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CYCLOMETALLATION. PALLADIUM 2-ARYLPYRIDINE COMPLEXES

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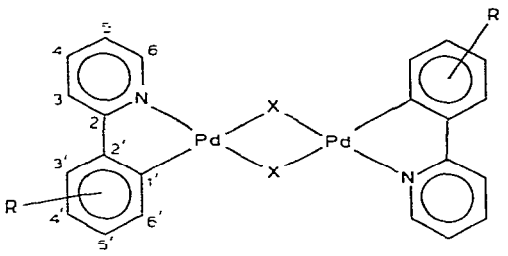
Summary

A number of new cyclometallated compounds of palladium with 2-arylpyridines have been synthesized and characterized. Palladium acetate has been proven to be a more useful starting material than Li_2PdCl_4, since the resulting acetato-bridged dimers, $[Pd(OAc)(2\text{-arylpyridine})]_2$, unlike the chloro-bridged dimers, are conveniently soluble in common organic solvents. The effect of varying substituents on the aryl nucleus supports the concept that after initial *N*-complexation, the 2-position of the aryl nucleus undergoes electrophilic attack by the palladium atom. Detailed NMR studies of the soluble acetato compounds showed that the 6-heteroaryl and "*ortho*" to the Pd—C bond protons in the complexes are shifted (~0.75 and 0.5 ppm, respectively) upfield from the ligand position. These shielding effects are believed to be due primarily to through-space interactions of overlying aromatic rings and secondarily to through-bond (Pd-to-ligand) effects. Both acetato- and chloro-bridged dimers will react with certain ligands to give mononuclear species containing the intact cyclometallated ligand.

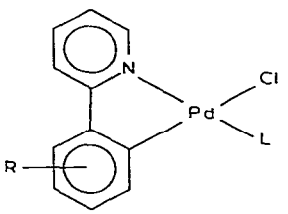
Introduction

Cyclometallation reactions, in which an organic ligand undergoes intramolecular metallation with the formation of a metal—carbon σ-bond, are relatively recent discoveries, but a large number of such reactions have now been carried out [1—5]. Cyclopalladation has been one of the more common reactions of this type, with $PdCl_4^{2-}$ generally being the source of the metal.

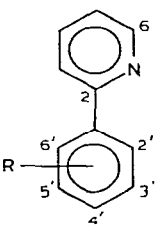
A brief communication [6] in 1968 reported the separate reactions of 2-phenylpyridine (6a) and 2-phenylquinoline with Na_2PdCl_4. The products were tentatively formulated as dinuclear chloro-bridged cyclometallated structures 1a. More recently, an additional palladium complex was reported [7] to contain both 6a and the polypyrazolylborate anion. A dimer of palladium



(1, X = Cl;
2, X = OAc;
3, X = SCN)



(4, L = $P(C_6H_5)_3$;
5, L = NH_3)



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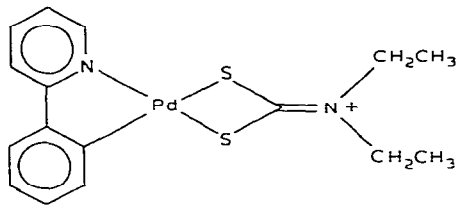
a, R = H
b, R = 2′-Me
c, R = 3′-Me
d, R = 4′-Me
e, R = 2′-OMe
f, R = 3′-OMe
g, R = 4′-OMe
h, R = 2′-NO_2
i, R = 3′-NO_2
j, R = 4′-NO_2
k, R = 2′-Cl
l, R = 4′-Cl
m, R = 4′-Br
n, R = 3′,5′-diOMe
o, R = 2′-Br



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acetate and 6a, $[Pd(OAc)6a]_2$, has been reported [8] but without supporting spectral or analytical data. The only other reported cyclometallation reactions involving 6a are preparations of complexes of rhodium(III), $RhCl_2(6a)(PBu_3)_2$, $[Rh_2Cl_2(6a)_4] \cdot 2\,CHCl_3$ [9]; manganese(I) and rhenium(I), $[M(CO)_4(6a)]$ (M = Mn or Re) [10]; titanium(III), $[cp_2Ti(6a)]$ [11]; and ruthenium(II), $[RuCl(6a)(CO)_2)_2$, $RuCl(6a)CO(PPh_3)_2$ and $RuCl(6a)(CO)_2$pic (where pic = γ-picoline) [12]. Related Cr^{III} complexes have been generated from 2-(2′-halophenyl)pyridine by initial lithium—halogen exchange, followed by chromium(III)—lithium exchange [13]; use of titanium(III), vanadium(III), iron(III), iron(II), and cobalt(II) were attempted, but the corresponding organometallic complex was not isolated.

