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Journal of Organometallic Chemistry 488 (1995) 79–83

Journal
of Organometallic
Chemistry

Synthesis, X-ray structure and reactivity of cyclopalladated complexes of hydrazones of 1*H*-indole-3-carboxaldehyde^{*}

Stefano Tollari^a, Giovanni Palmisano^b, Francesco Demartin^c, Maria Grassi^a,
Stefano Magnaghi^a, Sergio Cenini^{a,*}

^a Dipartimento di Chimica Inorganica, Metallorganica ed Analitica and Centro CNR, Via Venezian 21, 20133 Milano, Italy

^b Dipartimento di Chimica Organica ed Industriale, Via Venezian 21, 20133 Milano, Italy

^c Istituto di Chimica Strutturistica Inorganica, Via Venezian 21, 20133 Milano, Italy

Received 27 May 1994

Abstract

By reaction of $\text{Li}_2[\text{PdCl}_4]$ with substituted hydrazones of 1*H*-indole-3-carboxaldehyde the corresponding cyclopalladated complexes have been isolated and characterized. Compound **1a** [$\text{C}_{11}\text{H}_{10}\text{ClN}_3\text{OPd}$] reacts with PPh_3 by halogen displacement giving the cationic complex **5** the X-ray structure of which has revealed metallation at position 4 of the indole hydrazone, which is terdentate forming a [5,6]-fused ring system.

Keywords: Palladium; Cyclopalladation; X-ray structure; Aldehyde hydrazones; Metallation; Hydrazones

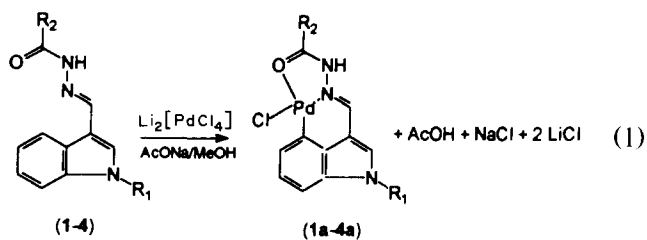
1. Introduction

Cyclometallation reactions have been the subject of many investigations in recent years [1,2], and cyclopalladated complexes have found various applications in organic synthesis [1,3]. Many examples are known for benzene and heteroaromatic derivatives but not for indole compounds. In particular, Nonoyama has studied the cyclopalladation of hydrazones derived from 1-[(4-methylphenyl)sulfonyl]-3-acetylpyrrole with acetylhydrazide and related derivatives [4]. We report here the attempted cyclopalladation of the indole ring by reaction of $\text{Li}_2[\text{PdCl}_4]$ with hydrazones of 1*H*-indole-3-carboxaldehyde.

2. Results and discussion

By reactions of $\text{Li}_2[\text{PdCl}_4]$ with the hydrazones **1–4** in methanol, the corresponding cyclopalladated com-

plexes have been isolated in good overall yield [Eq. (1)] (Table 1).



$\text{R}^1 = \text{H}$: (1) $\text{R}^2 = \text{Me}$; (2) $\text{R}^2 = \text{OEt}$; (3) $\text{R}^2 = \text{NH}_2$;
 $\text{R}^1 = \text{SO}_2\text{Me}$: (4) $\text{R}^2 = \text{Me}$

The proposed structure with palladation at position 4 of the terdentate indole residue (*peri*-metallation) which forms a doubly-chelated metallacycle, is supported by the reactivity of compound **1a** with PPh_3 (see later) and by spectroscopic data (Tables 1, 2 and 3).

In the IR spectra, $\nu(\text{C}=\text{O})$ shifts to lower frequencies upon formation of the complexes (Table 1), indicating coordination of the carbonyl group of the hydrazone, but the $\nu(\text{NH})$ shifts are not readily explicable. Compound **4a** showed the expected absorptions (Table 1) and bands due to the $-\text{SO}_2-$ group. The far IR spectrum of compound **1a** exhibited bands at 352 (m), 328.8 (m) and 287 (m) cm^{-1} . The absorption at 328.8

^{*} Dedicated to Professor Fausto Calderazzo on the occasion of his 65th birthday.

