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Cyclometallated compounds

VIII *. Double cyclopalladation of diacetylbenzene dioximes and 1,5-bis(dimethylamino)naphthalene

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Abstract

The dioximes of 1,3- and 1,4-diacetylbenzene readily undergo regioselective double cyclopalladation on reaction with lithium tetrachloropalladate. 1,5-Bis(dimethylamino)naphthalene has been singly and doubly cyclopalladated; attempts to prepare heterodicyclometallated derivatives of this ligand were not successful. An X-ray crystal structure of the singly cyclometallated Pd(acac) complex of 1,5-bis(dimethylamino)naphthalene has been determined.

Introduction

Nitrogen donor directed cyclometallation reactions have been much studied over the last twenty five years [2,3]. We recently described [4,5] the preparations of several doubly cyclopalladated complexes which represent organometallic analogues of well studied [6] binuclear coordination complexes. For example the dicyclopalladated complex **1** is readily prepared from 2,3-diphenylpyrazine and is a carbon analogue of the much studied [6,7] binuclear dipyridyl complexes **2**. However, in the absence of additional pendant nitrogen donors [8], we were unable to effect the double cyclopalladation of 2-phenylpyrimidines to produce analogues (**3**) of binuclear complexes (**4**) of 2,2′-bipyrimidine. This might suggest that the double metallation of a single phenyl ring is an unfavourable process. However, the successful double palladation on a single benzene ring has been previously claimed in an early report [9] of the reactions of tetraethyl α,α'-xylene diamines. We have therefore examined some other ligands which might undergo double cyclopalladation of a single benzene ring and herein report the successful double metallations of the diacetylbenzene dioximes **5** and **6** [10].

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* For Part VII see ref. 1.

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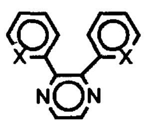

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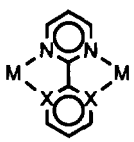
(2) X=N



(3) X=C
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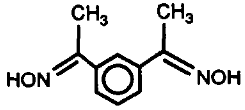

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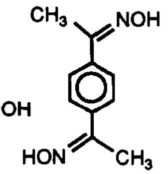

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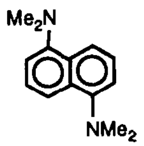


(7)

In view of the current interest in heterodinuclear complexes of bridging nitrogen containing ligands [6] it is perhaps surprising that no heterodicyclometallated analogues have been reported. We felt that a good ligand for the preparation of a doubly cyclometallated complex incorporating two different metals would be 1,5-bis(dimethylamino)naphthalene (7) since 1-dimethylaminonaphthalene readily undergoes cyclometallation with a variety of different metals [2] and the relative locations of the dimethylamino substituents should further activate a second metallation reaction. Thus we herein also describe some cyclometallation reactions of this ligand.

