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CYCLOMETALLATION

II *. ^{1}H NMR STUDIES OF PALLADIUM(II) AND RHODIUM(III) MIXED LIGAND COMPLEXES

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Summary

New cyclometallated compounds of Rh^{III} and Ir^{III} with 2-arylpyridines (1) have been prepared, including chloro-bridged dimers, $[M(1)_2Cl]_2$, and mononuclear species containing diethyldithiocarbamate (dtc), $[Rh(1)_2dtc]$. ^{1}H NMR studies have established a *trans*-nitrogen octahedral structure for all of these compounds. These studies have also strongly suggested that in the planar d^8 [Pd(1)dtc] complex there is metal-to-ligand back bonding, whereas in the octahedral d^6 $[Rh(1)_2dtc]$ no such bonding occurs. Furthermore, in the Pd^{II} complex the methyl groups are found to be in non-equivalent sites whereas the methylene protons seem to be in magnetically equivalent sites. The reverse is true for the Rh^{III} complex. These observations are explained by the different structures of the Pd and Rh complexes, and perhaps also by subtle differences in the metal—ligand bonding to both the arylpyridine and the dtc ligands.

Introduction

In a recent study [1] of cyclometallated palladium compounds containing 2-arylpyridines of type 1, we observed that upon cyclometallation the 6-pyridyl hydrogen, H(6) (see 2), exhibits a strong upfield shift ($\Delta\delta$ ~0.75 ppm). (Note that the numbering of the aryl carbons changes from isolated ligand, 1, to complex, 2). Likewise, the hydrogen "*ortho*" to the Pd—C bond (H(6′)) shows an upfield shift ($\Delta\delta$ ~0.5 ppm). We speculated that these dramatic shifts, reflecting enhanced shielding effects, result from two probable causes: (a) a flow of charge from the electron-rich (d^8) palladium atom into the

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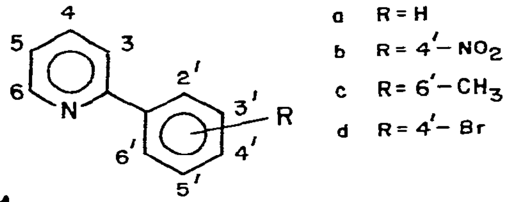
* For part I see ref. 1.



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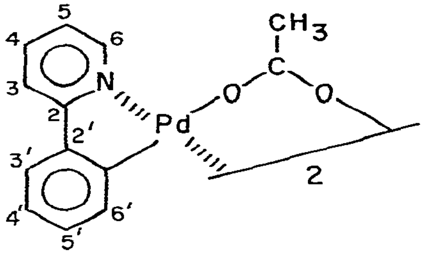

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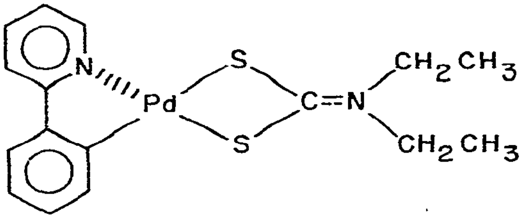
aromatic rings (π back bonding) and/or (b) a through-space shielding caused by an adjacent (*syn* juxtaposition) aromatic ring [2]. In order to eliminate the possibility of the latter effect, we prepared the mononuclear complex 3, having diethyldithiocarbamate (dtc) also as a ligand. Its NMR spectrum likewise shows upfield shifts for both the aromatic hydrogens in question (6 and 6′), but those shifts are not as pronounced as in the bridged dimers, being $\sim$0.3 ppm for H(6) and $\sim$0.4 ppm for H(6′). The through-space anisotropic shielding possible (and a likely contributing shift factor) in 2 is absent in 3 and thus the observed H(6) and H(6′) shifts are most likely due to palladium-to-nitrogen back bonding. (Note that the H(6) is much more affected, 2—3 = 0.45 ppm, than is H(6′), 2—3 = 0.1 ppm.) The smaller proton shifts in 3 could be due either to a dtc-altered electron density on palladium or to the loss of the shift contribution from through-space shielding, or, more likely, to both of these factors.



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The upfield shifts observed for 2 and 3 (in the protons under consideration here) are in marked contrast to the downfield shifts in these protons observed in a related rhodium(III) complex of 2-phenylpyridine (1a), RhCl$_2$(1a)(PBu$_3$)$_2$ [3]. Since Rh^{III} is a d^6 system, not capable in octahedral environments of π back bonding (nor is it as electron rich as the d^8 Pd^{II}, this reversal of electron flow appears to support the hypothesis that d^8 metal systems donate charge to the cyclometallated ligand via back donation.