^{*} Corresponding author.

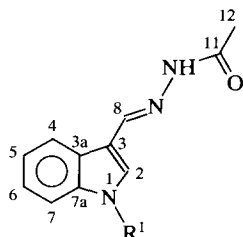
Table 1
Analytical data and selected IR absorptions ^a

Compound	C ^b	H ^b	N ^b	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$
1	65.4 (65.7)	5.5 (5.5)	20.8 (20.4)	3240–3140	1650	1574
1a	38.4 (38.2)	3.0 (2.8)	11.9 (12.1)	3272–3213	1625	1580
2	61.7 (62.3)	5.3 (5.6)	18.1 (18.2)	3260–3200	1715	1570
2a	38.8 (37.1)	3.2 (3.1)	10.7 (10.3)	3349–3174	1633	1580
3	58.8 (59.4)	5.0 (4.9)	27.1 (27.7)	3505–3485 to 3369–3200	1668	1575
3a	34.2 (35.0)	2.7 (2.6)	16.8 (16.4)	3300 (broad)	1622	1577
4 ^d	51.4 (51.6)	4.5 (4.7)	14.7 (15.0)	3245–3205	1656	1554
4a ^c	34.9 (34.3)	9.6 (10.1)	3.1 (2.9)	3172–3113	1622	1584
5 ^c	56.9 (56.8)	3.9 (4.1)	6.4 (7.0)	3325	1600	1557

^a cm^{-1} , Nujol mull. ^b Found (calc.) (%). ^c Cationic, cyclopalladated complex with PPh_3 as ligand $[\text{FAB}^+$, glycerine; m/z 568 ($\text{C}_{29}\text{H}_{25}\text{N}_3\text{OPd}^+$) 399, 358, 334, 306, 263]. ^d $\nu_{\text{asym}}(\text{SO}_2) = 1352$, $\nu_{\text{sym}}(\text{SO}_2) = 1124$. ^e $\nu_{\text{asym}}(\text{SO}_2) = 1350$, $\nu_{\text{sym}}(\text{SO}_2) = 1152$.

Table 2

¹H ^a NMR data (δ in ppm; J in Hz; $\text{DMSO-}d_6$) for **1–4**, cyclopalladated complexes **1a–4a** and the cationic complex **5**



Compound	H(1) ^d	H(2) ^c	H(4)	H(5)	H(6)	H(7)	H(8)	H(10)[NNHCO ^d]	H(12)
1	11.51	7.75 (d)	8.17 (d)	7.14 (m)	7.19 (m)	7.43 (d)	8.17	10.92	<i>MeCO</i> 2.26
b		7.77	8.21	7.13			8.31	11.00	1.93
1a	$J_{1,2} = 2.3$ 11.93	8.19	$J_{4,5} = 7.5$	$J_{5,6} = 7.3$ 7.81 (d)	$J_{6,7} = 7.2$ 6.92 (t)	7.21 (d)	8.41	13.52	<i>MeCO</i> 2.21
2	$J_{1,2} = 2.5$ 11.72	8.17 (d)	7.78 (d)	6.9 (m)	7.32 (t)	7.41 (d)	8.22	9.32 ^e	<i>OEt</i> 4.12, 1.21
2a	$J_{1,2} = 2.1$ 12.13	8.21 (d)	$J_{4,5} = 7.1$	$J_{5,6} = 7.2$ 7.68 (d)	$J_{6,7} = 7.4$ 6.89 (m) ^f	7.21 (d)	8.20	13.51	$J_{\text{CH}_2\text{CH}_3} = 7.6$ <i>OEt</i> 4.31, 1.32
3	$J_{1,2} = 2.2$ 11.42	7.61 (d)	8.12 (d)	6.85 (m)	7.21 (m)	7.42 (d)	8.16	9.81	NH_2 6.23 ^d
3a	$J_{1,2} = 2.1$ 11.42	7.61 (d)	8.12 (d)	6.85 (m)	7.21 (m)	7.42 (d)	8.16	9.81	NH_2 6.23 ^d
3a	^g	8.05 (d)	–	8.62 (d)	6.82 (m)	7.15 (d)	8.25	^g	NH_2 7.14 ^d
4				$J_{5,6} = 7.6$ 7.35–8.22	$J_{6,7} = 7.8$			^h	SO_2Me 3.49 <i>COMe</i> 2.26
4a		8.62	–	7.92 (d)	7.17 (t)	7.56 (d)	8.51	11.32	SO_2Me 3.65 <i>COMe</i> 2.18
5 ⁱ	12.32	8.31 (d)	–	$J_{5,6} = 7.8$	$J_{6,7} = 7.9$ 6.51 (m)	7.26 (d)	8.73	12.15	<i>COMe</i> 1.85
		$J_{1,2} = 1.8$			$J_{6,7} = 7.2$				

