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CYCLOMETALLATED COMPOUNDS

III *. CYCLOPALLADATION OF PHENYL PYRAZOLES. CRYSTAL STRUCTURE OF ACETYLACETONATO[2-(3-METHYL-5-PHENYLPYRAZOL-1-YL)PHENYL-C^1,$N^{2'}$]PALLADIUM(II)

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Summary

Six pyrazoles have been cyclopalladated by reaction with either lithium tetrachloropalladate or palladium acetate and the dimeric products converted to monomeric acetylacetonate complexes. The crystal structure of acetylacetonato[2-(3-methyl-5-phenylpyrazol-1-yl)phenyl-C^1,$N^{2'}$]palladium(II) has been determined. Crystals are monoclinic: a 15.035(3), b 8.541(1), c 16.340(4) Å, β 117.10(1)°, $P2_1/c$, $Z = 4$; the structure was refined to $R = 0.030$.

Introduction

The preparations [1] and applications in organic synthesis [2] of cyclopalladated compounds incorporating an internal nitrogen donor have been the subject of extensive research in recent years. In the preceeding paper [3] we reported unambiguous assignments of proton and carbon-13 NMR spectra of a number of cyclopalladated complexes. As part of that work we required the preparation of a number of cyclopalladated phenyl heterocycles as their acetylacetonate complexes. In the present work we describe the cyclopalladation of several *N*-phenyl pyrazoles and their conversion to the acetylacetonate complexes. An X-ray crystal structure of the complex from 1,5-diphenyl-3-methylpyrazole is also reported.

Results and discussion

The cyclopalladated chloro-bridged dimers **b** were prepared (Scheme 1) from the ligands **a** either directly, by reaction with lithium tetrachloropalladate, or by

* For part II see ref. 3.

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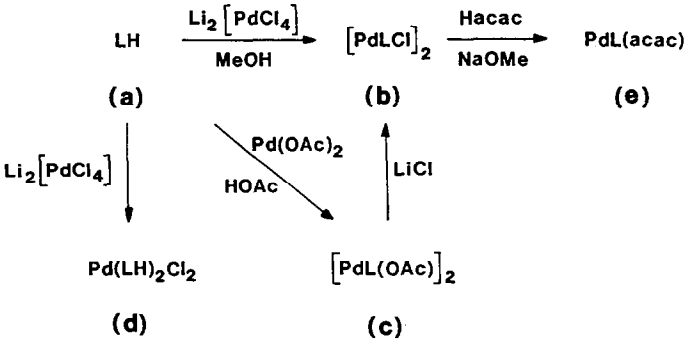

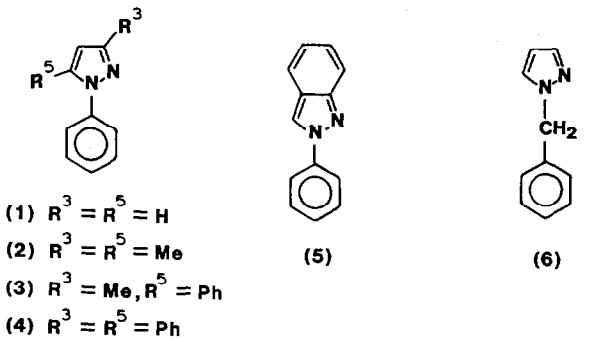

SCHEME 1

reaction with palladium acetate to give the acetate-bridged dimer **c** followed by anion exchange to the chloride. Thus 1-phenylpyrazole (**1a**), 3,5-dimethyl-1-phenylpyrazole (**2a**), 1,5-diphenyl-3-methylpyrazole (**3a**) and 2-phenylindazole (**5a**) were each converted directly to the chloro-bridged dimers **1b**, **2b**, **3b** and **5b** respectively. The reaction of **1a** has been previously reported [4–6]. Reaction of 1,3,5-triphenylpyrazole (**4a**) under the same conditions gave a mixture of the cyclopalladated chloro dimer **4b** and the non-cyclopalladated *trans*-dichloro-bis-pyrazole palladium complex **4d**. In the case of 1-benzylpyrazole (**6a**) no cyclopalladation was observed and the sole product of the reaction was the complex **6d**. This is consistent with the known [7–9] greater difficulty in effecting cyclometallation reactions that result in the formation of a six-membered ring compared to those that produce a five-membered metallocycle. The occurrence of cyclopalladation was readily monitored by infrared spectroscopy; in particular cyclopalladation results in the conversion of the out-of-plane C–H deformation pattern for a monosubstituted benzene to that of an *ortho*-disubstituted benzene ring.