We now wish to report the preparations and 200 MHz NMR studies of some cyclometallated complexes of Pd^{II}, Rh^{III}, and Ir^{III}, including both halo- or acetato-bridged dimers and mononuclear species derived from them in which diethyldithiocarbamate (dtc) replaces the two bridging groups in the coordination sphere: $[Pd(1b)Cl]_2$, $[Pd(1b)(CH_3COO)]_2$, $[Rh(1b)_2Cl]_2$, $[Rh(1c)_2Cl]_2$, $[Rh(1d)_2Cl]_2$, $[Ir(1b)_2Cl]_2$, $[Ir(1d)_2Cl]_2$, [Pd(1b)dtc], and $[Rh(1b)_2dtc]$. The new NMR results support our earlier findings on the palladium complexes [1] and speculations on the rhodium(III) complexes and suggest subtle but not insignificant electronic effects involving not only the two different metal species but the bidentate sulfur ligand itself.

Experimental

NMR spectra were obtained in $CDCl_3$ solutions, with Me_4Si as the internal standard ($\delta = 0$ ppm), and were recorded on either a Varian Associates A-60A or Bruker WP-200 NMR spectrometer. Chemical shifts (vide infra) are reported in parts per million on the δ scale. 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 [4] from $PdCl_2$. $Pd(C_2H_3O_2)_2$ was used as purchased from either Goldsmith Chemicals and Metal Corp. or SynMet, Inc. $RhCl_3 \cdot 3\ H_2O$ and $IrCl_3 \cdot 3\ H_2O$ were purchased from Matthey Bishop, Inc. and used as received.

The preparations of the various arylpyridines and of the palladium complexes containing both those ligands alone or mixed ligand complexes with diethyldithiocarbamate (dtc) have been previously described [1].

The rhodium- and iridium-bridged dimers were all prepared according to the following procedure, which uses $[Rh(1b)_2Cl]_2$ as the example. A stirred mixture of $RhCl_3 \cdot 3\ H_2O$ (145 mg, 0.55 mmol) and 2-(3'-nitrophenyl)pyridine (366 mg, 1.83 mmol) was refluxed in aqueous methanol (50%, 50 ml) for 12 h under nitrogen. Water (50 ml) was added to the orange solution which was then extracted with dichloromethane (3 × 100 ml). Extracts were combined and dried over anhydrous $MgSO_4$. The orange suspension was filtered and evaporated in vacuo to yield a yellow solid, which was column chromatographed on silica gel and eluted with dichloromethane to give $[Rh(1b)_2Cl]_2$, di-μ-chloro-tetra[4'-nitro-2'-(2-pyridyl)phenyl-*N*]dirhodium(III), as a powdery yellow solid: yield, 176 mg (60%), m.p. 406°C (decomp., DTA), IR (KBr), 1570s, 1500s, 1335vs(br), 993m, 783s, 755m, and 740m cm^{-1}. NMR data is summarized in Table 1.

Other chloro-bridged dimers prepared in the foregoing manner are listed in Table 2 along with the elemental analysis results.

The preparation of the mixed ligand mononuclear complex with dtc, $[Rh(1b)_2dtc]$, was as follows. A mixture of di-μ-chloro-tetra[4'-nitro-2'-(pyridyl)phenyl-*N*]dirhodium(III), $[Rh(1b)_2Cl]_2$ (74 mg, 0.070 mmol) and sodium *N*,*N*-diethyldithiocarbamate (dtc) trihydrate (31 mg, 0.14 mmol) in acetone (50 ml) was refluxed for 12 h under nitrogen. The yellow solution was

