Metallation of Aliphatic Carbon Atoms. Part 1. Synthesis and Characterization of the Cyclopalladated Complexes of 2-Neopentylpyridine

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Metallation of the methyl group in 2-neopentylpyridine occurs with palladium(II) acetate to afford a novel six-membered cyclopalladated complex $[\{\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2CH_2C_5H_4N}})(\mathrm{O_2CMe})\}_2]$. This complex is readily converted into the chloro-bridged analogue, $[\{\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2CH_2C_5H_4N}})\mathrm{Cl}\}_2]$, by metathetical reaction with LiCl. The chloro-bridged complex undergoes bridge-splitting reactions with 3,5-dimethylpyridine and thallium(I) acetylacetonate to give the corresponding mononuclear cyclopalladated complexes. All the complexes are characterized by means of elemental analysis and i.r. and ^{1}H n.m.r. spectroscopy. The inversion of the six-membered chelate ring in these complexes is discussed on the basis of temperature-dependent ^{1}H n.m.r. spectra.

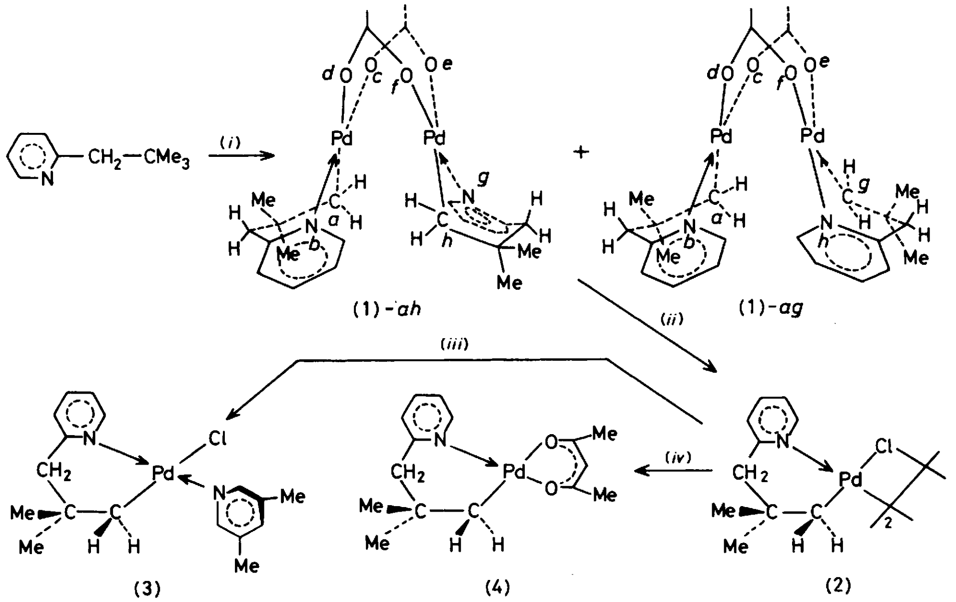
The activation of alkyl groups with transition-metal compounds has been one of the most important and challenging problems.[1,2] Many investigations have been reported concerning the activation of the alkyl groups through the cyclopalladation and cycloplatination of bulky tertiary alkylphosphines.[2,3] However, only a few papers have been published concerning the cyclopalladation of alkyl groups of nitrogen bases, *i.e.*, 8-alkylquinolines,[4,5] *o*-*NN*-dimethylaminotoluene,[6] alkyl t-butyl ketoxime,[7] and t-butyl methyl ketone dimethylhydrazone.[7] All the cyclopalladated complexes of these nitrogen bases had five-membered chelate structures.[4-7]

In this study, we present the activation of the t-butyl group in 2-neopentylpyridine using palladium(II) acetate, leading to the formation of a novel six-membered cyclopalladated complex. It has been reported recently from our laboratory that 2-benzyl- and 2-benzoyl-pyridines gave six-membered cyclopalladated complexes, which involved an aryl–palladium σ bond.[8,9]