For the titanium complex, the authors proposed that the cyclometallation occurs through the pyridine carbon adjacent to the nitrogen rather than through the 2-aryl position. This apparent fused 3-membered ring formation via cyclometallation is unique, since "metallation of nitrogen-donor ligands does not occur if the chelate ring produced has fewer than five atoms" [1].

We herein report preparation of several 2-arylpyridine complexes of palladium using both Li_2PdCl_4 and $Pd(C_2H_3O_2)_2$ as starting materials. We directly

prepared and interconverted the chloro-, acetato-, and thiocyanato-bridged palladium dimers. We have also converted these dimers into mononuclear species by reactions with other simple ligands, such as: ammonia, triphenylphosphine, and sodium *N*,*N*-diethyldithiocarbamate.

Experimental

NMR spectra were obtained in $CDCl_3$ solutions, with Me_4Si as the internal standard (δ = 0 ppm), and were recorded on either a Varian Associates A-60A or Bruker WP-200 NMR spectrometer. For preparative ThLC, 2 mm Brinkmann Silica gel P/UV-254-366 plates were used. Mass spectra (MS) were obtained on a Hewlett Packard Model 5968 GC/MS system with direct inlet attachment. 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.

Unless noted, all chemicals and solvents were reagent grade and were obtained from commercial sources. Li_2PdCl_4 was prepared by the method of Cope and Friedrich [14] from $PdCl_2$. $Pd(C_2H_3O_2)_2$ was used as purchased from either Goldsmith Chemicals and Metal Corp. or SynMet, Inc.

2-Phenylpyridine (**6a**) and 2-(*p*-tolyl)pyridine (**6d**) were prepared from pyridine and the corresponding aryllithium according to the procedure outlined in Vogel [15]. The other arylpyridines (**6**) were prepared from the corresponding diazonium salts and pyridine according to standard procedures [16]. This latter procedure generated mixtures of 2- and 4-arylpyridines (ca. 40%) and traces (ca. 10%) of the 3-isomer. These isomers were separated either by ThLC or HPLC. It was possible, in certain cases (e.g., **6k**), to employ the isomeric mixture in the reaction with palladium acetate, then separate the cyclometallated product via standard procedures, since neither the 3- or 4-isomer can cyclometallate.

Physical and/or spectral data for the 2-arylpyridine ligands are: **6a** (b.p. 130—132°C (8 mm), lit. [15] b.p. 140°C (12 mm); **6b** (b.p. 95°C (0.6 mm), lit. [17] b.p. 102°C (1.2 mm), NMR δ 2.34 ppm (Me), MS (70 eV) *m/e* 169 (37%, M^+)]; **6c** [b.p. 104—106°C (2 mm), lit. [17] b.p. 102°C (0.5 mm), NMR δ 2.35 ppm (Me)]; **6d** [b.p. 124°C (5 mm), lit. [17] b.p. 142°C (10 mm), NMR δ 2.38 ppm (Me)]; **6e** [b.p. 96—99°C (0.2 mm), lit. [18] b.p. 120—140°C (0.1 mm), NMR δ 3.78 ppm (OMe)]; **6f** (m.p. (picrate) 151—152°C, lit. [19] m.p. 154—155°C, NMR δ 3.78 ppm (OMe), MS (70 eV) *m/e* 185 (61%, M^+)]; **6g** (m.p. 49—50°C, lit. [19] m.p. 49—50°C, NMR δ 3.82 ppm (OMe), IR (KBr) 1257 cm^{-1}]; **6h** [m.p. 59—61°C, lit. [20] m.p. 60°C, IR (KBr) 1515, 1355, 795 cm^{-1}]; **6i** [m.p. 70—71°C, lit. [20] m.p. 74°C, IR (KBr) 1525, 1350 cm^{-1}]; **6j** [m.p. 128—130°C, lit. [20] m.p. 131°C, IR (KBr) 1520, 1355 cm^{-1}]; **6k**, **6n**, **6o** [not purified]; **6l** [m.p. 50—51°C, lit. [21] m.p. 52—53°C, MS (70 eV) *m/e* 191 (33%, M^+)]; **6m** [m.p. 60—61°C, lit. [21] m.p. 62°C, IR (KBr) 838, 770 cm^{-1}].