TABLE 1

200 MHz NMR DATA [a] FOR 2-ARYLPYRIDINE COMPLEXES OF $Rh^{(III)}$, $Ir^{(III)}$ AND $Pd^{(II)}$

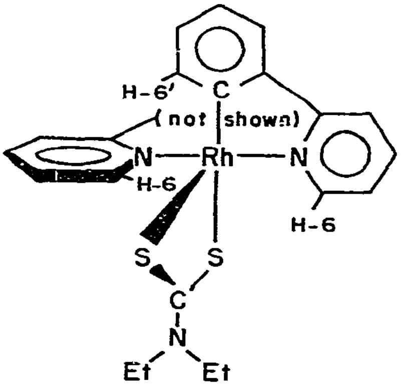
Compound	H(3′) or $CH(3')_3$	H(6′)	H(5′)	H(4′)	H(5)
$[Rh(1c)_2Cl]_2$	2.66,s	5.68,d,8	6.48,t,8	6.60,d,8	6.76,t,6
$[Rh(1b)_2Cl]_2$	8.46,d,3	6.04,d,9	7.57,dd,9,3	(NO_2)	7.01,ddd,8,6,2
$[Ir(1b)_2Cl]_2$	8.42,d,2.5	6.01,d,9	7.47,dd,9,2.5	(NO_2)	7.02,t,8
$[Rh(1d)_2Cl]_2$	7.44,d,9	5.97,d,2	(Br)	7.04,dd,9,2	6.84,ddd,6,6,3
$[Ir(1d)_2Cl]_2$	7.38,d,8	5.95,d,2	(Br)	6.97,dd,8	6.84,ddd,7,7,2
1b	8.84,t,2	7.61,t,8	8.33,m,—	(NO_2)	7.31,m,—
$[Rh(1b)_2dtc]$	8.45,d,2	6.47,d,8	7.60,dd,8,2	(NO_2)	7.43,ddd,8,6,2
$[Pd(1b)dtc]$	8.39,m,—	7.20—7.30,m,—	7.90—8.00,m,—	(NO_2)	7.20—7.30,m,—

[a] δ(ppm), splitting (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant(s).
[b] For first compound only.

evaporated in vacuo to yield a yellow solid, which was column chromatographed on silica gel and eluted with dichloromethane to give $[Rh(1b)_2dtc]$, *N,N*-diethyldithiocarbamato-bis-[4′-nitro-2′-(2-pyridyl)phenyl-*N*]rhodium(III), as a yellow solid. Yield, 48 mg (50%), m.p. 328°C (decomp. DTA); IR (KBr) 2605m, 1585s, 1565s, 1497vs(br), 1335vs(br), 781m, 753m, and 739m cm^{-1}. NMR data is summarized in Table 1.

Results and discussion

Several new cyclometallated complexes of Rh^{III} have been prepared: chloro-bridged dimers $[Rh(1b)_2Cl]_2$, $[Rh(1c)_2Cl]_2$, $[Rh(1d)_2Cl]_2$, and the mononuclear $[Rh(1b)_2dtc]$. A single NMR signal for each of the aromatic protons is strong evidence that the pyridyl nitrogens are *trans* to each other. (Table 1 summarizes the 200 MHz NMR data.) The significance of this *trans*-N octahedral structure for this work is that it means that in the Rh-dtc compound, $[Rh(1b)_2dtc]$, the two sulfur atoms are in equivalent molecular environments, which is clearly not the case in the corresponding Pd complex $[Pd(1b)dtc]$, where one sulfur is *trans* to a pyridyl nitrogen and the other is *trans* to an aryl carbon. Furthermore the octahedral structure of the Rh compound, in contrast to the square planar structure of the Pd compound, brings the 6-aryl proton (H(6′) in the complex) over the pyridyl ring current. (See 4). No such through-space interac-



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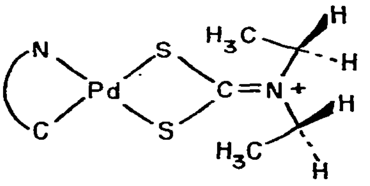
mpound	H(4)	H(3)	H(6)	—CH_2CH_3	—CH_2CH_3
h(1c)$_2$Cl]$_2$	6.60,d,8	8.09,d,6	9.37,d,6	—	—
h(1b)$_2$Cl]$_2$	8.13,m,—	8.13,m,—	9.18,d,6	—	—
(1b)$_2$Cl]$_2$	8.01,t,9	8.15,t,9	9,19,d,6	—	—
h(1d)$_2$Cl]$_2$	7.87,m,—	7.87,m,—	9,10,d,6	—	—
(1d)$_2$Cl]$_2$	7.82,m,—	7.82,m,—	9.12,d,7	—	—
	7.75—7.83,m,—	7.75—7.83,m,—	8.70,m,—	—	—
h(1b)$_2$dtc]	8.06,t,6	7.96,dd,6,2	9.60,d,6	1.24,t,7	3.71,dq,7 3.89,dq,7
l(1b)dtc]	7.90—8.00,m,—	7.90—8.00,m,—	8.42,m,—	1.34,t,7 1.38,t,7	3.89,q,7

tion is possible in the Pd compound. This structural feature serves to explain the observed upfield shift (from ligand to Rh complex) in H(6′), e.g., from 7.63 to 6.04 in [Rh(1b)$_2$Cl]$_2$ and to 6.47 in [Rh(1b)$_2$dtc]. Thus the upfield shift of this aromatic (aryl) proton in both the Pd and Rh complexes arises from entirely different interactions. It is due in the case of the Pd mainly to Pd-to-ligand back bonding [1], and in the case of Rh to through-space shielding by an adjacent aromatic ring.