Results and Discussion

Preparations and General Properties of the Cyclopalladated Complexes.—2-Neopentylpyridine reacted with palladium(II) acetate in acetic acid at 100 °C to give a novel six-membered cyclopalladated complex, $[\{\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2CH_2C_5H_4N}})(\mathrm{O_2CMe})\}_2]$ (1). This acetato-bridged complex (1) was readily converted into $[\{\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2CH_2C_5H_4N}})\mathrm{Cl}\}_2]$ (2), chloro-bridged analogue, by the metathetical reaction with excess lithium chloride. Complex (2) reacted with 3,5-dimethylpyridine (dmpy) and thallium(I) acetylacetonate, Tl(acac), to afford the corresponding mononuclear cyclopalladated complexes, $[\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2CH_2C_5H_4N}})\mathrm{Cl(dmpy)}]$ (3) and $[\overline{\mathrm{Pd}(\mathrm{CH_2CMe_2CH_2C_5H_4N}})(\mathrm{acac})]$ (4), respectively (Scheme).

The yields and microanalytical data of the complexes obtained in this study are summarized in Table 1. The microanalytical data of (1)—(4) are consistent with the struc-



Scheme. (*i*) $[\mathrm{Pd(O_2CMe)_2}]$ in acetic acid at 100 °C; (*ii*) LiCl in acetone–water (10 : 1); (*iii*) dmpy in $\mathrm{CH_2Cl_2}$; (*iv*) Tl(acac) in $\mathrm{CH_2Cl_2}$. Dotted lines represent the groups situated behind the plane of the paper

Table 1. Yields and elemental analyses of the cyclopalladated complexes

Complex	Yield (%)	M.p. (θ_c/°C)	Analysis [a] (%) C	H	N
(1)	33	204—208 [b]	45.8 (45.95)	5.5 (5.45)	4.3 (4.45)
(2)	94	241—244 [b]	41.15 (41.4)	4.85 (4.85)	4.8 (4.85)
(3)	82	171—173	50.85 (51.4)	5.75 (5.85)	6.75 (7.05)
(4)	34	109—111	50.7 (50.95)	6.05 (6.0)	4.1 (3.95)

[a] Calculated values are given in parentheses. [b] With decomposition.

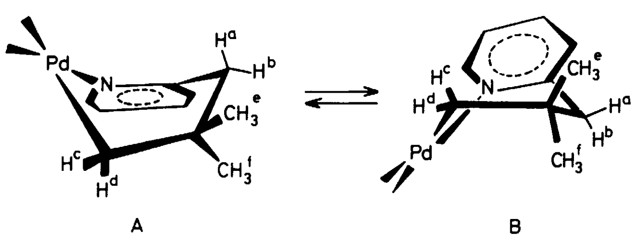


Figure 1. Inversion of the six-membered Pd–CH$_2$CMe$_2$CH$_2$CN ring

Table 2. Proton n.m.r. data [a] of the cyclopalladated complexes

Complex	Pd–CH$_2$CMe$_2$CH$_2$C$_5$H$_4$N moiety: Pd–CH$_2$	py–CH$_2$	CMe$_2$	H^6 (py)	H$^{3-5}$ (py)	Other ligands: Me	Others
(1)-*ah* [b]	1.81 (q) [c]	2.48 (q) [d]	0.82 (s) 0.44 (s)	8.93 (d) [e]	6.99 (d),[e] 7.43 (t) [e] 7.51 (t) [e]	1.98 (s)	—
(1)-*ag* [b]	2.16 (s)]	2.69 (s)	0.82 (s)	8.24 (d) [e]	6.61 (t),[e] 6.95 (m)	1.90 (s), 2.03 (s)	—
(3)	1.78 (s)	2.99 (s)	0.90 (s)	9.48 (d) [f]	7.58 (t),[f] 7.0—7.3 (m)	2.29 (s)	7.34 (s) [g] 8.47 (s) [h]
(4)	2.08 (s)	2.81 (s)	0.87 (s)	9.08 (d) [f]	7.65 (t), 7.15 (m) [f]	1.93 (s), 1.95 (s)	5.36 (s) [i]