Preparation of bridged palladium metallated complexes

Since the preparative procedure was the same for each of the chloro- and

acetato-bridged dimers, only a representative example for each specific type will be described. Although the chloro-bridged compounds (1) are generated in higher yields, their sparing solubility makes further spectral analysis difficult; thus, the acetate-bridged dimers were deemed superior for further spectral studies.

In a typical chloro-bridged complex preparation, to Li_2PdCl_4 (120 mg, 0.46 mmol) dissolved in absolute ethanol (30 ml), giving a reddish-brown solution, a solution of 2-(4′-nitrophenyl)pyridine (6j; 106 mg, 0.53 mmol) in absolute ethanol (50 ml) was added. The resultant solution immediately lightened and within a few minutes a yellow solid precipitated. The mixture was stirred for 12 h, filtered, and washed first with ethanol, then anhydrous diethyl ether. The solid product was dried in vacuo. The physical yield and analytical data for **1a, c, d, g, j, m,** and **n**, are given in Table 1.

In a typical acetato-bridged complex preparation, a mixture of $Pd(C_2H_3O_2)_2$ (135 mg, 0.60 mmol) and 2-(4′-methoxyphenyl)pyridine (6g; 127 mg, 0.69 mmol) suspended in glacial acetic acid (50 ml) was refluxed for 12 h under nitrogen. After cooling to 25°C, water (50 ml) was added and the desired complex extracted with dichloromethane (3 × 100 ml). The combined extract was dried over anhydrous sodium sulfate, then concentrated in vacuo to give a dark yellow solid which was column chromatographed on silica gel, eluting with dichloromethane (removal of unchanged starting materials). Elution with ethyl acetate gave the desired complex (2g), as a yellow powder after concentration.

TABLE 1

ANALYTICAL, YIELD, AND MELTING POINT DATA FOR PALLADIUM(II) COMPLEXES

Compound	Melting Point (Decomposition) (°C)	Yield [a] (%)	Analytical Data Found(Calcd.)(%)		
			C	H	N
2a	>220	52	48.71(48.83)	4.03(3.47)	4.18(4.39)
2b	273	66	50.71(50.37)	4.05(3.93)	4.09(4.20)
2c	160	72	51.53(50.37)	4.20(3.93)	4.11(4.20)
2d	244	48	50.94(50.37)	3.99(3.93)	3.84(4.20)
2e	251	62	46.67(48.07)	3.67(3.75)	3.78(4.01)
2f	249	41(80) [b]	48.46(48.07)	3.75(3.75)	3.87(4.01)
2g	230	60	48.05(48.07)	3.89(3.75)	3.87(4.01)
2h	278	42	43.89(42.80)	2.79(2.77)	7.40(7.69)
2i	325	35(66) [b]	42.39(42.80)	2.68(2.77)	7.37(7.69)
2j	260	37	42.10(42.80)	3.07(2.77)	7.19(7.69)
2k	258	19	44.06(44.08)	2.86(2.85)	3.83(3.96)
2l	275	31	44.30(44.08)	2.79(2.85)	3.79(3.96)
2m	273	67	39.59(39.16)	2.61(2.53)	3.44(3.52)
3f	300	81	43.91(44.76)	2.81(2.89)	7.69(8.04)
1a	327	— [c]	44.45(44.61)	2.75(2.73)	4.61(4.73)
1c	355	— [c]	46.10(46.46)	3.21(3.25)	4.34(4.52)
1d	324	— [c]	47.27(46.46)	3.54(3.25)	4.50(4.52)
1g	296	— [c]	44.31(44.18)	2.99(3.01)	4.26(4.30)
1j	405	— [c]	39.45(38.72)	1.94(2.07)	8.31(8.22)
1m	378	— [c]	35.35(35.22)	1.92(1.88)	3.61(3.74)

[a] Actual isolated yields in glacial acetic acid. [b] Yields in chloroform as reaction solvent. [c] Due to the insolubility, accurate yield data were not available.