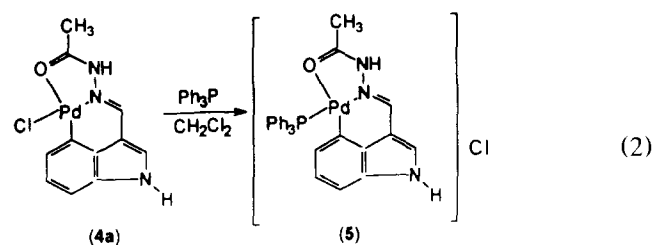
^a First-order analysis. ^b Values for the *syn* isomer. ^c On treatment with D_2O becomes a singlet. ^d On treatment with D_2O this signal disappeared. ^e At 8.61 ppm another signal due to the *anti* isomer was detected. ^f After treatment with D_2O this became a triplet. ^g Two signals were detected at 11.73 and 11.78 ppm. ^h Two signals were observed at 11.25 and 11.39 ppm, due to *syn/anti* isomers. ⁱ One signal at 42 ppm was observed in the ^{31}P NMR spectrum. ¹ Covered by absorption of PPh_3 at 7.44–7.84 ppm.

cm^{-1} is probably attributable to $\nu(\text{Pd}-\text{Cl})$, since it is absent in compound **5** where chlorine is not coordinated (see later). Finally, the out-of-plane bending region of the aromatic hydrogens was not useful for the structure determination, since we did not find a regular trend in the number of absorptions for either the free hydrazone or the cyclopalladated complexes.

Compounds **1–5** and **1a–4a** have been characterized by ^1H and ^{13}C NMR spectroscopy. Selected NMR data are listed in Tables 2 and 3. Owing to overlapping, particularly in the aromatic region, the assignment of ^1H and ^{13}C NMR spectra has required the combination of one- and two-dimensional techniques. For example, in the ^1H spectrum of complex **1a** the observation of two exchangeable broad singlets at 13.52 and 11.93 ppm as well as of NOE effect between the CH_3 -CO singlet at 2.21 ppm and the singlet at 13.52 ppm has allowed us to assign H(10) and H(1) (at 13.52 and 11.93 ppm, respectively). The assignment of the other resonances of the spectrum (Table 2) has been confirmed by ^1H 2D COSY and ^1H 2D NOESY experiments. From the ^1H NMR spectrum, the assignment of the protonated carbons has been straightforward on the basis of two-dimensional ^1H - ^{13}C correlation spectroscopy. The NMR findings of the corresponding free hydrazone **1** revealed the presence of *syn/anti* isomers (ca. 1:2.5 ratio). As expected, the two isomers exhibit very similar carbon and proton spectra and their different stereostructure mainly affects the chemical shifts of carbons C(12), C(8), C(11), as well as those of H(8), H(10), H(12). Obviously the *syn* converts to the *anti* isomer in order to give the cyclopalladated derivative. The characterization of the other compounds was made in a similar manner and their relative data are shown in Tables 2 and 3.