[a] δ Relative to SiMe$_4$; recorded at 100 MHz on a JEOL JNM-MH-100 spectrometer in CDCl$_3$, at 27 °C except for (1); s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. [b] Measured at −28 °C. [c] $\Delta\delta = 0.46$, ^2J(HH) = 8 Hz. [d] $\Delta\delta = 0.39$, ^2J(HH) = 13 Hz. [e] ^3J(HH) = *ca.* 6 Hz. [f] ^3J(HH) = 8 Hz. [g] γ-H(dmpy). [h] α-H(dmpy). [i] CH(acac).

tures drawn in the Scheme. The ^{1}H n.m.r. spectra of (1), (3), and (4) exhibited new resonances in the range δ 1.6—2.2, due to the palladium-bonded methylene protons (Table 2), indicating unambiguously that these complexes are cyclopalladated with one methyl group of 2-neopentylpyridine, forming a novel six-membered chelate ring.* All the complexes, having the aliphatic carbon–palladium σ bond, are fairly stable in air and water. It is noteworthy that the acetato-bridged complex (1) is stable also in acetic acid at 100 °C. The stability of the aliphatic carbon–palladium σ bond is probably due to both the cyclopalladated structure and the lack of β-hydrogen in the aliphatic moiety.

Acetato-bridged Binuclear Complexes (1).—The i.r. spectrum of (1) showed two bands at 1 580 and 1 420 cm^{-1}, characteristic of the bridging acetato-ligand.[10] The ^{1}H n.m.r. spectrum of (1) at 27 °C showed two sets of signals: one set consisting of stronger signals at δ 1.85 (s, br, 2.7 H, Pd–CH_2), 2.5 (s, br, 2.7 H, py-CH_2), 0.65 [s, br, 8 H, C(CH_3)$_2$], and 1.98 (s, 4 H, CH_3CO$_2$); the other consisting of weaker signals at δ 2.20 (s, 1.3 H, Pd–CH_2), 2.76 (s, 1.3 H, py-CH_2), 0.84 [s, 4 H, C(CH_3)$_2$], 1.95 (s, 1 H, CH_3CO$_2$), and 1.98 (s, 1 H, CH_3CO$_2$).‡ At −28 °C, the former two methylene signals at δ 1.85 and 2.5 changed into two AB quartets at δ 1.81 [$\Delta\delta = 0.46$, ^2J(HH) = 8 Hz] and 2.48 [$\Delta\delta = 0.39$, ^2J(HH) = 13 Hz], respectively, whereas the methyl proton signal at δ 0.65 separated into two sharp singlets at δ 0.44 (4 H) and 0.82 (4 H) (Table 2). The signals of the latter set changed very little above −50 °C. These data imply that (1) consists of an (*a*-C^1, *b*-N)-(*g*-N, *h*-C^1)-type (an *ah*-type) isomer and an (*a*-C^1, *b*-N)-(*g*-C^1, *h*-N)-type (an *ag*-type) one in a ratio of 2 : 1, which correspond to the stronger signals and the weaker ones, respectively (Scheme).[11] The temperature dependency of the ^{1}H n.m.r. spectra of the *ah*-type isomer indicates that the inversion of the six-membered chelate rings, Pd–CH$_2$CMe$_2$CH$_2$CN, took place rapidly on the n.m.r. time-scale above 20 °C (Figure 1), and was quenched below −28 °C.