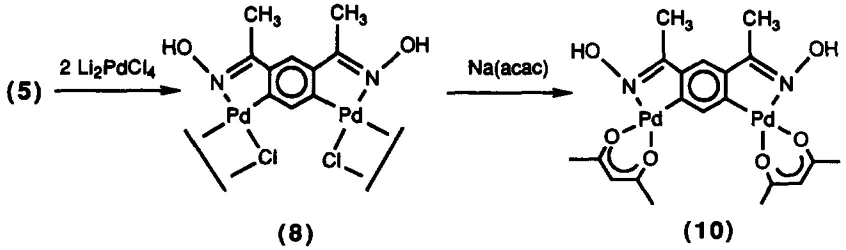
Results and discussion

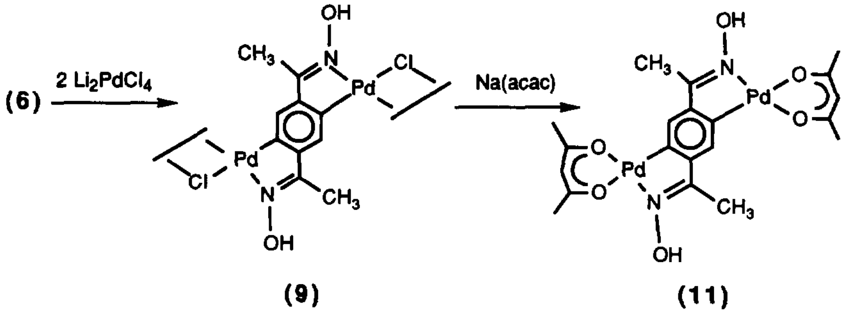
Cyclometallation reactions

The isomeric oximes **5** and **6** were each reacted with two equivalents of lithium tetrachloropalladate in methanol, in a procedure similar to that previously reported for the cyclopalladation of acetophenone oxime [11]. In each case this gave good yields of products with the stoichiometry LPd_2Cl_2 and which were assigned the chlorobridged polymeric structures **8** and **9**. The *meta* isomer was sufficiently soluble in dimethylsulfoxide to obtain a ^1H NMR spectrum, which showed two aromatic singlets consistent with the structure **8**. Ligand exchange with sodium acetylacetonate gave the more soluble binuclear complexes **10** and **11** whose ^1H NMR spectra contained two and one aromatic singlets respectively.

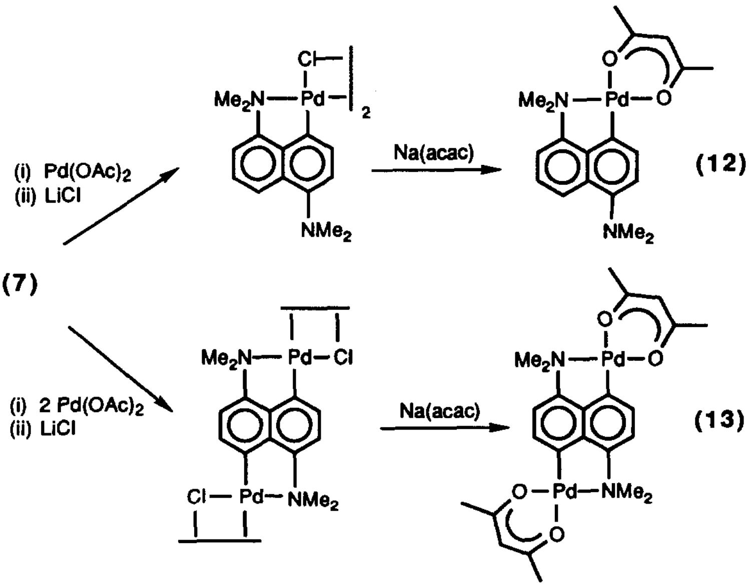
These reactions further demonstrate the feasibility of effecting the double cyclopalladation of a single benzene ring as had previously been described for xylene diamines [9]. It is notable that in both cases only a single regioisomer was observed. In the case of **8** no metallation of the 2-position was observed; metaxylene diamines have been metallated in the 2-position with a variety of different metals to give mononuclear complexes with *N,C,N*-tridentate coordination by the ligand [12]. The formation of a single product from **6** presumably reflects the more favourable para orientation of the two palladium substituents in **9** relative to the alternative sterically demanding ortho disubstitution pattern.

Reaction of 1,5-bis(dimethylamino)naphthalene (7) with two equivalents of lithium tetrachloropalladate in methanol, followed by ligand exchange with sodium acetylacetonate gave in low yield a mixture of the mono- and di-palladated products **12** and **13** in addition to $Pd(acac)_2$. More conveniently these products were selectively prepared by reaction of **7** with one and two equivalents respectively of palladium acetate, followed by sequential conversion to the chlorides and acetylacetonates. The NMR spectra fully supported the structures **12** and **13** and the X-ray crystal structure of **12** was determined and is described below.