The NMR data afford further evidence for the proposed structures. Obviously, the resonance of H(4) was absent in the spectra of **1a–4a** and **5**. Comparing the ^1H and ^{13}C NMR findings for **1–4** and **1a–4a**, in the latter a strong downfield shift for H(5), H(10) and

C(5) indicates that palladation occurs at position 4 of the indole and that the CO-NH-N- group is directly involved in coordination. Compound **1a** reacts with PPh_3 in CH_2Cl_2 by halogen displacement giving the cationic metallated complex **5** [Eq. (2)].



In the IR spectrum (Table 1), compound **5** shows the expected absorptions with a remarkable shift to lower frequencies of $\nu(\text{C}=\text{O})$ with respect to the free hydrazone. As already pointed out, $\nu(\text{Pd}-\text{Cl})$ was absent in the far IR spectrum.

The structure of compound **5** has been confirmed by X-ray diffraction. Crystals of $\text{5} \cdot \text{CHCl}_3$ derive from the packing of $[\text{C}_{29}\text{H}_{25}\text{N}_3\text{OPPd}]^+$ cations, Cl^- anions and clathrated CHCl_3 solvent molecules. The shortest interactions between cations and anions are: $\text{Cl}(1) \cdots \text{H}(\text{N}8)$, 2.22(5) Å; and $\text{Cl}(1) \cdots \text{H}(\text{N}3)$, 2.38(5) Å. The remaining contacts, including also those involving the chloroform molecules, are not shorter than the sum of the van der Waals radii. A perspective view of the $[\text{C}_{29}\text{H}_{25}\text{N}_3\text{OPPd}]^+$ cation is shown in Fig. 1. It contains a [5,6] fused-ring system, arising from terdentate coordination of the hydrazone. The six-membered metallacycle displays a boat-like conformation with the Pd and the C(6) atoms 0.14 and 0.04 Å, respectively, above the least-squares plane defined by the N(4), C(5), C(10) and C(11). The five-membered metallacycle possesses an envelope conformation; the Pd atom is 0.22 Å above the plane passing through N(4), N(3), C(2) and O(1), whereas the N(4)-N(3)-C(2)-O(1) torsion angle is 5.7(7)°. The coordination geometry around Pd is distorted towards tetrahedral. A similar situation

Table 3
 ^{13}C NMR data (δ in ppm; $\text{DMSO}-d_6$) for **1–4**, cyclopalladated complexes **1a–4a** and the cationic complex **5**

Compound	C(2)	C(3)	C(3a)	C(4)	C(5)	C(6)	C(7)	C(7a)	C(8)	C(11)	C(12)
1 ^b	129.9	111.5	124.0 (124.2)	121.4 (121.8)	120.3 (120.1)	122.3	111.8	136.8	139.8 (142.7)	171.0 (164.0)	20.3 (21.6)
1a	134.1	114.2	125.3	118.9	131.1	122.1	109.2	133.2	140.4	170.2	18.2
2	129.1	111.8	124.4	120.1	121.7	122.3	111.6	136.8	140.9	158.4	^a
2a	129.8	114.0	122.8	119.4	129.8	122.1	109.8	132.3	138.3	159.1	^a
3	129.7	113.6	123.9	121.7	122.3	120.2	114.2	136.8	137.5	157.9	
3a	125.6	115.7	125.3	120.3	127.5	122.3	110.3	132.3	135.8	160.1	
4 ^b	129.1	112.8	125.8 (125.3)	122.6 (122.2)	126.8 (126.3)	122.4	116.7	135.3	140.2 (141.3)	171.4 (165.2)	19.4 (20.2)
4a	129.6	114.3	126.4	120.8	132.4	121.8	114.3	132.4	138.6	172.6	18.3
5	134.4	114.2	124.9	120.1	131.1	122.2	109.3	133.4	140.5	170.2	18.2

^a For the OCH_2CH_3 group 14.5 and 59.9 ppm for compound **2**, 14.7 and 64.1 ppm for compound **2a**. ^b Values in parentheses are for the *anti* isomer.