The cyclopalladated chloro-bridged dimers **4b** and **6b** were prepared by the alternative procedure of reaction with the more reactive palladium acetate and subsequent acetate–chloride exchange. Each of the chloride dimers was then converted to the corresponding acetoacetonate monomer **1e**–**6e** by ligand exchange.

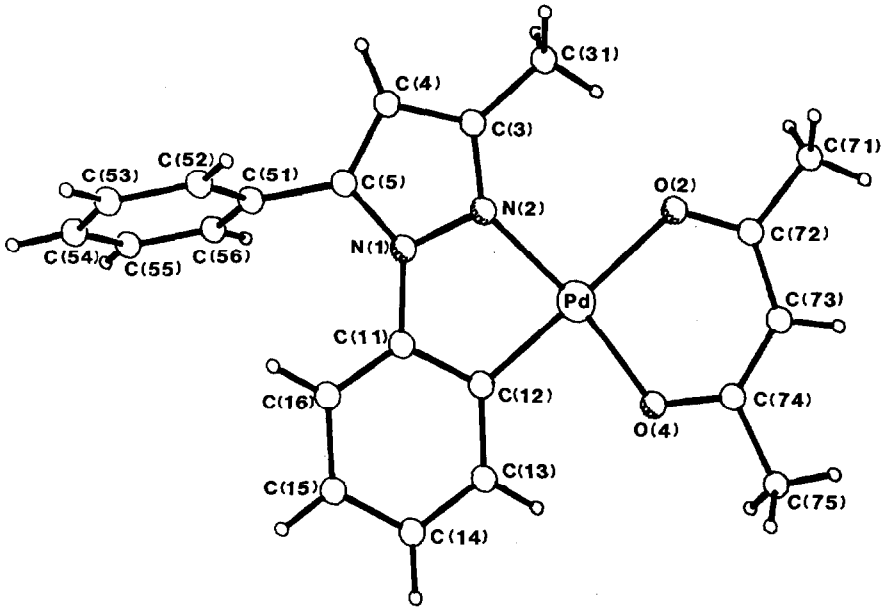

Fig. 1. Perspective view and atom labelling of **3e**.

Full assignments of the ^{1}H and ^{13}C NMR spectra of the acetoacetonate complexes **1e**–**6e** are described in the accompanying paper [3]. A notable feature of the NMR spectra of the complexes **3e** and **4e** is the existence of large upfield shifts of protons in the cyclopalladated phenyl ring. Such shifts are not observed in other cyclopalladated phenyl rings [3]. Thus in order to probe the origin of these effects and to confirm the structure of the complex a single-crystal X-ray structure determination of **3e** was carried out.

Figure 1 shows a perspective view of the structure of **3e** and includes the atom labelling. Tables 1 and 2 list bond lengths and angles respectively with standard deviations in parentheses. The structure is thus confirmed as acetylacetonato [2-(3-methyl-5-phenylpyrazol-1-yl)phenyl-$C^1,N^{2'}$]palladium(II). The coordination about the palladium atom is square planar, the maximum deviation from the meanplane described by the palladium and its four coordinated atoms being 0.043 Å (C(12)). Although most crystal structures of cyclopalladated complexes [10–17] have shown close to square planar coordination geometry, a recent example [18] described significant tetrahedral distortion about the palladium atom. The *O,O'*-bonded [19] acetylacetonate ligand is planar (maximum deviation from the meanplane: 0.044 Å) with its meanplane slightly tilted (3.2°) with respect to the (previous) coordination meanplane. The bonding geometry of the acetylacetonate ligand is similar to that of other Pd(acac) complexes [20–24]. The different *trans* influences of carbon and nitrogen are reflected in the unequal Pd–O(2) and Pd–O(4) bond lengths as has been observed in related structures [12–17,23,24].