On the other hand, the H(6) proton in the Rh complexes is strongly shifted downfield, e.g., from 8.70 to 9.18 in [Rh(1b)$_2$Cl]$_2$ and to 9.60 in [Rh(1b)$_2$dtc]. Thus in the Pd compounds this aromatic (pyridyl) proton is shifted upfield due, we suggest, to Pd-to-ligand back bonding [1], and it is shifted downfield in the Rh compounds due, we suggest, to the straight N → Rh coordinate sigma bond with no superimposed metal-to-ligand back bonding.

The 200 MHz proton NMR spectra for both the square planar Pd-dtc complex and the analogous octahedral Rh^{III}-dtc complex are shown in Fig. 1. As can be seen from this figure, in the Pd complex the methylene protons appear to be in magnetically equivalent sites (one quartet), whereas the methyl groups appear to be in non-equivalent sites (two triplets). These triplets do not merge up to 90°C. These results are probably fortuitous and due to an undetectable chemical shift difference in the case of the methylene protons, which are, after all, not exactly chemically (symmetry) equivalent. However, the fact that the methyl protons show up in the NMR experiment to be non-equivalent whereas the methylene protons seem to be magnetically equivalent is tentatively explained as follows. If the methyl groups are positioned near the sulfur atoms (see 5), which are themselves non-equivalent (vide supra), then the non-equivalence of the methyl groups is enhanced by a through-space interaction. The "equivalent" appearing methylene protons are apparently far enough away



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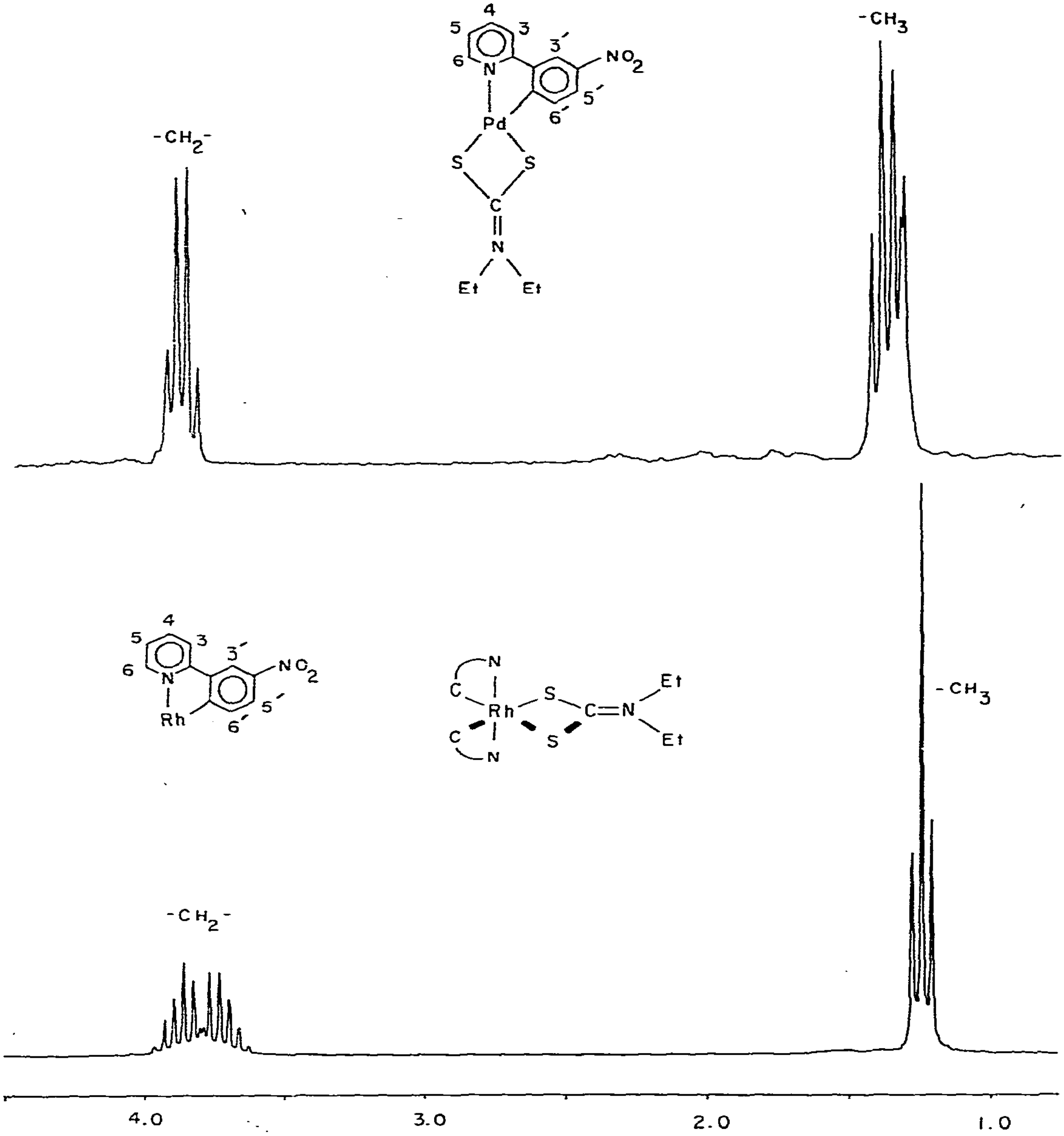