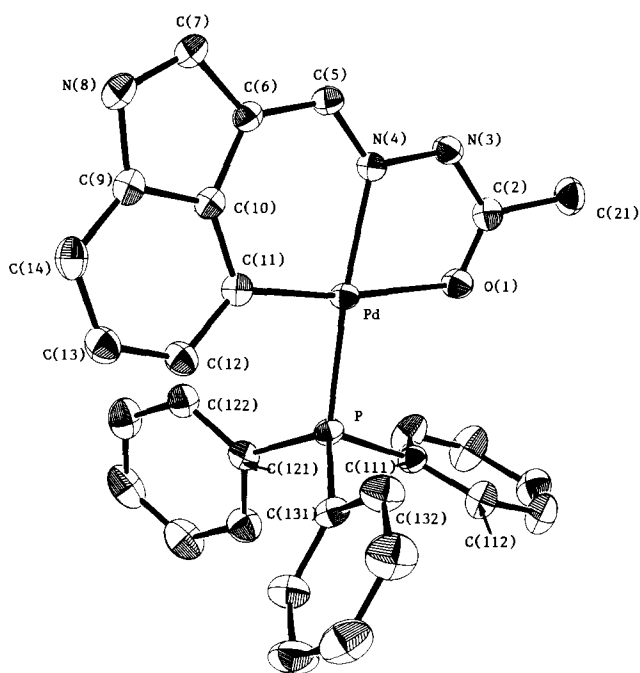


Fig. 1. Perspective view of the $[C_{29}H_{25}N_3OPPd]^+$ cation.

in a cyclometallated complex of Pd containing a terdentate ligand has been reported [5]. Selected interatomic distances within the cation are reported in Table 4.

We are currently investigating the reactivity of compounds **1a–4a** with several electrophiles, and the reactions of $Li_2[PdCl_4]$ with other indole derivatives.

Table 4

Selected interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses

Pd–P	2.247(1)	N(4)–C(5)	1.296(4)
Pd–O(1)	2.153(2)	N(8)–C(7)	1.342(5)
Pd–N(4)	2.074(3)	N(8)–C(9)	1.389(5)
Pd–C(11)	2.005(3)	C(2)–C(21)	1.496(5)
C(5)–C(6)	1.410(5)	C(9)–C(10)	1.414(5)
C(6)–C(7)	1.394(5)	C(9)–C(14)	1.387(5)
C(6)–C(10)	1.439(5)	C(10)–C(11)	1.403(5)
O(1)–C(2)	1.240(4)	C(11)–C(12)	1.408(5)
N(3)–N(4)	1.383(4)	C(12)–C(13)	1.385(5)
N(3)–C(2)	1.328(5)	C(13)–C(14)	1.382(6)
P–Pd–O(1)	94.71(7)	C(5)–C(6)–C(7)	125.8(3)
P–Pd–N(4)	170.55(8)	C(5)–C(6)–C(10)	126.5(3)
P–Pd–C(11)	94.7(1)	C(7)–C(6)–C(10)	107.3(3)
O(1)–Pd–N(4)	76.7(1)	N(8)–C(7)–C(6)	109.3(3)
O(1)–Pd–C(11)	170.4(1)	N(8)–C(9)–C(10)	107.9(3)
N(4)–Pd–C(11)	94.1(1)	N(8)–C(9)–C(14)	128.9(3)
C(10)–C(9)–C(14)	123.2(3)	C(9)–C(10)–C(11)	121.0(3)
C(6)–C(10)–C(9)	105.7(3)	Pd–C(11)–C(10)	115.8(2)
C(6)–C(10)–C(11)	133.3(3)	Pd–C(11)–C(12)	129.3(3)
Pd–O(1)–C(2)	112.1(2)	C(10)–C(11)–C(12)	114.8(3)
N(4)–N(3)–C(2)	118.0(2)	C(11)–C(12)–C(13)	123.0(4)
Pd–N(4)–N(3)	111.2(2)	C(12)–C(13)–C(14)	122.6(4)
Pd–N(4)–C(5)	131.2(2)	C(9)–C(14)–C(13)	115.3(3)
N(3)–N(4)–C(5)	117.7(3)	O(1)–C(2)–C(21)	121.7(3)
C(7)–N(8)–C(9)	109.8(3)	N(3)–C(2)–C(21)	117.3(3)
O(1)–C(2)–N(3)	121.0(3)	N(4)–C(5)–C(6)	118.4(3)