The metallated phenyl ring and the pyrazole ring are both planar (maximum deviations: 0.020 and 0.005 Å, respectively) but are not mutually coplanar (angle between meanplanes: 7.8°). The relatively short Pd–C(12) bond length suggests the

TABLE 1

BOND LENGTHS (Å) FOR **3e**

Pd–N(2)	2.020(3)	Pd–C(12)	1.962(4)
Pd–O(2)	2.083(3)	Pd–O(4)	2.010(2)
N(1)–N(2)	1.377(4)	N(1)–C(5)	1.347(4)
N(1)–C(11)	1.431(4)	N(2)–C(3)	1.332(4)
C(3)–C(4)	1.396(6)	C(3)–C(31)	1.486(6)
C(4)–C(5)	1.373(5)	C(5)–C(51)	1.484(5)
C(11)–C(12)	1.405(5)	C(11)–C(16)	1.385(5)
C(12)–C(13)	1.384(4)	C(13)–C(14)	1.380(5)
C(14)–C(15)	1.389(5)	C(15)–C(16)	1.389(4)
C(51)–C(52)	1.377(4)	C(51)–C(56)	1.384(4)
C(52)–C(53)	1.388(6)	C(53)–C(54)	1.363(5)
C(54)–C(55)	1.387(5)	C(55)–C(56)	1.381(6)
C(71)–C(72)	1.490(6)	C(72)–C(73)	1.403(4)
C(72)–O(2)	1.271(5)	C(73)–C(74)	1.379(5)
C(74)–C(75)	1.511(5)	C(74)–O(4)	1.279(5)

existence of multiple bonding due to metal-to-ligand back bonding [14,15], a conclusion which is supported by the NMR data [3]. The geometry of the pyrazole ring is normal [25].

The phenyl ring at C(5) is planar (maximum deviation: 0.008 Å and inclined to the pyrazole and palladated phenyl rings at angles of 80.4 and 77.8°, respectively. The unusual ^{1}H NMR chemical shifts observed for this compound are thus

TABLE 2

BOND ANGLES (°) FOR **3e**

N(2)–Pd–C(12)	80.7(1)	N(2)–Pd–O(2)	97.1(1)
C(12)–Pd–O(2)	176.9(1)	N(2)–Pd–O(4)	171.2(1)
C(12)–Pd–O(4)	90.8(1)	O(2)–Pd–O(4)	91.5(1)
N(2)–N(1)–C(5)	110.4(3)	N(2)–N(1)–C(11)	114.9(3)
C(5)–N(1)–C(11)	134.7(3)	Pd–N(2)–N(1)	114.4(2)
Pd–N(2)–C(3)	138.7(3)	N(1)–N(2)–C(3)	106.5(3)
N(2)–C(3)–C(4)	109.4(3)	N(2)–C(3)–C(31)	122.9(4)
C(4)–C(3)–C(31)	127.7(3)	C(3)–C(4)–C(5)	106.9(3)
N(1)–C(5)–C(4)	106.9(3)	N(1)–C(5)–C(51)	124.5(3)
C(4)–C(5)–C(51)	128.7(3)	N(1)–C(11)–C(12)	113.8(3)
N(1)–C(11)–C(16)	123.6(3)	C(12)–C(11)–C(16)	122.5(3)
Pd–C(12)–C(11)	115.9(2)	Pd–C(12)–C(13)	126.8(3)
C(11)–C(12)–C(13)	117.2(3)	C(12)–C(13)–C(14)	121.4(3)
C(13)–C(14)–C(15)	120.2(3)	C(14)–C(15)–C(16)	120.3(3)
C(11)–C(16)–C(15)	118.3(3)	C(5)–C(51)–C(52)	119.5(3)
C(5)–C(51)–C(56)	121.4(3)	C(52)–C(51)–C(56)	119.0(4)
C(51)–C(52)–C(53)	120.5(3)	C(52)–C(53)–C(54)	120.3(3)
C(53)–C(54)–C(55)	119.8(4)	C(54)–C(55)–C(56)	120.0(3)
C(51)–C(56)–C(55)	120.4(3)	C(71)–C(72)–C(73)	119.5(4)
C(71)–C(72)–O(2)	115.5(3)	C(73)–C(72)–O(2)	125.0(3)
C(72)–C(73)–C(74)	127.4(4)	C(73)–C(74)–C(75)	119.1(4)
C(73)–C(74)–O(4)	127.3(3)	C(75)–C(74)–O(4)	113.6(3)
Pd–O(2)–C(72)	124.3(2)	Pd–O(4)–C(74)	124.3(2)

explained by the fact that this phenyl ring is approximately orthogonal to the conformationally fixed cyclometallated ring. Thus the unusually high-field position of H(16) is due to its lying in the shielding region above the C(5) phenyl ring. Furthermore a comparison of the NMR spectra of **4e** with those of **3e** clearly shows that it is the *N*-phenyl ring of **4a** that has undergone palladation rather than the C(3)-phenyl ring, which is also suitably disposed for cyclopalladation.