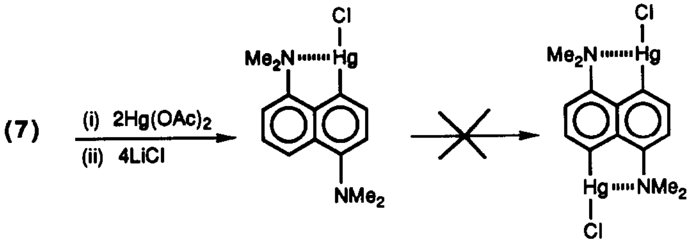


Having established that 7 can be selectively mono- and di-cyclopalladated, we examined the possibility of preparing a heterodicyclometallated derivative of 7. To this end we attempted to prepare cycloplatinated derivatives of 7 by reaction with potassium tetrachloroplatinate(II) in methanol/water, and in refluxing acetic acid,



and with *cis*-dichloro-bis(dimethylsulfoxide)platinum(II) in refluxing methanol [13]. In no case were we able to isolate cycloplatinated products; the NMR spectra indicated the formation of non-cyclometallated coordinated complexes of **7** which showed broadening of some of the aromatic proton signals possibly due to agostic Pt–H interaction [14]. The contrast between the reactions with palladium(II) and platinum(II) can be related to the different reaction mechanisms for the cyclometallations, the former reaction occurs by electrophilic substitution and the latter by oxidative addition [3]. In a similar way reaction with stannic chloride in boiling toluene [15] gave only a non-cyclometallated product of stoichiometry [$7 \cdot Sn_2Cl_8$].

Since cyclomercurated compounds can be readily transmetallated with a variety of transition metals [16], selective sequential transmetallations with different metals was considered as an alternative approach to a heterodicyclometallated derivative of **7**. However reaction of **7** with two equivalents of mercuric acetate followed by lithium chloride gave only the monomercurated product **14** rather than the desired dimercurated product **15**. Thus although **7** readily undergoes single and double cyclopalladation reactions we have so far been unable to prepare a heterodicyclometallated derivative.



(14) **(15)**

X-Ray crystal structure of 12

In order to confirm the structure of the monopalladated product from 1,5-bis(dimethylamino)naphthalene, a single crystal X-ray analysis was carried out. Figure 1

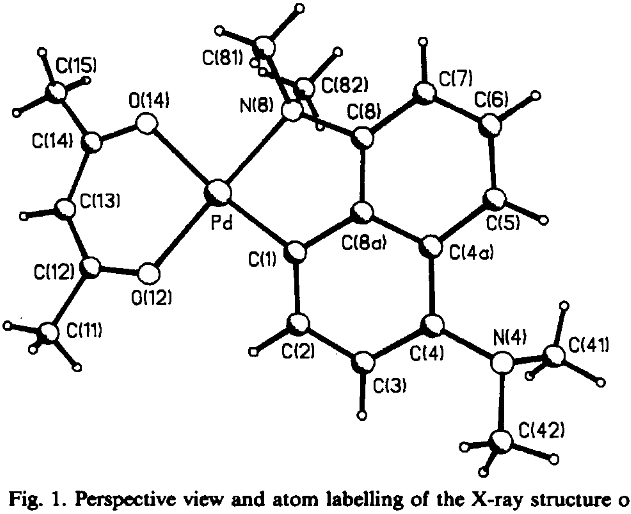


Fig. 1. Perspective view and atom labelling of the X-ray structure of **12**.

Table 1

Bond lengths (Å) and bond angles (°) for **12**

Pd–C(1)	1.934(14)	Pd–N(8)	2.077(10)	Pd–O(12)	2.023(8)
Pd–O(14)	2.103(11)	C(1)–C(2)	1.339(23)	C(1)–C(8A)	1.433(20)
C(2)–C(3)	1.403(23)	C(3)–C(4)	1.405(21)	C(4)–N(4)	1.414(19)
C(4)–C(4A)	1.425(22)	N(4)–C(41)	1.481(20)	N(4)–C(42)	1.455(23)
C(4A)–C(5)	1.421(22)	C(4A)–C(8A)	1.432(20)	C(5)–C(6)	1.339(24)
C(6)–C(7)	1.378(24)	C(7)–C(8)	1.390(24)	C(8)–N(8)	1.493(21)
C(8)–C(8A)	1.407(22)	N(8)–C(81)	1.479(17)	N(8)–C(82)	1.432(24)
O(12)–C(12)	1.307(19)	O(14)–C(14)	1.260(20)	C(11)–C(12)	1.493(22)
C(12)–C(13)	1.372(22)	C(13)–C(14)	1.414(23)	C(14)–C(15)	1.494(23)