TABLE 2

200 MHz NMR DATA FOR LIGAND AND THE CORRESPONDING ACETATO-BRIDGED COMPLEX (2) [a]

Aryl Functional Group		σ [b] Constant	Ligand (6), δ (ppm)		Complex (2), δ (ppm)		
			H-5′	py-6	H-6′	py-6	OAc
4′-OMe	(g)	−0.27	6.98	8.63	6.42	7.85	2.28
4′-Me	(d)	−0.17	7.22	8.62	6.75	7.89	2.28
3′-Me	(c)	−0.07	7.35	8.68	6.77	7.82	2.28
H	(a)	0	7.92—8.25	8.70	6.62—6.95	7.88	2.24
3′-OMe	(f)	0.12	7.32	8.63	6.76	7.82	2.34
4′-Cl	(l)	0.23	7.42	8.70	~6.76	7.97	2.28
4′-Br	(m)	0.23	7.57	8.68	6.82—6.95	7.98	2.30
3′-NO_2	(i)	0.71	7.63	8.70	7.11	7.96	2.32
2′-Me	(b)	—	— [c]	8.66	6.87	7.97	2.28
2′-OMe	(e)	—	— [c]	8.70	6.60	7.86	2.25
2′-NO_2	(h)	—	— [c]	8.65	6.90—7.03	7.96	2.24
2′-Cl	(k)	—	— [d]	—	6.93—6.98	7.95	2.26

[a] Ligands were run as 10% solutions in $CDCl_3$. Palladium compounds were run as 0.1 mmol solutions. [b] σ-Values from ref. 38. [c] Values not assigned. [d] Ligand mixtures not separated, but rather transformed directly to complex 2k.

The analytical, yield, and melting point data are given for 2 in Table 1 and selected NMR data are given in Table 2.

Preparation of mononuclear palladium cyclometallated complexes

In general, the bridged dichloro- or acetato-complexes can be converted into the corresponding mononuclear species (7, 4, and 5) using either sodium *N,N*-diethyldithiocarbamate, triphenylphosphine, or ammonia, respectively, in acetone as solvent.

A mixture of bis-(μ-acetato-*O*:*O*′)-bis[4′-nitro-2′-(2-pyridyl)phenyl-*N*]-dipalladium (2j; 72 mg, 0.10 mmol) and sodium *N,N*-diethyldithiocarbamate trihydrate (45 mg, 0.20 mmol) in acetone (20 ml) was stirred at 25°C for 12 h and then evaporated to dryness to give a dark yellow solid, which was chromatographed on a silica gel column, eluting with dichloromethane, to give a yellow solid upon concentration. Recrystallization from CH_2Cl_2 : CCl_4 (1 : 3) gave (36%) *N,N*-diethyldithiocarbamato-[4′-nitro-2′-(2-pyridyl)phenyl-*N*]palladium(II), 7j, as yellow needles: 32 mg; m.p. 224°C (dec); NMR, Figure 1A. Anal. Found: C, 40.89; H, 3.68; N, 8.91. calcd. for $C_{16}H_{17}N_3O_2S_2Pd$: C, 42.32; H, 3.78; N, 9.26%.

Results and discussion

Synthesis

Treatment of 2-arylpyridines (6) with lithium tetrachloropalladate(II) in alcohol at ambient temperature gave (62—94%) the corresponding chloro-bridged dimer 1, as a sparingly soluble precipitate. In regard to alternative palladium reagents, it was found that: (a) $Pd(acetylacetonate)_2$ did not react with 6; (b) $PdCl_2(C_6H_5CN)_2$ did not metallate, but did give a 2 : 1 (ligand-metal) adduct; and (c) both $PdCl_4^{2-}$ and $Pd(CH_3COO)_2$ (hereafter $Pd(OAc)_2$) gave the

