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CYCLOMETALLATION

IV. PALLADIUM(II) COMPOUNDS WITH BENZO[*h*]QUINOLINE AND SUBSTITUTED 2,6-DIARYLPYRIDINES

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Summary

The first cyclometallated compounds of some 2,6-diarylpyridines (**2**) and the related ligand, 5,6,8,9-tetrahydrodibenz[*c*,*h*]acridine (**3**) were prepared and characterized as acetato-bridged palladium(II) dimers: [Pd(**2** or **3**)OAc]$_2$. Inseparable isomers (*syn,trans* and *syn,cis*) were indicated by NMR, with the *syn,trans* isomer invariably predominating. With an unsymmetrical **2**, both isomers resulting from metallation of either one ring or the other dissimilar ring were observed in relative amounts which support the hypothesis that palladium makes an electrophilic attack on the aryl ring during cyclopalladation. Efforts to force *trans*-dimetallation, previously only observed with 2,6-dialkylpyridines, were unsuccessful. NMR evidence for palladium-to-carbon multiple bonding ($M_{d\pi} \rightarrow L_{\pi^*}$) (and a shorter than single Pd–C bond determined from an X-ray crystal structure), coupled with the near 120° angle restriction on sp^2 carbons, suggests that these diarylpyridines are not sterically suited for dimetallation. The benzo[*h*]quinoline (**1**) cyclopalladated complexes. [Pd(**1**)OAc]$_2$, and [Pd(**1**)dtc] (dtc = *N*,*N*-diethyldithiocarbamate) have been fully characterized by 200 MHz NMR.

Introduction

The first preparation of a cyclopalladated compound of benzo[*h*]quinoline (**1**) was the insoluble chloro-bridged dimer, [Pd(**1**)Cl]$_2$ [1]. This complex was later prepared by two other groups [2,3] and all groups [2–4] cleaved the dimer with mono- or bi-dentate ligands, L or L–L, to produce several (generally more soluble) monomers, [Pd(**1**)LCl] and [Pd(**1**)(L–L)]. Very little characterizational data or structural evidence accompanied these early reports. A later study [5] of the ^{13}C NMR spectra of [Pd(**1**)aca] and [Pd(**1**)cp] (where aca = acetylacetonate and cp = cyclopentadienyl ion), while not assigning the observed ^{13}C resonances, did at least

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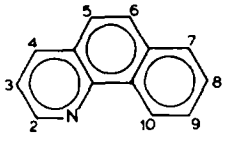
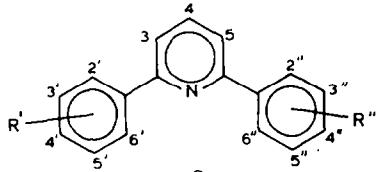
establish that cyclometallation had occurred. Brief mention of the preparation of $[Pd(\mathbf{1})OAc]_2$ and [Pd(**1**)dtc] (where OAc = acetate and dtc = *N*,*N*-diethyldithiocarbamate) appeared in 1979 [6], but even less characterizational information was in that report which was only concerned with the latter compound as a synthetic intermediate.

Only two types of metal compounds have been previously reported with 2,6-diarylpyridine: pyridinium salts, such as $(\mathbf{2H})_2PtCl_6$ and $(\mathbf{2H})AuCl_4$ [7], and compounds involving π-complex formation with the aryl rings, such as **2** (R′ = R″ = H)-$Cr(CO)_3$ [8]. There are no reported metal complexes with 5,6,8,9-tetrahydrodibenz[*c*,*h*]acridine (**3**); and with dibenz[*c*,*h*]acridine (**4**), only salts $(\mathbf{4H})_2PtCl_6$ [9] and $(\mathbf{4H})AuCl_4$ [10] have been reported.

We now report the preparation and characterization of the acetato-bridged dimer, $[Pd(\mathbf{1})OAc]_2$, its conversion via the chloro-bridged dimer to the monomeric [Pd(**1**)dtc] and its characterization. We also report the first cyclometallated compounds containing 2,6-diarylpyridines, **2a**–**2d**, and the related ligand **3**. These five new compounds are all acetate-bridged dimers, $[Pd(\mathbf{2})OAc]_2$ and $[Pd(\mathbf{3})OAc]_2$. Compound **4** did not yield even a simple adduct with $Pd(OAc)_2$.