C(1)–Pd–N(8)	85.4(6)	C(1)–Pd–O(21)	93.1(5)
N(8)–Pd–O(12)	178.2(4)	C(1)–Pd–O(14)	173.4(5)
N(8)–Pd–O(14)	88.9(5)	O(12)–Pd–O(14)	92.6(4)
Pd–C(1)–C(2)	131.3(12)	Pd–C(1)–C(8A)	12.7(10)
C(2)–C(1)–C(8A)	116.0(14)	C(1)–C(2)–C(3)	123.8(16)
C(2)–C(3)–C(4)	121.6(15)	C(3)–C(4)–N(4)	123.3(13)
C(3)–C(4)–C(4A)	117.3(13)	N(4)–C(4)–C(4A)	119.3(12)
C(4)–N(4)–C(41)	111.8(12)	C(4)–N(4)–C(42)	117.9(13)
C(41)–N(4)–C(42)	111.3(13)	C(4)–C(4A)–C(5)	124.5(13)
C(4)–C(4A)–C(8A)	118.4(13)	C(5)–C(4A)–C(8A)	117.1(14)
C(4A)–C(5)–C(6)	121.7(15)	C(5)–C(6)–C(7)	122.5(16)
C(6)–C(7)–C(8)	117.8(15)	C(7)–C(8)–N(8)	123.3(14)
C(7)–C(8)–C(8A)	122.2(15)	N(8)–C(8)–C(8A)	114.4(13)
Pd–N(8)–C(8)	108.4(10)	Pd–N(8)–C(81)	108.3(7)
C(8)–N(8)–C(81)	109.9(14)	Pd–N(8)–C(82)	111.3(10)
C(8)–N(8)–C(82)	108.4(11)	C(81)–N(8)–C(82)	110.5(14)
C(1)–C(8A)–C(4A)	122.7(13)	C(1)–C(8A)–C(8)	119.0(13)
C(4A)–C(8A)–C(8)	118.2(14)	Pd–O(12)–C(12)	122.1(10)
Pd–O(14)–C(14)	123.7(10)	O(12)–C(12)–C(11)	112.2(13)
O(12)–C(12)–C(13)	127.7(15)	C(11)–C(12)–C(13)	119.9(14)
C(12)–C(13)–C(14)	128.8(15)	O(14)–C(14)–C(13)	124.5(15)
O(14)–C(14)–C(15)	117.2(14)	C(13)–C(14)–C(15)	118.2(14)

shows a minimum overlap view of the structure and includes the atom labelling. Table 1 lists all bond lengths and bond angles. The structure is confirmed as **12** in which the ligand has undergone monocyclopalladation. The coordination about the palladium atom is square planar with Pd–C and Pd–N bond lengths similar to those in related cyclopalladated complexes which incorporate an internal nitrogen donor [4,5,17,18]. The geometry of the acetylacetonate ligands is similar to that in other Pd(acac) complexes [4,5,18]. The different *trans* influences of carbon and nitrogen are reflected in the unequal Pd–O bond lengths, with that *trans* to carbon being significantly longer than that *trans* to nitrogen. In the solid state the potential C_s symmetry of the complex is destroyed by the conformation of the non-coordinated dimethylamino substituent, with C(41) 1.377 Å above and C(42) 0.287 Å below the naphthalene meanplane. No unusually short intermolecular contacts exist.

Experimental

For general procedures and instrumentation see ref. 19.