Experimental

Infrared spectra were recorded with a Shimadzu IR27G spectrophotomer. ^1H and ^{13}C NMR spectra were recorded with a Varian XL300 spectrometer for $CDCl_3$ solutions with Me_4Si as internal standard. NMR assignments were made as described in ref. 3. The ligands were prepared according to the literature procedures: **1a**, **2a** [26], **3a**, **4a** [27], **5a** [28], and **6a** [29].

Preparation of chloro-bridged dimers

A. From lithium tetrachloropalladate

A solution of one equivalent of palladium chloride and three equivalents of lithium chloride in methanol was refluxed for 2 h and then filtered. The filtrate was then added to a methanol solution containing one equivalent of the ligand. After 24 h stirring, the precipitate was filtered off and washed with methanol. Yield: typically 80%.

*Di-μ-chloro-bis[2-(pyrazol-1-yl)phenyl-C^1,$N^{2'}$]dipalladium(II) (**1b**).* Reaction of 1-phenylpyrazole **1a** as above gave **1b**, as previously reported [4–6].

*Di-μ-chloro-bis[2-(3,5-dimethylpyrazol-1-yl)phenyl-C^1,$N^{2'}$]dipalladium(II) (**2b**).* Reaction of 3,5-dimethyl-1-phenylpyrazole (**2a**) as above gave **2b**. m.p. > 250 °C. ν(KBr) 745 cm^{-1} (1,2-C_6H_4). Found: C, 46.0; H, 4.0; N, 9.7. $C_{22}H_{22}N_4Cl_2Pd_2$ calc: C, 46.7; H, 3.9; N, 9.9%.

*Di-μ-chloro-bis[2-(3-methyl-5-phenylpyrazol-1-yl)phenyl-C^1,$N^{2'}$]dipalladium(II) (**3b**).* Reaction of 1,5-diphenyl-3-methylpyrazole (**3a**) as above gave **3b**. m.p. 311–313 °C (dec). ν(KBr) 765 and 695 (C_6H_5), 750 cm^{-1} (1,2-C_6H_4). Found: C, 51.3; H, 3.5; N, 7.5 calc.: C, 51.2; H, 3.5; N, 7.5%.

*Di-μ-chloro-bis[2-(indazol-2-yl)phenyl-C^1,$N^{1'}$]dipalladium(II) (**5b**).* Reaction of 2-phenylindazole (**5a**) as above gave **5b**. m.p. > 300 °C. ν(KBr) 750 cm^{-1} (1,2-C_6H_4). Found: C, 47.0; H, 2.7; N, 8.4. $C_{26}H_{18}N_4Cl_2Pd_2$ calc: C, 46.6; H, 2.7; N, 8.4%.

Reaction of 1,3,5-triphenylpyrazole (**4a**) as above gave a mixture of **4b** and **4d**. Reaction of 1-benzylpyrazole (**6a**) as above gave only the non-cyclopalladated complex *trans*-dichlorobis[1-benzylpyrazole]palladium(II) (**6d**). m.p. 196 °C. ν(KBr) 770 and 705 cm^{-1} (C_6H_5). Found: C, 48.7; H, 4.0; N, 11.4. $C_{20}H_{20}N_4Cl_2Pd$ calc: C, 48.7; H, 4.1; N, 11.4%.

B. From palladium acetate

A solution of equimolar quantities of palladium(II) acetate and the ligand in glacial acetic acid was heated on a steam bath for ca. 4 h. After removal of the acetic acid under vacuum the residue was suspended in acetone and an aqueous solution containing three equivalents of lithium chloride was added. After 24 h stirring the product was isolated by filtration and washed with acetone.

Di-μ-chloro-bis[2-(3,5-diphenylpyrazol-1-yl)phenyl-C^1,$N^{2'}$]dipalladium(II) ***(4b)***. Reaction of 1,3,5-triphenylpyrazole (**4a**) as seen above gave **4b**. m.p. 280–283°C (dec). ν(KBr) 765 and 695 (C_6H_5), 750 cm^{-1} (1,2-C_6H_4). Found: C, 58.4; H, 3.5; N, 6.3. $C_{42}H_{30}N_4Cl_2Pd_2$ calc: C, 57.7; H, 3.5; N, 6.4%.