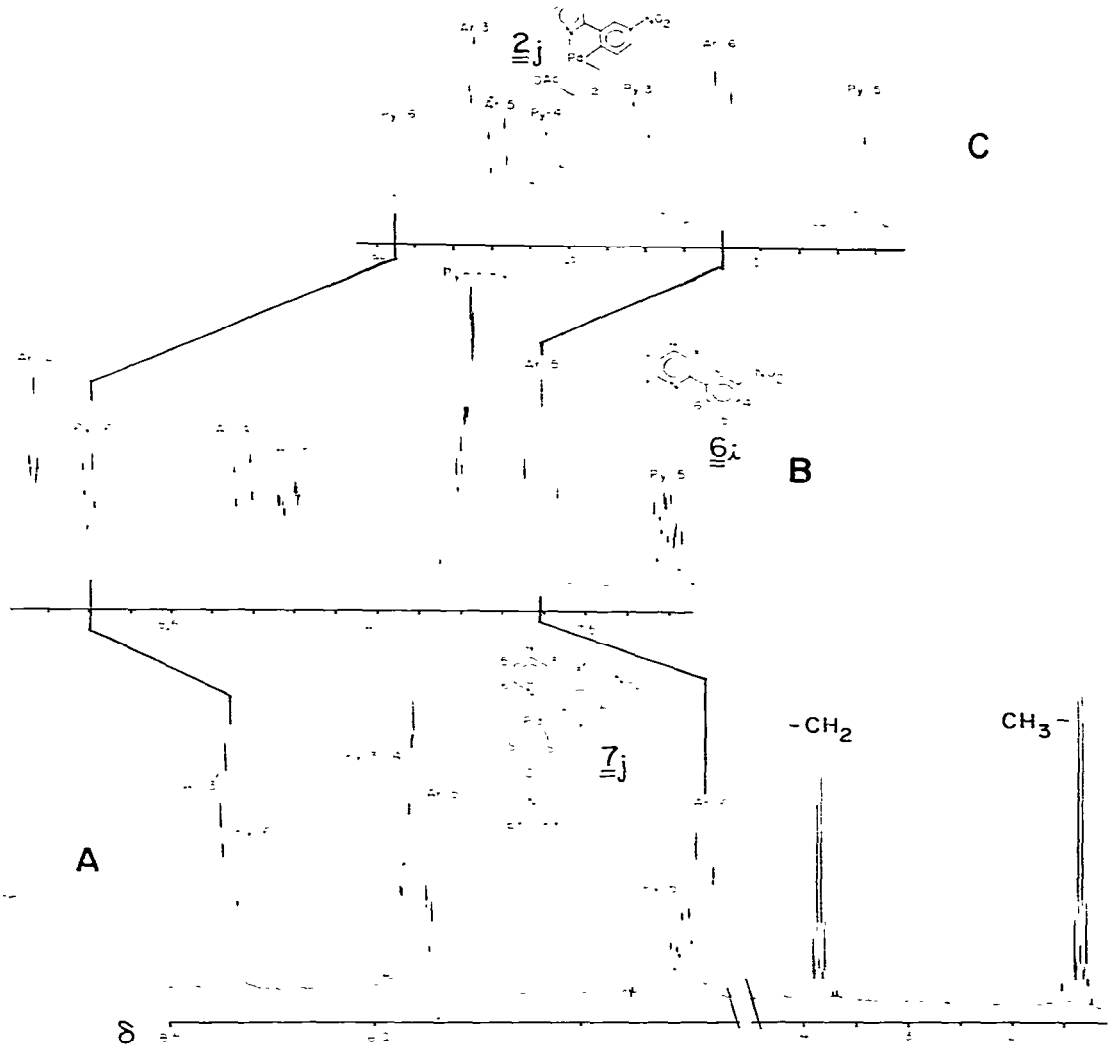


Fig. 1. NMR (200 MHz) comparison of ligand 6i (B) with complexes 7j (A) and 2j (C) in $CDCl_3$.

desired cyclometallated products 1 and 2, respectively. When $Pd(OAc)_2$ is utilized, cyclometallation proceeded at a slower rate; thus, the reaction was conducted in refluxing glacial acetic acid, however, refluxing chloroform proved to be a better solvent choice. These related metallation reaction rates are best explained by the nature of the palladium reagent, in which $Pd(OAc)_2$ is trimeric and $PdCl_4^{2-}$ is mononuclear. Yield data for the formation of 2 with (six) different ring-activating substituents averaged 58%, whereas, for six compounds with ring-deactivating groups averaged only 38%. These results suggest that the controlling factor in formation of 2 may be electrophilic attack on the aryl ring by palladium, after initial *N*-complexation. Previous workers [23,24] have also suggested that palladium undertakes electrophilic substitution reactions.