1,3-Diacetylbenzene dioxime was prepared from the diketone [20]. M.p. 205 ° C; lit. [20] 204 ° C. ^{1}H NMR (dmso-d_6): δ 2.29 (6H, s, CH_3); 7.50 (1H, t, H5); 7.75

(2H, d, H4,6); 8.03 (1H, s, H2); 11.34 (2H, s, OH). ^{13}C NMR (dmso-d_6): δ 11.6 (CH_3); 122.7 (C2); 125.9 (C4,6); 128.5 (C5); 137.1 (C1,3); 152.8 (CNOH). 1,4-Diacetylbenzene dioxime was prepared from the diketone [21]. M.p. 255 °C; lit. [21] 248–250 °C. ν(KBr) 820 cm^{-1}. ^{1}H NMR (dmso-d_6) δ 2.28 (6H, s, CH_3); 7.76 (4H, s, H2,3,5,6); 11.36 (2H, s, OH). ^{13}C NMR (dmso-d_6): δ 11.5 (CH_3); 125.5 (C2,3,5,6); 137.1 (C1,4). 1,5-Bis(dimethylamino)naphthalene was prepared from 1,5-diaminonaphthalene [22]. M.p. 89 °C; lit. [22] 87–88 °C. ^{1}H NMR ($CDCl_3$): δ 2.88 (s, CH_3); 7.05 (d, H2,6); 7.38 (t, H3,7); 7.93 (d, H4,8). ^{13}C NMR ($CDCl_3$): δ 45.3 (CH_3); 113.8 (C2,6); 119.0 (C4,8); 124.9 (C3,7); 130.3 (C4a,8a); 151.2 (C1,5).

Preparation and spectra of complexes

Cyclopalladations were carried out by reaction of the ligand with lithium tetrachloropalladate or palladium acetate according to previously described procedures for cyclometallations of related ligands [5].

Reaction of 1,3-diacetylbenzene dioxime (**5**) with two equivalents of lithium tetrachloropalladate in methanol gave, in 93% yield, catena-μ-(1,3-diacetylbenzene dioxime-$C^4,N:C^6,N'$)di-μ-chloro-dipalladium(II) (**8**). M.p. > 300 °C. ν(KBr) 870 cm^{-1}. ^{1}H NMR (dmso-d_6): δ 2.39 (s, CH_3); 7.21 (s, H2); 7.95 (s, H5). Found: C, 25.10; H, 2.09; N, 5.52. $(C_{10}H_{10}N_2O_2Cl_2Pd_2)_n$ calc.: C, 25.34; H, 2.13; N, 5.91%. Ligand exchange with sodium acetylacetonate gave, in 91% yield, μ-(1,3-diacetylbenzenedioxime-$C^4,N:C^6,N'$)-bis(acetylacetonato)dipalladium(II) (**10**). M.p. > 300 °C. ν(KBr) 875 cm^{-1}. ^{1}H NMR (dmso-d_6): δ 2.08 and 2.10 (s, acac-CH_3); 2.39 (s, CH_3); 5.52 (s, acac-CH); 7.20 (s, H2); 7.63 (s, H5).

Reaction of 1,4-diacetylbenzene dioxime (**6**) with two equivalents of lithium tetrachloropalladate in methanol gave, in 95% yield, catena-μ-(1,4-diacetylbenzenedioxime-$C^2,N:C^5,N'$)di-μ-chloro-dipalladium(II) (**9**). M.p. > 300 °C. ν(KBr) 860 cm^{-1}. Found: C, 25.49; H, 2.15; N, 5.63. $(C_{10}H_{10}N_2O_2Cl_2Pd_2)_n$ calc.: C, 25.34; H, 2.13; N, 5.91%. Ligand exchange with sodium acetylacetonate gave, in 61% yield, μ-(1,4-diacetylbenzene dioxime-$C^2,N:C^5,N'$)-bis(acetylacetonato)dipalladium(II) (**11**0. m.p. > 300 °C. ν(KBr) 880 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.02 and 2.11 (s, acac-CH_3); 2.33 (s, CH_3); 5.39 (s, acac-CH); 7.18 (s, H3,6); 8.55 (s, OH). Found: C, 38.55; H, 3.88; N, 4.51.$C_{20}H_{24}N_2O_6Pd_2 \cdot H_2O$ calc: C, 38.79; H, 4.23; N, 4.52%.