Di-μ-chloro-bis[2-(pyrazol-1-ylmethyl)phenyl-C^1,$N^{2'}$]dipalladium(II) ***(6b)***. Reaction of 1-benzylpyrazole (**6a**) as above gave **6b**. m.p. 253–255°C (dec). ν(KBr) 755 cm^{-1} (1,2-C_6H_4). Found: C, 40.0; H, 3.0; N, 9.3. $C_{20}H_{18}N_4Cl_2Pd_2$ calc: C, 40.2; H, 3.0; N, 9.4%.

Preparation of acetylacetonate complexes

The chloro-bridged dimer was added to a methanol solution containing sodium methoxide and excess acetylacetone and the resulting mixture stirred for 24 h. The precipitated product was filtered and recrystallised from dichloromethane/petroleum ether. Yield: typically 85%.

Acetylacetonato[2-(pyrazol-1-yl)phenyl-C^1,$N^{2'}$]palladium(II) ***(1e)***. m.p. 235°C (dec); lit. [5] m.p. 231°C. ^{1}H NMR δ 2.05 and 2.10, s, acac-CH_3; 5.41, s, acac-CH; 6.45, dd, $^3J_{4',3'}$ 2.7, $^3J_{4',5'}$ 2.2 Hz, H(4'); 7.06, 7.07 and 7.12, m, H(3), H(4) and H(5); 7.55, m, H(6); 7.78, dd, $^3J_{3',4'}$ 2.2, $^4J_{3',5'}$ 0.8 Hz, H(3'); 7.90, dd, $^3J_{5',4'}$ 2.7, $^4J_{5',3'}$ 0.8 Hz, H(5'). ^{13}C NMR δ 27.5 and 27.8, acac-CH_3; 100.5, acac-CH; 106.5 C(4'); 110.5, C(3); 124.8, C(5'); 124.9 C(4); 125.1, C(5); 132.0, C(6); 138.7, C(3'); 135.1 and 143.4, C(1) and C(2); 186.4 and 188.3, acac-CO.

Acetylacetonato[2-(3,5-dimethylpyrazol-1-yl)phenyl-C^1,$N^{2'}$]palladium(II) ***(2e)***. m.p. 157–158°C. ^{1}H NMR δ 2.00 and 2.09, s, acac-CH_3; 2.54, s, C(3')-CH_3; 2.63, s, C(5')-CH_3; 5.39, s, acac-CH; 5.92, s, H(4'); 7.01, ddd, $^3J_{5,4}$ 7.5, $^3J_{5,6}$ 7.3, $^4J_{5,3}$ 1.3 Hz, H(5); 7.08, ddd, $^3J_{4,3}$ 7.7, $^3J_{4,5}$ 7.5, $^4J_{4,6}$ 1.7 Hz, H(4); 7.13, dd, $^3J_{3,4}$ 7.7, $^4J_{3,5}$ 1.3 Hz, H(3) 7.60, dd, $^3J_{6,5}$ 7.3, $^4J_{6,4}$ 1.7 Hz, H(6). ^{13}C NMR δ 12.0, C(3')-CH_3; 14.1, C(5')-CH_3; 27.6 (2C), acac-CH_3; 99.9, acac-CH; 109.1, C(4'); 111.5, C(3), 123.8, C(5) 124.8, C(4); 131.5, C(6) 152.5, 144.8 and 139.2, C(2), C(3') and C(5'); 186.3 and 187.9, acac-CO. Found: C, 51.1; H, 5.0; N, 7.6. $C_{16}H_{18}N_2O_2Pd$ calc: C, 51.0; H, 4.8; N, 7.4%.