3. Experimental details

IR spectra were recorded on Perkin-Elmer 1310 and Nicolet MX-1 FT-IR spectrophotometers. NMR measurements were made on a Bruker AC-200 200 MHz spectrometer using standard [6] pulse sequences for JMOD and two-dimensional experiments. Mixing times of 1 s were used in the NOESY measurements. MS spectra was performed on a VG 7070 EQ instrument. Solvents were distilled before use. The solution of $Li_2[PdCl_4]$ in methanol was prepared by stirring a suspension of 1 equiv. of $PdCl_2$ and 2 equiv. of $LiCl$ in the appropriate amount of methanol overnight.

3.1. Preparation of hydrazones 1–4

For the preparation of compound **1**, a mixture of 10 mmol of 1*H*-indole-3-carboxaldehyde, 10 mmol of acetohydrazide and 0.1 ml of acetic acid in 20 ml of methanol was warmed on a steam bath for 2 h and allowed to stand overnight at $-10^\circ C$. The white crystalline precipitate obtained was washed with cold ethanol and dried in air. Compounds **2** and **3** were prepared similarly by the use of semicarbazide or ethyl carbazate [7], whereas **4** was obtained by reaction of 1-(methylsulfonyl)-indole-3-carboxaldehyde with acetohydrazide.

Table 5

Crystallographic data for compound (5)·CHCl₃

Formula	$C_{30}H_{26}Cl_4N_3OPPd$
F.W.	723.75
Crystal system	monoclinic
Space Group	$P2_1/c$
<i>a</i> (Å)	17.735(2)
<i>b</i> (Å)	9.696(2)
<i>c</i> (Å)	18.171(2)
β (°)	99.56(1)
<i>V</i> (Å ³)	3081(1)
<i>Z</i>	4
<i>D</i> _{calc.} (g cm ⁻³)	1.560
μ (cm ⁻¹)	10.2
Min. transmis. factor	0.92
Scan mode	ω
ω -scan width (°)	$1.0 + 0.35 \tan \theta$
θ -range (°)	1–25
reciprocal space explored	+ <i>h</i> , + <i>k</i> , ± <i>l</i>
measured reflections	5752
unique observed refl.	
with $I > 3\sigma(I)$	3888
Final R and <i>R</i> _w indices ^a	0.041, 0.058
No. of variables	370
GOF ^b	1.82

^a $R = [\sum w(F_o - k|F_c|) / \sum F_o]$ $R_w = [\sum w(F_o - k|F_c|)^2 / \sum wF_o^2]^{1/2}$.

^b $GOF = [\sum w(F_o - k|F_c|)^2 / (N_{\text{observations}} - N_{\text{variables}})]^{1/2}$ $w = 1/(\sigma(F_o))^2$, $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{1/2} / 2F_oLp$.

Table 6
Fractional atomic coordinates for compound (5)·CHCl₃ with e.s.d.'s in parentheses