Reaction of 1,5-bis(dimethylamino)naphthalene (**7**) with one equivalent of palladium acetate in refluxing acetic acid followed by ligand exchange with lithium chloride gave di[1,5-bis(dimethylamino)naphthalene-C^4,N^5]di-μ-chlorodipalladium(II) in 50% yield. M.p. > 300 °C. ^{1}H NMR (dmso-d_6): δ 2.87 (s, $N^1(CH_3)_2$); 3.46 (s, $N^5(CH_3)_2$); 7.03 (d); 7.60 (t); 7.87 (d); 7.47 (d); 8.05 (d). Ligand exchange with sodium acetylacetonate gave acetylacetonato[1,5-bis(dimethylamino)naphthalene-C^4,N^5]palladium(II) (**12**) which was recrystallised from methanol to give the crystals used for the X-ray structure determination. M.p. 159–160 °C. ^{1}H NMR ($CDCl_3$): δ 2.00 and 2.07 (s, acac-CH_3); 2.85 (s, $N^1(CH_3)_2$); 3.35 (s, $N^5(CH_3)_2$); 5.35 (s, acac-CH); 6.98 (d); 7.31 (t); 7.32 (d); 7.37 (d); 7.99 (d). Found: C, 54.00; H, 5.67; N, 6.57. $C_{19}H_{24}N_2O_2Pd$ calc.: C, 54.49; H, 5.78; N, 6.69%.

Reaction of 1,5-bis(dimethylamino)naphthalene (**7**) with two equivalents of palladium acetate in refluxing acetic acid followed by ligand exchange with lithium chloride gave catena-μ-[1,5-bis(dimethylamino)naphthalene-$C^4,N^5:C^8,N^1$]di-μ-chloro-dipalladium(II) in 55% yield. M.p. > 250 °C. Found: C, 33.14; H, 3.13; N, 5.59. $(C_{14}H_{16}N_2Cl_2Pd_2)_n$ calc.: C, 33.9; H, 3.25; N, 5.65%. Ligand exchange with

Table 2

Crystal data and X-ray experimental details for **12**

Formula	$C_{19}H_{24}N_2O_2Pd$
Molecular weight	418.8
Crystal system	orthorhombic
Space group	$Pca2_1$
a (Å)	15.039(12)
B (Å)	7.538(5)
C (Å)	15.886(11)
V (Å^3)	1801(2)
D_c (g cm^{-3})	1.54
Z	4
$F(000)$	856
μ (cm^{-1})	10.3
Radiation	Mo-K_α
Wavelength (Å)	0.71069
Temperature (°C)	−110
Crystal dimensions (mm)	0.41×0.22×0.02
Scan mode	ω
2θ range (°)	3–55
Unique reflections	2131
Observed reflections ($I > 3\sigma(I)$)	1196
Number of parameters	101
R	0.058
R_w	0.054

sodium acetylacetonate gave μ-[1,5-bis(dimethylamino)naphthalene-$C^4,N^5:C^8,N^1$] bis(acetylacetonato)dipalladium(II) (**13**) in 63% yield. M.p. >250 °C. ^{1}H NMR (dmso-d_6); δ 2.08 and 2.11 (s, acac-CH_3); 3.32 (s, $N(CH_3)_2$); 5.52 (s, acac-CH); 7.16 (d, H2,6); 7.47 (d, H3,7). ^{1}H NMR ($CDCl_3$): δ 2.01 and 2.06 (s, acac-CH_3); 3.30 (s, $N(CH_3)_2$); 5.35 (s, acac-CH); 7.15 (d, H2,6); 7.25 (d, H3,7).

1,5-Bis(dimethylamino)naphthalene (**7**) and two equivalents of $SnCl_4 \cdot 5H_2O$ were refluxed in toluene for 24 h to give a green solid in 43% yield. M.p. 255–260 °C ^{1}H NMR (dmso-d_6): δ 3.15 (s, $N(CH_3)_2$; 7.74 (m, 4H); 8.30 (d, 2H). Found: C, 22.87; H, 2.54; N, 3.80. $C_{14}H_{18}N_2Cl_8Sn_2$ calc.: C, 22.87; H, 2.47; N, 3.81%.