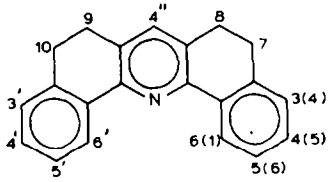


1



2

a R′ = R″ = 3′(″)—CH_3 c R′ = R″ = 4′(″)—Br
b R′ = R″ = 4′(″)—Cl d R′ = H ; R″ = 4″—OCH_3



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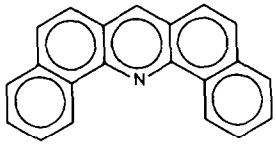

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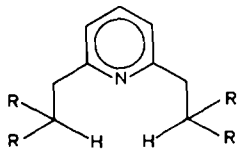

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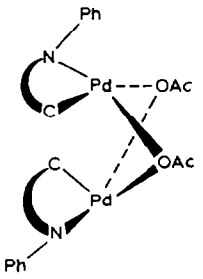
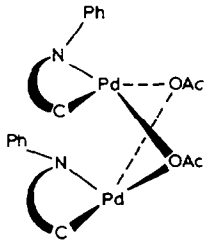
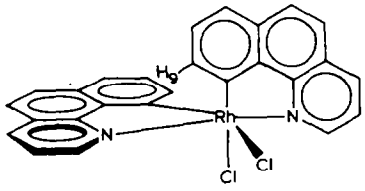
R = $COOCH_3$ or $COOC_2H_5$



6a



6b



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What we were seeking with compounds **2** and **3** was the first demonstration of *trans*-dimetallation (i.e. *trans* carbon–metal–carbon complexation) involving aryl carbons. The only known examples of such *trans*-dimetallation are those in which the cyclometalled ring contains the more flexible sp^3 carbons of a 2,6-dialkylpyridine (**5**), e.g. Pd(**5**-2H)py. Although the sp^2 carbons of the 2,6-diarylpyridines are not as flexible for forming five-membered rings, the existance of planar palladium(II)-terpy compounds (where terpy = 2,6-di-2-pyridylpyridine), and in particular the crystal structure [12] of [Pd(terpy)Cl]Cl which proves coordination by all three nitrogens, was the impetus to attempt to see if the structurally related compounds, **2** and **3**, could likewise serve to *trans*-dimetallate.

Experimental

A. Measurements

NMR spectra (200 MHz) were obtained in $CDCl_3$ solutions, with Me_4Si as the internal standard ($\delta = 0$ ppm), and were recorded on a Bruker WP-200 NMR spectrometer. Chemical shifts are reported in parts per million on the δ scale. Mass spectra (MS) were obtained on a Hewlett Packard Model 5968 GC/MS system with direct inlet attachment. They were run by Mr. Don Patterson in these laboratories. Infrared (IR) spectra were recorded on a Perkin–Elmer 621 spectrophotometer. A Dupont Model 900/Thermal Analyzer was used to obtain differential thermal analyses (DTA) from which decomposition and/or melting points were obtained. Elemental analyses were performed by Mr. R. Seab in these laboratories. Pd analyses were determined by thermogravimetric analysis.

B. Preparation of compounds

The five ligands **2a**, **2b**, **2c**, **2d** and **3** were all obtained from Prof. G.R. Newkome (LSU) and their melting points all were within 1–2°C of their literature [13,15] values. NMR spectra were obtained for all ligands and resonances were assigned [14]. Dibenz[*c*,*h*]acridine, **4**, was prepared by refluxing a mixture of **3** and an equal weight of palladium on carbon (10%) in *p*-cymene: m.p. 188–189°C (Lit. [15] m.p. 188°C). Benzo[*h*]quinoline was a commercial product.