It was further established that $Pd(OAc)_2$ could serve to separate the 2-arylpyridines from the isomeric mixture derived from the treatment of pyridine

with the appropriate diazonium salt, since only the 2-isomer can undergo cyclometallation. $PdCl_4^{2-}$ will not suffice since a mixture of insoluble metallated *and* simple adducts readily precipitates.

In electrophilic substitution reactions, electron-rich aryl rings are very susceptible to attack, thus **6n** was prepared to test this effect in cyclopalladation. Under a variety of conditions, only unchanged starting ligand was isolated when $Pd(OAc)_2$ was used and a 2 : 1 adduct $[Pd(\mathbf{6n})_2Cl_2]$ was obtained with $PdCl_4^{2-}$. Although initial *N*-complexation is possible, subsequent electrophilic substitution is retarded by the 3- (or 5-) methoxy groups. Similar steric effects were observed for 6c, 6f, and 6i in that only a single cyclometallated product ($J_{5'-6'}$ = 7 Hz (d)] was obtained and it was derived from only "*para*" palladation to the functional group.

Simple 2-phenylpyridine (6a) exists in solution in a mobile but non-planar conformation (ca 58° out-of-plane) [25], thus, introduction of a 2′-substituent will greatly contribute to this steric inhibition of resonance. From isomerization studies of chiral biphenyls, it was concluded that the effective substituent capacity to retard racemization is roughly parallel to the order of size of groups as determined by X-ray measurements, that is: Br >> Me > Cl > NO_2 > CO_2H >> OMe > F [26]. Since cyclometallation was possible with 6e (2′-OMe), 6h (2′-NO_2), 6k (2′-Cl), and 6b (2′-Me) but not with 6o (2′-Br), the steric bulk of a bromine atom at the 2-position was sufficient to prevent rotation to give the necessary near planarity of the aryl moieties and thereby to obviate subsequent electrophilic substitution.

The bridging acetato complexes were converted quantitatively to the corresponding chloro or thiocyanato compounds (1 or 3, respectively) upon treatment with the appropriate sodium salt in acetone. Conversion of 1 to 2 (ca. 80%) was realized by treatment with silver acetate in refluxing acetone. Similarly, 1 was readily transformed to the mononuclear species, such as 7, by the use of certain monodentate ligands, e.g., ammonia, triphenylphosphine, or bidentates such as sodium *N*,*N*-diethyldithiocarbamate.

Spectral analysis

The acetato complexes exhibit two intense broad IR bands at ca. 1580 and 1410 cm^{-1}, as expected for bridging acetates [27,28]. The bands are absent in the corresponding spectra of 1 or 3. The bridging thiocyanate exhibits a sharp peak at 2145 cm^{-1}, suggesting that bridging involves *both* sulfur *and* nitrogen [29a]. The dithiocarbamate complex exhibits an intense broad band at 1505 cm^{-1} and a weak band at ca. 990 cm^{-1}, as expected for bidentate coordination [29b].

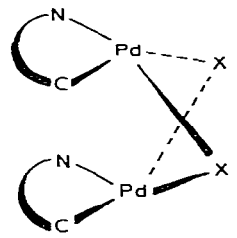
The bridging acetate shows as a sharp spike in the NMR of 2 in the range δ 2.24—2.32 ppm. The distinct downfield shift compared to $Pd(OAc)_2$ (δ 2.04 ppm) and the non-cyclometallated acetato-bridged palladium dimers $[PdX(PMe_2Ph)(OAc)]_2$ (δ 1.80—1.89 ppm) and $[PdX(AsMe_2Ph)(OAc)]_2$ (δ 1.74—1.89 ppm) [30] is indicative of the bridging acetato moiety. In Figure 1 are shown pertinent portions of the 200 MHz spectra of complexes 7j and 2j and the common ligand 6i, with a comparison of the positions of the most perturbated pyridyl and aryl protons. Although the ligand H-5′ proton (Table 2) demonstrates a reasonable σ—ρ correlation to the ring functionality,

there appears to be no other such relationship detected in either the ligand or related complex. Upon cyclometallation with $Pd(OAc)_2$ the 6-pyridyl hydrogen in 2 exhibits a strong upfield shift ($\Delta\delta$ 0.75 ppm) and the hydrogen "*ortho*" to the Pd—C bond (H-6′) similarly shows an upfield shift ($\Delta\delta$ 0.5 ppm), reflecting enhanced shielding effects. These dramatic shifts result from two probable causes: (a) a flow of charge from the electron-rich (d^8) palladium atom into the aromatic rings (π back bonding) and/or (b) a through-space shielding caused by an adjacent (*syn* juxtaposition) aromatic ring.