It is possible that the six-membered chelate ring has two conformations, *i.e.*, ' half-boat ' and ' half-chair ' types, as in the case of cyclohexene.[12] However, the half-chair type is unfavourable, since molecular models indicate that it must hold remarkable ring strain owing to the relatively small bond angle CH$_2$–Pd–N(py) (almost 90°), in contrast to cyclohexene involving two sp^3 carbons adjacent to the olefinic bond. Accordingly, the six-membered chelate ring is ascribed to the half-boat type [8] having little ring strain, shown in the Scheme. Considering that two co-ordination planes in an acetato-bridged cyclopalladated dimer are combined by two mutually *cis* μ-acetato-ligands with a dihedral angle of *ca.* 24°,[13] (1)-*ah* was expected to have three conformations (C, D, and E) at low temperature, as shown in Figure 2. However, D is less favourable, because molecular models indicate that one of the pyridyl protons (H^6) and protons of an inner methyl group in D are located very close to each other. Compound (1)-*ah* looks unlikely to have conformation E, since two methylene groups in E are very close to each other. Since a new set of signals for D did not appear in the ^{1}H n.m.r. spectra at low temperature, D is probably a quasi-stable conformation, formed in a limited proportion only at high temperature. On the other hand, the inversion of the six-membered chelate rings in the *ag*-type isomer was not quenched even at −50 °C, as for the mononuclear complexes (3) and (4) (see below).

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* The ^{1}H n.m.r. spectrum of (2) could not be obtained owing to its poor solubility.

‡ This signal overlapped with the acetato-methyl proton signal for the stronger set (see before).

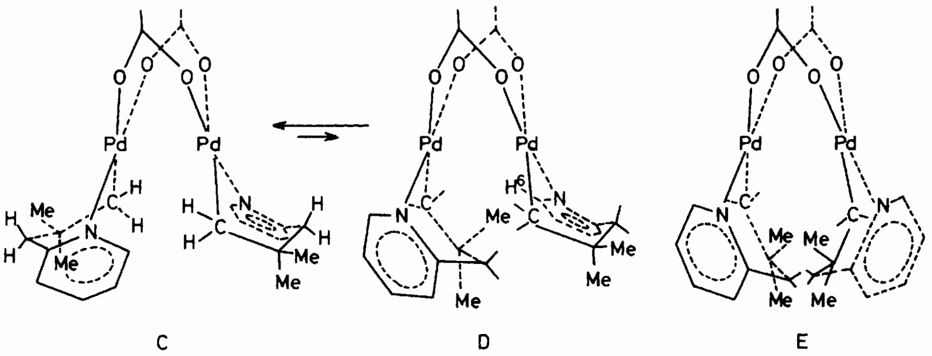

Figure 2. Possible conformations for (1)-*ah*. Dotted lines represent the groups situated behind the plane of the paper

Mononuclear Complexes.—Each of the mononuclear complexes $[Pd(CH_2CMe_2CH_2C_5H_4N)Cl(dmpy)]$ (3) and $[Pd(CH_2CMe_2CH_2C_5H_4N)(acac)]$ (4) showed only one sort of ^1H n.m.r. spectrum without temperature dependency in the range 27 to −50 °C, indicating that the inversion of the six-membered chelate ring is rapid. The i.r. spectrum of (4) exhibited two bands at 1 590 and 1 400 cm^{-1} characteristic of *OO'*-chelating acac ligand. The mass spectrometry of (4) gave the parent peak at *m/e* 354 corresponding to ^{106}Pd.

Conclusions

It is concluded that 2-neopentylpyridine reacts with palladium(II) acetate to give the acetato-bridged binuclear cyclopalladated complex (1), which consists of the *ah*- and *ag*-type isomers in the ratio of 2 : 1, and that (1) and its derivatives (3) and (4) have a six-membered chelate ring, which exhibits the inversion motion. Only the (1)-*ah* isomer shows the temperature-dependent ^1H n.m.r. spectra due to quenching of the inversion motion.