(1) Bis(μ-acetate-*O*:*O'*)-bis(benzo[*h*]quinolin-10-yl-*N*)dipalladium(II), [Pd(**1**)-OAc]$_2$: A stirred mixture of palladium(II) acetate (127 mg, 0.57 mmol) and benzo[*h*]quinoline (117 mg, 0.65 mmol) in glacial acetic acid (50 ml) was refluxed for 12 h under N_2. Water (50 ml) was added to the yellow solution, which was then extracted with dichloromethane (3 × 100 ml). Extracts were combined, dried over anhydrous Na_2SO_4, filtered and the filtrate was evaporated to dryness in vacuo to give a yellow solid, which was column chromatographed on silica gel and eluted with dichloromethane to remove organic impurities. Elution with ethyl acetate gave, upon concentration, a yellow solid: 154 mg (75%); m.p. 276°C (decomp.); IR(KBr): 1565(vs,br), 1325(m), 830(m,br) and 710(m)cm^{-1}; MS (70eV): *m/e* 343 (20, $C_{15}H_{11}NO_2Pd^+$), 284 (98, $C_{13}H_8NPd^+$), and 178 (*100*, $C_{13}H_8N^+$): Anal. Found: C, 52.63; H, 3.20; N, 3.92. $[C_{15}H_{11}NO_2Pd]_2$ calcd.: C, 52.40; H, 3.23; N, 4.08%.

(2) Di-μ-chlorobis(benzo[*h*]quinolin-10-yl-*N*)dipalladium(II), [Pd(**1**)Cl]$_2$: A mixture of [Pd(**1**)OAc]$_2$ (100 mg, 0.15 mmol) and sodium chloride (17 mg, 0.30 mmol) in acetone (20 ml) was stirred for 12 h, then filtered. The light yellow solid was washed

first with ethanol, then diethyl ether and dried in vacuo: 92 mg (96%); m.p. 405°C (decomp.); IR (KBr): 1399(vs), 1322(vs), 820(s), 811(s), 743(m), 702(m) cm^{-1}; Anal. Found: C, 48.61, H, 2.46; N, 4.38. $[C_{13}H_8NClPd]_2$ calcd.: C, 48.76; H, 2.52; N, 4.38%.

(3) *N,N'*-Diethyldithiocarbamato(benzo[*h*]quinolin-10-yl-*N*]palladium(II) [Pd(**1**)-dtc]: A mixture of $[Pd(\mathbf{1})Cl]_2$ (59 mg, 0.09 mmol) and sodium *N,N*-diethyldithiocarbamate trihydrate (42 mg, 0.19 mmol) in acetone (20 ml) was stirred for 36 h. The yellow suspension was evaporated in vacuo to yield a yellow solid which was column chromatographed on silica gel and eluted with methylene chloride: 46 mg (57%); m.p. 208°C (decomp.); IR (KBr): 1495(vs,br), 1399(vs), 1322(s), 980(m), 845(m), 825(vs), 815(sv), 780(m), 750(m), 712(s) cm^{-1}; Anal. Found: C, 49.30; H, 4.21; N, 6.26. $[C_{18}H_{18}N_2S_2Pd]$ calcd.: C, 49.01; H, 4.12; N, 6.36%.

(4) The four compounds $[Pd(\mathbf{2})OAc]_2$, with ligands **2a**, **2b**, **2c** and **2d**, were all prepared by the same general procedure outlined in (1) above, from palladium acetate and the ligand in refluxing glacial acetic acid.

(a) Bis(μ-acetato-*O:O'*)bis[4'-methyl-2'-(6-(3''-methylphenyl)-2-pyridyl)phenyl-*N*]dipalladium(II), $[Pd(\mathbf{2a})OAc]_2$: yellow solid, 60%; m.p. 217°C (decomp.); IR (KBr): 1580(vs,br), 1560(vs,br), 1407(s,br), 810(m), 783(m) cm^{-1}; MS (70eV): *m/e* 423 (19, $C_{21}H_{19}NO_2Pd^+$), 363 (71, $C_{19}H_{15}NPd^+$), 259 (*100*, $C_{19}H_{17}N^+$), 257 (28, $C_{19}H_{15}N^+$), 256 (50, $C_{19}H_{14}N^+$), and 242 (28, $C_{18}H_{12}N^+$): Anal. Found: C, 59.30; H, 4.71; N, 3.13. $[C_{21}H_{19}NO_2Pd]_2$ calcd.: C, 59.50; H, 4.52; N, 3.31%.

(b) Bis(μ-acetato-*O:O'*)-bis[5-chloro-2'-(6-4''-chlorophenyl)-2-pyridyl phenyl-*N*]-dipalladium(II), $[Pd(\mathbf{2b})OAc]_2$: yellow solid, 88%; m.p. 253°C (decomp.); IR (KBr): 1581 (vs,br), 1560(vs,br), 1543(s), 1467(m), 1430(s), 1405(s,br), 1085(s), 790(s) cm^{-1}; Anal. Found: C, 49.56; H, 3.21; N, 2.82; Pd, 23.1. $[C_{19}H_{13}NCl_2O_2Pd]_2$ calcd.: C, 49.09; H, 2.82; N, 3.02; Pd, 22.9%.