Acetylacetonato[2-(3-methyl-5-phenylpyrazol-1-yl)phenyl-C^1,$N^{2'}$]palladium(II) ***(3e)***. m.p. 148–150°C. ^{1}H NMR δ 2.03 and 2.10, s, acac-CH_3; 5.42, s, acac-CH; 6.10, s, H(4'); 6.34, dd, $^3J_{3,4}$ 8.0, $^4J_{3,5}$ 1.5 Hz, H(3); 6.74; ddd, $^3J_{4,3}$ 8.0, $^3J_{4,5}$ 7.4, $^4J_{4,6}$ 1.5 Hz, H(4) 6.93, ddd, $^3J_{5,4}$ 7.4, $^3J_{5,6}$ 7.3, $^4J_{5,3}$ 1.5 Hz, H(5); 7.44–7.52, m, C(5')-C_6H_5; 7.55, dd, $^3J_{6,5}$ 7.3, $^4J_{6,4}$ 1.5 Hz, H(6). ^{13}C NMR δ 12.1, C(3')-CH_3; 27.5$_9$ and 27.6$_3$, acac-CH_3; 100.0, acac-CH; 109.9, C(4'); 112.7, C(3); 124.0, C(5); 124.3, C(4); 128.9, 5'-*ortho*; 129.4, 5'-*meta*; 129.7, 5'-*para*; 129.9, 5'-*ipso*; 131.2, C(6); 134.9 and 143.0, C(1) and C(2); 152.6, C(3); 186.3 and 187.9, acac-CO. Found: C, 57.8; H, 4.8; N, 6.6. $C_{21}H_{20}N_2O_2Pd$ calc: C, 57.5; H, 4.6; N, 6.4%.

Acetylacetonato[2-(3,5-diphenylpyrazol-1-yl)phenyl-C^1,$N^{2'}$]palladium(II) ***(4e)***. m.p. 193–194.5°C. ^{1}H NMR δ 1.42 and 2.03, s, acac-CH_3; 5.23, s, acac-CH; 6.39, dd, $^3J_{3,4}$ 8.0, $^4J_{3,5}$ 1.0 Hz, H(3); 6.40, s, H(4'); 6.76, ddd, $^3J_{4,3}$ 8.0, $^3J_{4,5}$ 7.4, $^4J_{4,6}$ 1.5 Hz, H(4); 6.96, ddd, $^3J_{5,4}$ 7.4, $^3J_{5,6}$ 7.7, $^4J_{5,3}$ 1.0 Hz, H(5); 7.36–7.40, m, 3'-*meta* and 3'-*para*; 7.49–7.53, m, 5'-C_6H_5; 7.57, dd, $^3J_{6,5}$ 7.7, $^4J_{6,4}$ 1.5 Hz, H(6); 7.73, m, 3'-*ortho*. ^{13}C NMR δ 26.9 and 27.3, acac-CH_3; 99.8, acac-CH; 109.6, C(4'); 113.4, C(3); 124.3, C(4); 124.5, C(5); 127.6, 3'-*meta*; 128.9, 3'-*para*; 129.0, 5'-*meta*; 129.4, 5'-*ortho*; 129.7, 3'-*ortho*; 129.9, 5'-*para*; 129.6 and 130.2, 3'-*ipso* and 5'-*ipso*; 131.4, C(6); 135.8, 143.3 and 144.3, C(1), C(2) and C(5'); 154.8, C(3') 185.4 and 187.7,

acac-CO. Found: C, 61.1; H, 4.4; N, 5.5 $C_{26}H_{22}N_2O_2Pd$ calc: C, 62.3; H, 4.4; N, 5.6%.

Acetylacetonato[2-(indazol-2-yl)phenyl-C^1,$N^{1'}$]palladium(II) (5e). m.p. > 280°C. ^1H and ^{13}C: not soluble in $CDCl_3$. Found: C, 54.0; H, 4.0; N, 7.0. $C_{18}H_{16}N_2O_2Pd$ calc: C, 54.2; H, 4.0; N, 7.0%.

Acetylacetonato[2-(pyrazol-1-ylmethyl)phenyl-C^1,$N^{2'}$]palladium(II) (6e). m.p. 171–172°C. ^1H NMR δ 2.03 and 2.08, acac-CH_3; 5.31, CH_2; 5.42, acac-CH; 6.33, dd, H(4); 6.96, dd, $^3J_{3,4}$ 7.8, $^4J_{3,5}$ 1.3 Hz, H(3); 7.00, ddd, $^3J_{4,3}$ 7.8, $^3J_{4,5}$ 7.4, $^4J_{4,6}$ 1.2 Hz, H(4); 7.10, ddd, $^3J_{5,4}$ 7.4, $^3J_{5,6}$ 7.8, $^4J_{5,3}$ 1.3 Hz, H(5); 7.52, dd, $^3J_{6,5}$ 7.8, $^4J_{6,4}$ 1.2 Hz, H(6); 7.59, dd, H(5); 7.84, dd, H(3') ^{13}C NMR δ 27.7 and 28.0, acac-CH_3; 58.7, CH_2, 100.3, acac-CH; 106.6, C(4'); 124.2, C(4); 125.1, C(3); 126.8, C(5); 131.0, C(5'), 134.2, C(6); 140.9, C(3'); 134.7 and 140.1, C(1) and C(2); 186.6 and 188.1, acac-CO. Found: C, 49.0; H, 4.4; N, 7.7. $C_{15}H_{16}N_2O_2Pd$ calc: C, 49.7; H, 4.5; N, 7.7%.