Atom	x	y	z
Pd	0.18599(2)	0.05479(4)	0.14390(2)
Cl(1)	0.95036(7)	0.7607(2)	0.45941(7)
Cl(2)	0.2942(2)	0.7382(4)	0.0992(2)
Cl(3)	0.2486(2)	0.6839(3)	-0.0461(2)
Cl(4)	0.4032(1)	0.7514(3)	0.0118(2)
P	0.28931(7)	0.1896(1)	0.17567(7)
O(1)	0.1971(2)	0.0419(4)	0.0279(2)
N(3)	0.0932(2)	-0.0904(5)	0.0233(2)
N(4)	0.0993(2)	-0.0800(4)	0.1000(2)
N(8)	0.0179(2)	-0.1479(5)	0.3210(2)
C(2)	0.1431(3)	-0.0211(6)	-0.0095(3)
C(5)	0.0528(3)	-0.1532(6)	0.1321(3)
C(6)	0.0542(3)	-0.1361(5)	0.2093(3)
C(7)	0.0050(3)	-0.1991(6)	0.2514(3)
C(9)	0.0750(3)	-0.0487(6)	0.3271(3)
C(10)	0.1001(3)	-0.0392(5)	0.2573(3)
C(11)	0.1584(3)	0.0529(5)	0.2465(3)
C(12)	0.1870(3)	0.1345(6)	0.3090(3)
C(13)	0.1594(3)	0.1266(7)	0.3758(3)
C(14)	0.1033(3)	0.0340(6)	0.3876(3)
C(21)	0.1318(3)	-0.0242(7)	-0.0929(3)
C(99)	0.3097(5)	0.784(1)	0.0138(5)
C(111)	0.3331(3)	0.2188(6)	0.0929(3)
C(112)	0.3175(3)	0.3363(6)	0.0490(3)
C(113)	0.3480(4)	0.3519(7)	-0.0151(3)
C(114)	0.3929(3)	0.2516(8)	-0.0383(3)
C(115)	0.4079(4)	0.1332(8)	0.0043(4)
C(116)	0.3786(3)	0.1164(7)	0.0697(3)
C(121)	0.3689(3)	0.1184(6)	0.2417(3)
C(122)	0.3584(3)	0.0026(6)	0.2822(3)
C(123)	0.4206(4)	-0.0538(7)	0.3302(4)
C(124)	0.4909(4)	0.0061(8)	0.3378(4)
C(125)	0.5022(3)	0.1205(9)	0.2970(4)
C(126)	0.4416(3)	0.1767(7)	0.2476(3)
C(131)	0.2691(3)	0.3629(6)	0.2072(3)
C(132)	0.1986(3)	0.4187(6)	0.1783(4)
C(133)	0.1788(4)	0.5478(7)	0.1983(5)
C(134)	0.2279(4)	0.6245(8)	0.2485(4)
C(135)	0.2979(5)	0.5707(7)	0.2794(4)
C(136)	0.3192(4)	0.4384(7)	0.2581(4)

3.2. General conditions for cyclopalladation reactions

To a solution consisting of 0.5 mmol of Li₂[PdCl₄] prepared in situ in 10 ml of methanol, 0.5 mmol of hydrazones 1–4 and 0.5 mmol of AcONa in 5 ml of methanol were added dropwise. The yellow product formed immediately. It was filtered off, washed with methanol and dried in vacuo.

3.3. Formation of compound 5

Cyclopalladated hydrazone 1a (150 mg, 0.473 mmol) was suspended in 10 ml of CH₂Cl₂ and 115 mg (0.473 mmol) of PPh₃ were added. The solution became orange in colour and after 17 h a yellow product precipi-

tated. It was filtered off. The product was dissolved in CH₂Cl₂ and precipitated by addition of Et₂O; 170 mg (64.3%) of a yellow product ($R_f = 0.47$ in AcOEt/MeOH 49:1) was obtained. Suitable crystals of 5 were obtained from a chloroform solution, n-pentane being added by solvent diffusion.

3.4. X-Ray data collection and structure determination

Crystal data and other experimental details are summarized in Table 5. A prismatic crystal of approximate dimensions 0.12–0.10 × 0.22 mm was used. The diffraction measurements were carried out on an Enraf-Nonius CAD4 diffractometer at room temperature, using graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å). The diffracted intensities were corrected for Lorentz polarization and absorption (empirical correction) [8] but not for extinction. Scattering factors for all the atomic species and anomalous dispersions corrections for scattering factors of non-hydrogen atoms were taken from Ref. [9]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares, minimizing the function $\sum w(|F_o| - k|F_c|)^2$. An anisotropic thermal parameter was assigned to all the non-hydrogen atoms. The hydrogen atoms were introduced into the structural model at calculated positions (C–H, 0.95 Å), with the exception of those bonded to N(3) and N(8) which were also refined. The final difference Fourier synthesis showed maxima residuals of 0.8 e Å⁻³. The atomic coordinates are listed in Table 6. All the calculations were performed on a HP Vectra 486/33 computer using the Personal SDP Structure Determination Package [10]. Full lists of atomic coordinates, bond lengths and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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