(c) Bis(μ-acetato-*O:O'*)-bis[5'-bromo-2'-(6-(4''-bromophenyl)-2-pyridyl)phenyl-*N*]dipalladium(II), $[Pd(\mathbf{2c})OAc]_2$: yellow solid, 60%; m.p. 190°C (decomp.): IR (KBr): 1580(vs,br), 1560(vs), 1431(s), 1410(s,br), 790(m), 745(m) cm^{-1}; Anal. Found: C, 41.47; H, 2.53; N, 2.34; Pd, 18.6. $[C_{19}H_{13}NBr_2O_2Pd]_2$ calcd.: C, 41.20; H, 2.37; N, 2.53; Pd, 19.2%.

(d) The reaction of $Pd(OAc)_2$ with **2d** yielded a yellow solid (75% yield) which appeared to be a mixture of the two possible mono-cyclometallated isomeric products, i.e. with the ligand bonded either through ArC(6') or ArC(6''). From the NMR spectrum of the mixture, which exhibits two (unequal intensity) acetato and two methoxy resonances, it is possible to tentatively deduce that the isomer having the Pd bonded to the ArC(6'') is produced in larger amount (by roughly a 2/1 mole ratio). That is, the isomer in which the cyclometallation occurs with the substituted aromatic ring appears to be the more thermodynamically stable one. Anal. Found: C, 56.40; H, 3.84; N, 3.27. $[C_{20}H_{17}NO_2Pd]_2$ calcd.: C, 56.40; H, 4.03; N, 3.29%.

(e) Bis(μ-acetato-*O:O'*)-bis(5,6,8,9-tetrahydrodibenz[*c,h*]acridin-1-yl-*N*)dipalladium(II), $[Pd(\mathbf{3})OAc]_2$. This was prepared by the same general procedure detailed in 1 above: yellow solid, 67%; m.p. 210°C (decomp.); IR (KBr): 1580(vs,br), 1555(m), 1410(vs,br), 763(m), 733(m) cm^{-1}; MS (70eV): *m/e* 447 (3,$C_{23}H_{19}NO_2Pd^+$), 388 (12,$C_{21}H_{16}NPd^+$), 283 (*100*, $C_{21}H_{17}N^+$), 282 (46, $C_{21}H_{16}N^+$), 281 (47, $C_{21}H_{15}N^+$), 280 (60, $C_{21}H_{14}N^+$), and 279 (75, $C_{21}H_{13}N^+$). Anal. Found: C, 61.22; H, 4.43; N, 2.92. $[C_{23}H_{19}NO_2Pd]_2$ calcd.: C, 61.67; H, 4.28; N, 3.13%.

Results and discussion

Treatment of $Pd(OAc)_2$ with **1** in refluxing glacial acetic acid yielded the acetato-bridged dimer $[Pd(\mathbf{1})OAc]_2$. This is converted (nearly 100%) into the chloro-bridged dimer, $[Pd(\mathbf{1})Cl]_2$, by treatment with NaCl in acetone. This product could then be cleaved to the monomeric [Pd(**1**)dtc] by reaction with Nadtc in acetone. Reactions of **2a**–**2d** and **3** with $Pd(OAc)_2$ in glacial acetic acid yielded the five new compounds [Pd(**2a**–**2d**) or (**3**)OAc]$_2$, and these products will be discussed first. We should note here that all efforts to obtain cyclometallated products of the ligands **2** with rhodium(III), iridium(III) or gold(III) failed, with reduction of the metal to the metallic state a common result.