In support of the latter effect being the major contributor to these upfield shifts, we offer the following observations.

(1) Acetato-bridged dimers, whose crystalline structures have been determined [31—34], exhibit a "boat" form of the bridging acetates, to permit greater electron delocalization. The remaining ligands attached to the two planar bridged palladium atoms are brought into a close proximity of each other. After substitution of these ligands with 2-arylpyridines, the CPK models indicate that the protons in question are in the shielding environment of the *syn*-juxtaposed aromatic rings (see 8).

(2) In order to remove the effect caused by the *syn*-aromatic nuclei, the mononuclear complex 7 was prepared. The NMR spectrum of 7 shows upfield



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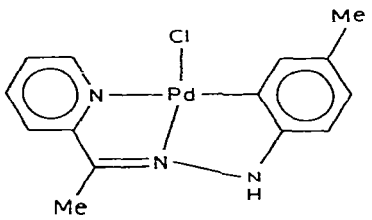

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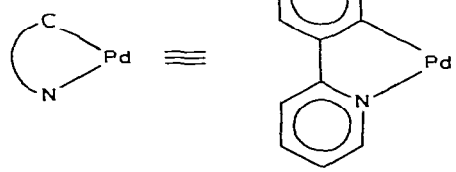

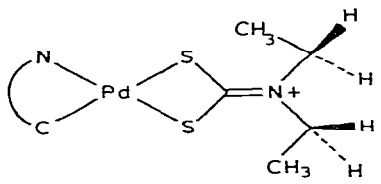

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shifts for both of the aromatic hydrogens in question but not as severe as those seen in the bridged acetato-compounds 2i. The 6-pyridyl hydrogen is shifted upfield by ~0.3 ppm in 7 versus ~0.75 ppm in 2i. The aryl proton is similarly shifted by ~0.4 ppm and ~0.5 ppm in 7 and 2i, respectively. While there is no through-space anisotropic shielding possible in 7, it is possible that any palladium-to-nitrogen back bonding, which might occur, is diminished by the dithiocarbamate moiety.

There is, nevertheless, some contribution to the proton chemical shift caused by metal-ligand back-bonding. (1) For example, in 9, the NMR spectra for both the ligand and complex reveal an upfield shift (~0.2 ppm) for the α-pyridyl hydrogen, which must be due to metal back-bonding [35]. (2) The upfield shifts observed for 2 are in contrast to the downfield shifts of the α-pyridyl proton and the proton "*ortho*" to the rhodium—carbon bond in $RhCl_2(6a)(PBu_3)_2$ [9]. Since Rh^{III}, a d^6 system, is not as electron rich as Pd(II), this reversal in electron flow suggests that d^8 systems donate to the ligand via back donation. (3) The distinct upfield shifts for the aromatic protons in question are still present in 7 but are not as large as those in 2i.

The NMR data [36] for 2 further reveal considerable non-bonding interaction between the 3′-aryl substituent and the 3-pyridyl hydrogen. The shifts for H-3 from δ 7.07 (R = H) downfield to 7.32 (R = Me), 7.82 (R = OMe), and 8.30 ppm (X = Cl) are indicative of increased electron-density of the 3′-substituent on H-3, compounded with a possible deviation of the rings from planarity caused by the 3′-substituent, and not simply increasing substituent size (Me > Cl > MeO > H). When R = NO_2, the H-3 chemical shift showed a slight upfield shift (δ 6.90—7.03 ppm), reflecting of a diminished electron-density at the atom adjacent to the aryl ring on H-3.

Finally, for the mixed ligand complex 7j, the expanded 200 MHz NMR spectrum (see Figure 1A) shows that the methylene protons are equivalent whereas the methyl protons are not. A forthcoming paper [37] will deal with this observation and related ones for analogous Rh^{III} complexes.

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