Fig. 1. The 200 MHz proton NMR spectra for [Pd(1b)dtc] and [Rh(1b)$_2$dtc] in the region 1.0 to 4.5 ppm.

from the non-equivalent sulfur atoms so that they are not similarly affected by such through-space interaction.

On the other hand, we see from the NMR spectrum of the Rh^{III} complex that an opposite effect is observed; namely, the methyl groups appear to be in equivalent sites (one triplet), but the methylene protons clearly appear to be in non-equivalent sites (two sets of a double quartet that overlap so that only 12 of the 16 lines appear). In the Rh^{III} complex the methylene protons are still,

TABLE 2

ANALYTICAL, YIELD AND MELTING POINT DATA FOR NEW RHODIUM(III) AND IRIDIUM(III) COMPLEXES [a]

Compound	Melting point (°C) (Decomposition) [b]	Yield (%)	Analytical data: Found (calcd.) (%)		
			C	H	N
$[Rh(1b)_2Cl]_2$ [c]	406	60	47.63(49.21)	2.61(2.63)	9.92(10.45)
$[Rh(1c)_2Cl]_2$ [d]	362	30	54.18(53.64)	3.86(3.94)	5.01(5.01)
$[Rh(1d)_2Cl]_2$	473	12	43.25(43.69)	2.27(2.33)	4.56(4.64)
$[Ir(1b)_2Cl]_2$	453	14	40.93(42.19)	1.99(2.26)	8.86(8.95)
$[Ir(1d)_2Cl]_2$	298	5	36.57(35.45)	2.14(2.07)	3.54(3.60)
$[Rh(1b)_2dtc]$	328	50	47.87(47.71)	3.47(3.64)	10.03(10.13)

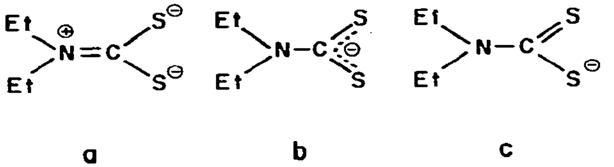
[a] Additional characterizing data (NMR, IR, TGA, DTA, MS) available in M. Gutierrez, Ph.D. Dissertation, Louisiana State University, Baton Rouge, LA 70803.

[b] By DTA.

[c] By TGA residue the metal was 19.30% (calcd. 19.18%).

[d] By TGA residue the metal was 20.37% (calcd. 21.68%).

of course, chemically non-equivalent but in this case the non-equivalence is clearly magnetically monitored in the NMR spectrum. We might also (on less firm ground) speculate that either or both of the other two possible structures of dtc, 6b and 6c, contributes more to the dtc in the Rh^{III} complex than in the



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Pd^{II} complex. If this were the case, the lone pair on the nitrogen may serve to enhance the non-equivalence of the methylene protons so that the chemical shift difference becomes detectable in the Rh^{III} complex. Finally, the magnetic equivalence of the methyl protons in the Rh^{III} complex may simply be due to the fact that the sulfur atoms are chemically equivalent here (4), as opposed to their non-equivalence in the Pd^{II} complex (5).

Finally, the first complexes of iridium with 2-arylpyridines have been prepared: $[Ir(1b)_2Cl]_2$ and $[Ir(1d)_2Cl]_2$. Yields were low (Table 2) and the quantities of material limited our studies to simply establishing by NMR that the Ir^{III} species were very similar to those of Rh^{III} (see Table 1).

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