From elemental analyses and IR and NMR spectral data it was clear (vide infra) that these five compounds were all acetate-bridged dimers, and that cyclopalladation had occurred, but with only one of the two aryl rings. Extended refluxing of the products with ethyldiisopropylamine (12 h) or with sodium acetate in 1/1 ethanol/water (48 h) failed to remove an *ortho*-proton of the free ring and permit formation of a second (*trans*)-Pd–C bond. The compounds all exhibited strong, broad IR bands at 1580 and ~ 1410 cm^{-1}, expected of bridging acetates [16], and in the NMR spectrum (Table 1) of each is a sharp singlet in the δ 1.33–1.45 ppm range. It should be noted that the methyl signals of the bridging acetates in the 2-arylpyridinepalladium(II) [17] fall in the range 2.24–2.32 ppm. The substantial upfield shifts can be explained by the fact that these methyl groups are now in the (through-space) shielding environment of the unmetallated aryl ring (where, for example, the CH_3... aryl distances are 3.679 and 3.650 Å), from the recently determined crystal stucture of the **2b** complex [18]. Two small side bands, most clearly discernable with $[Pd(\mathbf{2c})OAc]_2$ and absent with $[Pd(\mathbf{2b})OAc]_2$, were observed just to either side of the acetate methyl spike. These bands were also seen with all the acetate-bridged 2-arylpyridine dimers we studied [14,17], and varying the spinning rate did not shift their peak positions (eliminating "spinning side bands"). Note that if the bridging acetate methyl groups have similar chemical environments, as in **6a**, a singlet is expected, whereas if their environments are different, as in **6b**, then two singlets should appear. Thus we conclude that these side bands (except in the compound containing the unsymmetrical 2,6-diarylpyridine (**2d**) vide infra) must be due to the less thermodynamically stable *cis*-isomer (**6b**). Integration areas of the three peaks suggest that the *trans*-isomer (**6a**) is the dominant isomer by a roughly 10/1 mole ratio. Examination of the crystals under a microscope reveals the presence of two slightly different crystals with one form in great predominance. We have now verified by single crystal X-ray diffraction [18] that $[Pd(\mathbf{2b})OAc]_2$ and a 2-arylpyridine complex, [Pd{4'-nitro-2'-(2-pyridyl)phenyl-*N*}OAc], do indeed have the *trans* (**6a**) configuration.

In the case of the unsymmetrical ligand, **2d**, the possibility exists for four isomeric products of $[Pd(\mathbf{2d})OAc]_2$, since here it is possible for the cyclometallation to occur either with the unsubstituted phenyl ring (I) or with the methoxysubstituted ring (II). That either metallation can take place is proven by the NMR spectrum for this (unseparated) isomeric mixture. That spectrum shows two singlets for the acetate methyls (at 1.35 and 1.40) and two singlets for the methoxy methyls (at 3.82 and 3.92) and integration shows roughly 2/1 mole ratios in each pair. With no further information concerning these isomers, but with the evidence [17,20] that palladium(II)