Experimental

2-Neopentylpyridine,[14] and Tl(acac) [15] were prepared according to literature methods. General procedures were as described previously.[11]

Preparations.—$[\{Pd(CH_2CMe_2CH_2C_5H_4N)(O_2CMe)\}_2]$ (1). An acetic acid (20 cm^3) suspension containing palladium(II) acetate (4.45 mmol) and 2-neopentylpyridine (4.91 mmol) was heated at 100 °C for 5 h, and filtered. The filtrate was diluted with water (100 cm^3), and then extracted with dichloromethane (50 cm^3). The concentrated extract was chromatographed on a silica gel column (200 mesh, 12 × 180 mm) to give a yellow fraction by eluting with diethyl ether–acetone (1 : 1). The yellow fraction was evaporated to dryness to give (1) as yellow crystals.

$[\{Pd(CH_2CMe_2CH_2C_5H_4N)Cl\}_2]$ (2). An acetone–water suspension (10 : 1, 33 cm^3) containing (1) (0.77 mmol) and lithium chloride (3.85 mmol) was stirred for 15 h at room temperature. The resulting precipitates were filtered off and washed with methanol–water (1 : 1, 20 cm^3) to give (2) as pale yellow solids.

Reactions of (2).—(*a*) *With* 3,5-*dimethylpyridine*. A clear solution was obtained immediately by adding dmpy (0.88 mmol) to a suspension of (2) (0.43 mmol) in dichloromethane (15 cm^3). After stirring for 20 h at room temperature, addition of hexane to the mixture gave $[Pd(CH_2CMe_2CH_2C_5H_4N)Cl(dmpy)]$ (3) as pale yellow crystals.

(*b*) *With* Tl(acac). A dichloromethane suspension (15 cm^3) containing (2) (0.43 mmol) and thallium(I) acetylacetonate (0.92 mmol) was stirred at room temperature for 1 d. After centrifuging the resulting milky suspension, the supernatant solution was purified by passing through a silica gel column (200 mesh, 12 × 50 mm) with dichloromethane as an eluant, and white needles of $[Pd(CH_2CMe_2CH_2C_5H_4N)(acac)]$ (4) were obtained.

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References

1 J. Halpern, *Discuss. Faraday Soc.*, 1968, **46**, 7.
2 D. E. Webster, ' Advances in Organometallic Chemistry,' eds. F. G. A. Stone and R. West, Academic Press, London, 1977, vol. 15, pp. 147—188.
3 I. Omae, *Coord. Chem. Rev.*, 1980, **32**, 235.
4 G. E. Hartwell, R. V. Lawrence, and M. J. Smas, *Chem. Commun.*, 1970, 912.
5 V. I. Sokolov, T. A. Sorokina, L. L. Troitskaya, L. I. Solovieva, and O. A. Reutov, *J. Organomet. Chem.*, 1972, **36**, 389.
6 C. Mutet and M. Pfeffer, *J. Organomet. Chem.*, 1979, **171**, C34.
7 A. G. Constable, W. G. McDonald, L. C. Sawkins, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 1992.
8 K. Hiraki, Y. Fuchita, and K. Takechi, *Inorg. Chem.*, 1981, **20**, 4316.
9 Y. Fuchita, K. Hiraki, and Y. Kage, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 955.
10 H. Onoue and I. Moritani, *J. Organomet. Chem.*, 1972, **43**, 431.
11 K. Hiraki, Y. Fuchita, H. Nakaya, and S. Takakura, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2531.
12 J. B. Hendrickson, D. J. Cram, and G. S. Hammond, ' Organic Chemistry,' 3rd edn., McGraw-Hill, London, 1970.
13 M. R. Churchill, H. J. Wasserman, and G. J. Young, *Inorg. Chem.*, 1980, **19**, 762.
14 R. Bokalski and A. R. Katritzky, *J. Chem. Soc. B*, 1968, 836.
15 W. H. Nelson, W. J. Randall, and D. F. Martin, *Inorg. Synth.*, 1971, **9**, 53.

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