1,5-Bis(dimethylamino)naphthalene (**7**) was refluxed with two equivalents of $Hg(AcO)_2$ in ethanol for 24 h. Lithium chloride (4 equivalents) in methanol was added and the mixture heated for a further 15 min. Addition of water afforded a dark brown precipitate of chloro[1,5-bis(dimethylamino)naphthalene-C^4,N^5]-mercury(II) (**14**) in 86% yield. ^{1}H NMR (dmso-d_6): δ 2.90 (s, $N^1(CH_3)_2$); 3.41 (s, $N^5(CH_3)_2$) 7.22 (d); 7.60 (t); 7.66 (d); 7.77 (d); 8.16 (d).

Crystallography

Table 2 lists crystal data and X-ray experimental details for **12**. Intensity data were collected with a Nicolet $R3m$ four-circle diffractometer by using monochromatized Mo-K_α radiation. Cell parameters were determined by least squares refinement, the setting angles of 25 accurately centred reflections ($2\theta > 20°$) being used. Throughout data collection the intensities of three standard reflections were moni-

Table 3

Atomic coordinates ($\times 10^4$) and thermal parameters ($Å^2 \times 10^3$) for **12**

	x	y	z	U
Pd	6683(1)	1901(1)	5000 [a]	[b]
C(1)	5884(9)	2744(19)	5866(9)	13(3)
C(2)	5896(12)	4222(25)	6334(11)	27(4)
C(3)	5233(10)	4666(21)	6918(10)	19(4)
C(4)	4504(10)	3544(18)	7069(10)	15(3)
N(4)	3837(8)	3919(17)	7672(8)	18(3)
C(41)	2956(10)	4171(22)	7272(11)	26(4)
C(42)	4017(12)	5294(23)	8292(12)	32(5)
C(4A)	4490(9)	1885(23)	6639(9)	17(3)
C(5)	3859(11)	518(21)	6789(11)	22(4)
C(6)	3851(11)	−977(23)	6333(11)	27(4)
C(7)	4472(11)	−1326(22)	5717(11)	24(4)
C(8)	5111(11)	−37(23)	5555(10)	19(4)
N(8)	5825(7)	−250(13)	4909(11)	13(3)
C(81)	6338(7)	−1885(18)	5078(15)	19(3)
C(82)	5416(11)	−334(23)	4096(11)	26(4)
C(8A)	5166(9)	1540(19)	6026(9)	16(3)
O(12)	7486(5)	4045(10)	5098(8)	16(2)
O(14)	7424(8)	846(15)	3994(7)	27(3)
C(11)	8615(10)	6028(20)	4754(10)	28(4)
C(12)	8115(10)	4372(22)	4551(10)	25(4)
C(13)	8371(11)	3344(21)	3881(9)	24(3)
C(14)	8038(10)	1675(23)	3625(10)	23(4)
C(15)	8406(12)	862(22)	2840(10)	27(4)

[a] Origin defining parameter. [b] $U_{11}(1) = 12$, $U_{22}(1) = 20$, $U_{33}(1) = 20$, $U_{23}(1) = 6$, $U_{13} = 2(1)$, $U_{12} = -1(1)$.

tored at regular intervals and this indicated no significant crystal decomposition. The intensities were corrected for Lorentz and polarization effects and for absorption by a procedure based on azimuthal ψ scans.

The structure was solved by conventional Patterson and Fourier methods, and refined by blocked cascade least-squares procedures. In view of the paucity of observed data, associated with the relatively poor crystal quality, only the palladium atom was refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to those of their carrier atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + 0.0004F_o^2]^{-1}$. The absolute structure was not determined. All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL [23]. Final atom coordinates and thermal parameters are listed in Table 3. Tabulations of structure factors, hydrogen atom coordinates and equations of meanplanes are available from the author P.J.S.

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