TABLE 1

200 MHz NMR DATA AND ASSIGNMENTS FOR CYCLOPALLADATED COMPOUNDS AND THEIR HETEROCYCLIC LIGANDS

Compound	δ(ppm) [a]	Assignment [b]	Compound	δ (ppm) [a]	Assignment [b]
1	7.63(dd,1)	H(3)	**2b**	7.45(dd,4)	H(2′(′),6′(″))
	7.87(m,5)	H(5,6,7,8,9)		7.63(dd,2)	H(3,5)
	8.32(dd,1)	H(4)		7.79(dd,1)	H(4)
	9.09(dd,1)	H(2)		8.06(dd,4)	H(3′(″),5′(″))
	9.47(dd,1)	H(10)	[Pd(**2b**)OAc]$_2$	1.43(s,3)	OAc
[Pd(**1**)OAc]$_2$	2.38(s,3)	OAc		6.75(dd,1)	H(3)
	6.43(dd,1)	H(3)		6.80(t,1)	H(4′)
	6.92(d,1)	H(5)		6.92(m,2)	H(3′,6′)
	7.06(dd,1)	H(8)		7.21(dd.1)	H(5)
	7.20(m,3)	H(6,7,9)		7.40(m,4)	H(2″,6″,3″,5″)
	7.40(dd,1)	H(4)		7.51(t,1)	H(4)
	7.78(dd,1)	H(2)	**2c**	7.61(dd,4)	H(2′(″),6′(″))
[Pd(**1**)dtc]	1.33(t,3)	CH_3		7.66(m,2)	H(3,5)
	1.38(t,3)	CH_3		7.78(dd,1)	H(4)
	3.89(q,4)	CH_2		7.99(dd,4)	H(3′(″),5′(″))
	7.39(dd,1)	H(9)	[Pd(**2c**)OAc]$_2$	1.45(s,3)	OAc
	7.43(dd,1)	H(3)		6.77(d,1)	H(3)
	7.48(t,1)	H(8)		6.85(d,1)	H(3′)
	7.55(d.1)	H(5)		6.94(d,1)	H(6′)
	7.61(dd,1)	H(7)		7.08(dd,1)	H(4′)
	7.76(d,1)	H(6)		7.22(d,1)	H(5)
	8.26(dd,1)	H(4)		7.51(t,1)	H(4)
	8.64(dd,1)	H(2)		7.57(m,4)	H(2″,6″,3″,5″)
2a	2.46(a,b)	CH_3(3′)(″))	**3**	2.93(m,8)	7,8,9,10-CH_2-
	7.24(m,2)	H(4′(″))		7.40(m,7)	H(3(′),4(′),5(′))
	7.38(t,2)	H(5′(″))		8.52(d,2)	H(6(′))
	7.65(dd,2)	H(3,5)	[Pd(**3**)OAc]$_2$	1.14(s,3)	OAc
	7.79(dd,1)	H(4)		2.70(m,8)	7,8,9,10-CH_2-
	7.93(m,4)	H(2′(″),6′(″))		6.55(m,3)	H(4,5,6)
[Pd(**2a**)OAc]$_2$	1.33(s,3)	OAc		6.91(a,1)	H(4″)
	2.31(s,3)	CH_3(4′)		7.16(d,1)	H(3′)
	2.42(s,3)	CH_3(3″)		7.26(t,1)	H(4′)
	6.54(d,1)	H(3)		7.39(t,1)	H(5′)
	6.80(m,3)	H(3′,5′,6′)		8.52(d,1)	H(6′)
	7.14(d,1)	H(5)			
	7.26(m,4)	H(2″,4″,5″,6″)			
	7.42(t,1)	H(4)			

[a] The splitting and the number of hydrogens are given in parentheses: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet (for which the center value only is given). [b] Note that the numbering system of the aromatic carbons changes for the ring attached to the metal.

normally attacks aryl rings electrophilically and hence should prefer to attack the electron-richer ring (II), we tentatively suggest that the stronger peaks at 3.92 and 1.35 belong to the isomer where palladium is cyclometallated to the methoxyphenyl ring (ring II) and the peaks at 3.82 and 1.40 belong to the isomer where the phenyl ring (I) has been metallated. Perhaps the most surprising result is that the isomer ratio is not greater than 2/1, considering the powerful electron-donating capacity of the methoxy group. However, in our compound that methoxy group is *meta* to the

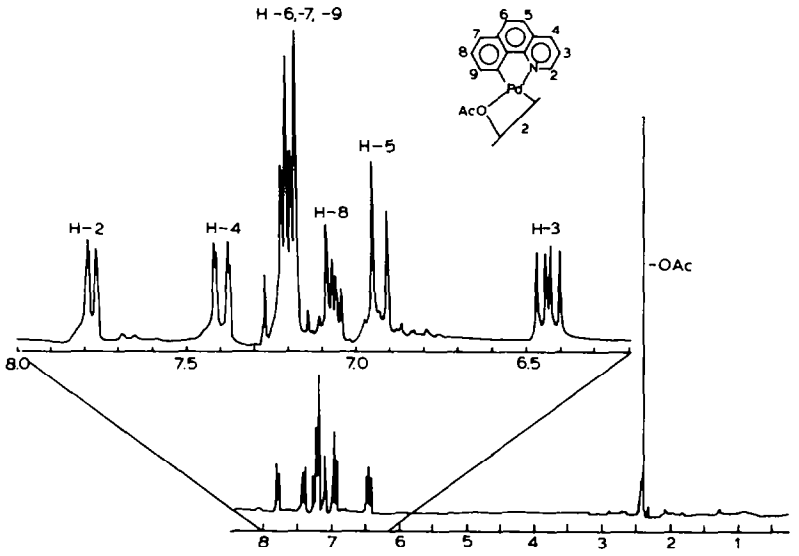

Fig. 1. The 200 MHz proton NMR spectrum of $[Pd(\mathbf{1})OAc]_2$ in $CDCl_3$ at 300 K in the region 0–8 ppm.

two carbons (2″ and 6″ in **2d**) susceptible to metallation. Were this methoxy group *para* to one of those carbons, i.e. were it situated at either position 3″ or 5″ in **2d**, we should expect a much higher isomer ratio.

