbond angles.

Table 2
Interatomic distances in Angstroms

Bond distances	Å
Pd–C(0)	2.019(4)
Pd–N(11)	2.092(2)
Pd–O(121)	2.140(2)
Pd–C(1)	1.971(2)
N(11)–C(12)	1.346(3)
N(11)–C(16)	1.342(3)
C(12)–C(121)	1.524(3)
C(12)–C(13)	1.378(4)
C(121)–O(121)	1.268(3)
C(121)–O(122)	1.223(3)
C(13)–C(14)	1.384(4)
C(14)–C(15)	1.371(5)
C(15)–C(16)	1.381(5)
C(1)–N(2)	1.347(3)
C(1)–N(5)	1.348(3)
N(2)–C(21)	1.456(4)
N(2)–C(3)	1.380(3)
C(3)–C(4)	1.339(4)
C(4)–N(5)	1.374(3)
N(5)–C(51)	1.461(4)

Table 1
Atomic positional and isotropic displacement parameters

Atom	*x/a*	*y/b*	*z/c*	*U*(eq) A**2
Pd	0.24302(1)	0.17857(2)	0.13543(3)	0.03697(8)
C(0)	0.1694(3)	0.0362(6)	0.3925(6)	0.068(1)
N(11)	0.0870(2)	0.2453(3)	0.0163(3)	0.0417(7)
C(12)	0.1033(2)	0.3665(3)	−0.1498(4)	0.0402(7)
C(121)	0.2295(2)	0.4260(3)	−0.2286(4)	0.0435(8)
O(121)	0.3081(2)	0.3471(3)	−0.1343(3)	0.0535(7)
O(122)	0.2451(2)	0.5401(3)	−0.3760(3)	0.0619(8)
C(13)	0.0107(3)	0.4339(4)	−0.2464(5)	0.055(1)
C(14)	−0.1017(3)	0.3692(5)	−0.1776(6)	0.066(1)
C(15)	−0.1181(3)	0.2430(5)	−0.0108(6)	0.066(1)
C(16)	−0.0227(2)	0.1858(4)	0.0840(5)	0.055(1)
C(1)	0.3986(2)	0.1275(3)	0.2223(3)	0.0349(6)
N(2)	0.4716(2)	0.2387(2)	0.2567(3)	0.0369(6)
C(21)	0.4399(3)	0.4108(3)	0.2638(6)	0.055(1)
C(3)	0.5794(2)	0.1666(3)	0.2905(4)	0.0413(7)
C(4)	0.5725(2)	0.0065(3)	0.2793(4)	0.0404(7)
N(5)	0.4616(2)	−0.0160(2)	0.2385(3)	0.0354(5)
C(51)	0.4180(3)	−0.1761(3)	0.2202(5)	0.0462(8)
H(0a)	0.128(6)	−0.026(8)	0.35(1)	0.14(3)
H(0b)	0.226(3)	−0.037(5)	0.477(6)	0.07(1)
H(0c)	0.107(4)	0.105(6)	0.431(7)	0.09(1)
H(13)	0.023(3)	0.515(4)	−0.356(5)	0.045(8)
H(14)	−0.166(2)	0.427(4)	−0.252(5)	0.046(8)
H(15)	−0.199(5)	0.191(6)	0.054(8)	0.11(2)
H(16)	−0.028(3)	0.112(4)	0.193(5)	0.047(8)
H(3)	0.634(3)	0.229(4)	0.306(5)	0.053(9)
H(4)	0.635(3)	−0.079(4)	0.271(5)	0.06(1)
H(21a)	0.406(4)	0.412(5)	0.390(7)	0.09(1)
H(21b)	0.385(3)	0.467(4)	0.150(5)	0.059(9)
H(21c)	0.507(3)	0.477(4)	0.251(5)	0.049(8)
H(51a)	0.390(4)	−0.226(5)	0.305(7)	0.07(1)
H(51b)	0.355(3)	−0.148(4)	0.149(5)	0.06(1)
H(51c)	0.491(3)	−0.247(4)	0.188(5)	0.058(9)

Table 3
Interbond angles in degrees

Bond angles	Degrees
C(0)–Pd–N(11)	97.4(1)
C(0)–Pd–O(121)	174.5(1)
C(0)–Pd–C(1)	88.3(1)
N(11)–Pd–O(121)	78.67(8)
N(11)–Pd–C(1)	174.21(8)
O(121)–Pd–C(1)	95.61(8)
Pd–N(11)–C(12)	112.9(2)
Pd–N(11)–C(16)	129.0(2)
C(12)–N(11)–C(16)	118.1(2)
N(11)–C(12)–C(121)	117.1(2)
N(11)–C(12)–C(13)	121.9(2)
C(121)–C(12)–C(13)	120.9(2)
C(12)–C(121)–O(121)	115.3(2)
C(12)–C(121)–O(122)	117.8(2)
O(121)–C(121)–O(122)	126.9(2)
Pd–O(121)–C(121)	115.0(2)
C(12)–C(13)–C(14)	119.5(3)
C(13)–C(14)–C(15)	118.7(3)
C(14)–C(15)–C(16)	119.2(3)
N(11)–C(16)–C(15)	122.6(3)
Pd–C(1)–N(2)	126.1(2)
Pd–C(1)–N(5)	128.9(2)
N(2)–C(1)–N(5)	104.6(2)
C(1)–N(2)–C(21)	124.7(2)
C(1)–N(2)–C(3)	111.1(2)
C(21)–N(2)–C(3)	124.2(2)
N(2)–C(3)–C(4)	106.4(2)
C(3)–C(4)–N(5)	107.1(2)
C(1)–N(5)–C(4)	110.9(2)
C(1)–N(5)–C(51)	125.1(2)
C(4)–N(5)–C(51)	124.0(2)

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