Crystallography

Table 3 lists crystal data and X-ray experimental details for **3e**. 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 centered reflections ($2\theta > 20°$) being used. Throughout data collection the intensities of three standard reflections were moni-

TABLE 3

CRYSTAL DATA AND X-RAY EXPERIMENTAL DETAILS FOR **3e**

Formula	$C_{21}H_{20}N_2O_2Pd$
Molecular weight	438.8
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	15.035(3)
b (Å)	8.541(1)
c (Å)	16.340(4)
β (°)	117.10(1)
V (Å^3)	1867.9(6)
D_c (g cm^{-3})	1.560
Z	4
F(000)	888
μ (cm^{-1})	9.95
Radiation	Mo-K_α
Wavelength	0.71069
Temperature (°C)	−130
Crystal dimensions (mm)	0.63×0.40×0.26
Scan mode	$\theta/2\theta$
2θ range (°)	3–50
Unique reflections	3269
Observed reflections ($I > 3\sigma(I)$)	2910
Number of parameters	235
g	0.00027
R	0.030
wR	0.042

TABLE 4

ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($Å^2 \times 10^3$) FOR **3e**

Atom	x	y	z	U_{eq} [a]
Pd	1866(1)	5395(1)	5320(1)	26(1)
N(1)	3015(2)	6742(3)	4492(2)	27(1)
N(2)	2610(2)	7145(3)	5068(2)	28(1)
C(3)	2923(3)	8593(4)	5360(2)	33(1)
C(4)	3541(3)	9107(4)	4985(2)	37(1)
C(5)	3582(2)	7920(3)	4437(2)	29(1)
C(11)	2774(2)	5199(3)	4114(2)	26(1)
C(12)	2236(2)	4309(3)	4462(2)	26(1)
C(13)	1984(2)	2796(4)	4136(2)	30(1)
C(14)	2229(2)	2197(4)	3481(2)	35(1)
C(15)	2732(2)	3120(4)	3126(2)	33(1)
C(16)	3002(2)	4645(3)	3435(2)	30(1)
C(31)	2632(3)	9459(4)	5990(3)	43(2)
C(51)	4139(2)	7866(3)	3886(2)	28(1)
C(52)	3746(2)	8587(4)	3039(2)	33(1)
C(53)	4244(3)	8524(4)	2504(2)	39(1)
C(54)	5137(2)	7765(4)	2817(2)	41(1)
C(55)	5551(2)	7063(4)	3676(2)	40(1)
C(56)	5051(2)	7111(4)	4205(2)	35(1)
C(71)	711(3)	7198(4)	7139(4)	45(2)
C(72)	912(2)	6103(4)	6533(2)	32(1)
C(73)	543(2)	4568(4)	6412(2)	32(1)
C(74)	712(2)	3373(4)	5933(2)	31(1)
C(75)	275(3)	1774(4)	5919(2)	41(1)
O(2)	1449(2)	6652(2)	6183(2)	34(1)
O(4)	1229(2)	3436(2)	5492(1)	32(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalised U_{ij} tensor.

tored at regular intervals and this indicated no significant crystal decomposition. The intensities were corrected for Lorentz and polarization effects and an empirical absorption correction, based on azimuthal φ scans, was applied. The space group followed from systematic absences.

The structure was solved by conventional Patterson and Fourier methods, and refined by blocked cascade least-squares procedures. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to the isotropic of their carrier atoms. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, with $w = [\sigma^2(F_0) + gF_0^2]^{-1}$. All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL [30].

Final atom coordinates are listed in Table 4. Tabulations of structure factors, hydrogen atom coordinates, anisotropic thermal parameters and equations of meanplanes are available from the author P.J.S.

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