That only one aryl carbon has bonded to palladium is indicated by the NMR spectral data (Table 1) which shows that the singlet at 2.46 assigned to the methyl protons in **2a** becomes two singlets in the complex at 2.42 and 2.31 (each representing 3 protons), with simultaneous loss of a signal from only one ligand proton. Note also that the equivalence of H(3) and H(5) (pyridine protons) in **2a** (7.65) is clearly lost in the complex, with H(3) at 6.54 and H(5) at 7.14. NMR data for the complexes of **2b**, **2c**, **2d** and **3** (Table 1) leads to the same conclusion regarding mono-cyclopalladation; and as already noted, the X-ray structure determination of the **2b** complex confirms this conclusion as well as the "boat" form (**6**) of the acetato-bridged dimers. The latter configuration apparently permits greater electron delocalization.

Now that we know the molecular structure for one of our 2,6-diarylpyridine complexes, $[Pd(\mathbf{2b})OAc]_2$ [18], as well as for a 2,6-dialkylpyridine complex, [Pd(**5**-2H)py] [11], and [Pd(terpy)Cl]Cl [12], it is possible to speculate on why the sought-for *trans*-dimetallation did not occur in our complexes. The metal–nitrogen bonds *trans* to each other in [Pd(terpy)Cl]Cl are slightly longer than single bond length (2.044 and 2.104 Å vs. a calculated 2.01 Å) [12], whereas in $[Pd(\mathbf{2b})OAc]_2$ a shortened metal–carbon bond is found (1.944 Å vs. a calculated single bond length of 2.05 Å) [18], which suggests some multiple bond character in these Pd–C(aryl) linkages. In the [Pd(**5**-2H)py] complex [11] the Pd–C(alkyl) length (2.140 Å) is in slight excess of the calculated single bond length (2.08 Å). Thus after the first Pd–C bond forms in our compounds and pulls the Pd atom away from the other ring (where *ortho* carbons are now at 2.427 and 2.252 Å) dimetallation is apparently prevented. Furthermore, in the complex with **5** (with $R = CO_2C_2H_5$) the cyclometallated (mean) ring angles Pd–C–C and C–C–C, which involve sp^3 carbons, are 102.2

and 110.8°, respectively [11], whereas the corresponding ring angles in our **2b** complex, which involve sp^2 carbons, are 114.7 and 114.6°. These latter angles and the approximate 120° angles which constrain the unmetallated aromatic ring system, coupled with the shortened Pd–C(aryl) bond, must all combine to prevent dimetallation.

The *syn*-juxta position of the aromatic rings in the complexes is undoubtedly a major source of the shielding (through-space) experienced by all the aromatic protons (Table 1). Additional shielding of certain protons (e.g., H(3), shifted by $\Delta\delta$ 1.11 in the **2a** complex) arises from the near planar rigidity imposed by metallation of one ring (bringing H(3) and H(3′) near one another) whereas a lesser shielding occurs at other protons (e.g., H(5), shifted only by $\Delta\delta$ 0.51 in the **2a** complex) because of the freedom of the unmetallated ring. Finally there is evidence, as there was with the 2-arylpyridine complexes [17], that some of the proton shielding in the rings arises from palladium-to-ligand π back-bonding. For example, note that for $[Pd(\mathbf{3})OAc]_2$ the largest shielding effect ($\Delta\delta$ 0.95) is experienced by the three ring protons of the metallated aryl ring and the second largest shielding effect is experienced by the lone pyridine proton (H(4″), $\Delta\delta$ 0.49). These four protons are the only ones to experience through-bond shielding effects as well as through-space from the adjacent (*syn* juxtaposition) aromatic rings. The resonances of the remaining protons which are bound to carbons not connected through delocalized bonds to the metal are either not shifted at all (e.g. H(6′) and H(5′)) or are slightly shielded ($\Delta\delta$ 0.14–0.24) by through space effects.

Turning now to the NMR spectra of the benzo[*h*]quinoline complexes, we note first (Fig. 1, Table 1) that the bridging acetate methyl protons appear as a sharp singlet at 2.38, much closer to the 2.24–2.32 range for 2-arylpyridine complexes [17] than to the 1.33–1.45 range for 2,6-diarylpyridine complexes. Furthermore, small side bands are present suggesting (from integration) that roughly 3% of the *cis* isomer (**6b**) has formed. In the spectrum of the dtc monomer, [Pd(**1**)dtc], we find that the methyl groups are inequivalent, appearing as two triplets (which a higher temperature, 90°C, did not cause to merge), whereas the methylene protons appear to be in magnetically equivalent sites (one quartet). We [21] found this same strange result with [Pd(2-arylpyridine)dtc] compounds and the opposite result with $[Rh(2\text{-arylpyridine})_2dtc]$ (viz. one triplet for the methyl protons, but two sets of double quartets for the methylene protons). We have no better an explanation for these observations now than we have when we first observed them [21].

The other NMR data for the complexes of **1** (Table 1) provide further evidence for but do not move, palladium *d* to ligand π^* "back-bonding". All 8 protons of the complexed ligand **1** are strongly shielded (by $\Delta\delta$ 0.67–1.30) in the bridged dimer $[Pd(\mathbf{1})OAc]_2$. Shielding is expected from through-space interactions alone because of the *syn* juxtaposed ring systems, so it is difficult to deduce any through-bond contributions to these upfield shifts. However, in the mononuclear complex [Pd(**1**)dtc], where all 8 aromatic proton resonances are clearly discernable (Fig. 2) and no such through-space shieldings are possible, all aromatic proton resonances are still shifted upfield by ($\Delta\delta$ 0.06–0.48) with the largest shifts occurring in the ring which carries the shortened Pd–C bond ($\Delta\delta$ values: H(9) 0.48, H(8) 0.39, H(7) 0.26). In this connection it is noteworthy that in an analogous rhodium(III) complex, $[Rh(\mathbf{1})Cl]_2$ [20], some of the protons are deshielded (in particular H(2) by $\Delta\delta$ 0.24), which is what would be expected if only sigma bonding were operative. The t_{2g}^6

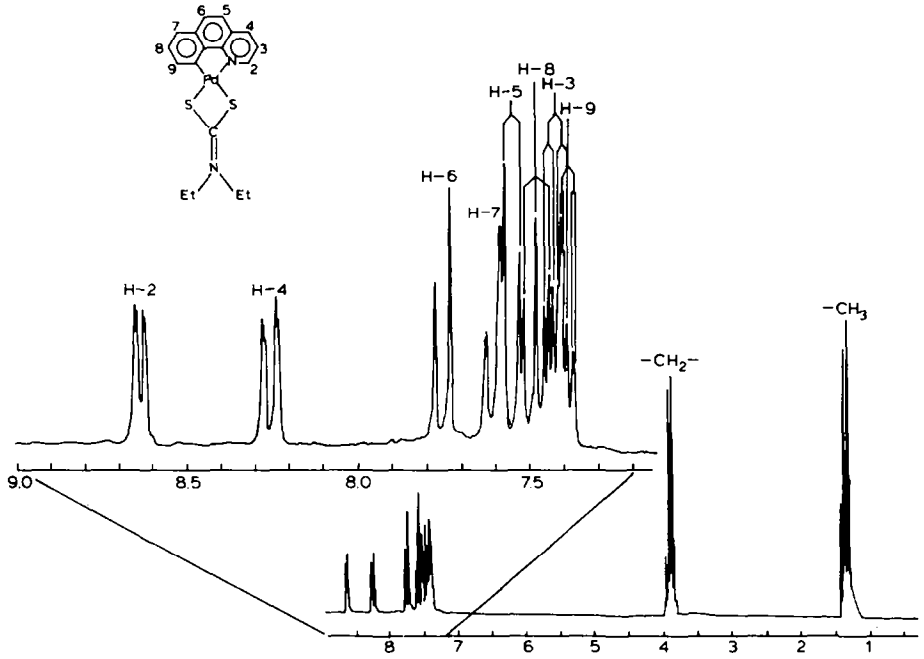

Fig. 2. The 200 MHz proton NMR spectrum of [Pd(**1**)dtc] in $CDCl_3$ at 300 K in the region 0–9 ppm.

rhodium(III) is incapable of π back-bonding whereas such is possible with d^8 palladium(II). A very strong shielding of the H(9) proton in the chloro-bridged rhodium dimer (by $\Delta\delta$ 1.88) is observed [20], but this must surely be due to its position in the octahedral rhodium compound close to the ring current of the adjacent ligand (see **7**).

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