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Reactions of the novel Schiff's base 2-(3-nitrobenzylidene)-benzimidazole (3a) with Rh, Ir and Pt. X-ray crystal structure of [Rh(3a)(4-picoline)(1,5-COD)](CF_3SO_3).

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Abstract

The chemistry of the Schiff's base 2-(3-nitrobenzylidene)benzimidazole (**3a**), with rhodium(I) is described, and the molecular structure of the cationic complex [Rh(3a)(4-picoline)(1,5-COD)](CF_3SO_3) (**4b**) is reported. The complex has a distorted square planar geometry with the benzimidazole imine-*N* coordinated; relevant bond distances (Å) and angles (°) are: Rh–N(1), 2.100(6), Rh–N(6), 2.095(6), Rh–C(16), 2.117(11), Rh–C(17), 2.131(9), Rh–C(20), 2.131(9), Rh–C(21), 2.112(9) Å; N(1)–Rh–N(6), 88.0(2), N(1)–Rh–C(16), 89.5(3), N(1)–Rh–C(17), 92.6(3), N(6)–Rh–C(20), 90.6(3), N(6)–Rh–C(21), 91.7(3)°.

Ligand **3a** reacts with [M(μ-Cl)(cyclooctene)$_2$]$_2$ (M = Rh, Ir) in the presence of PPh_3 to afford rhodium(III) and iridium(III) complexes in which the imine C–H bond has oxidatively added. This type of addition also takes place with 2-(4-methylbenzylidene)benzimidazole and several derivatives are reported. Ligand **3a** when coordinated to platinum(II) in *trans*-$PtCl_2$(3a)(PhCH=CH_2) does not give rise to Pt←H–C interactions, in contrast to 2-(3-nitrobenzylidene)3-methylpyridine (**2**). Reasons for this are suggested, and a steric boundary condition is proposed for this weak Pt←H–C interaction, the 5- and 6-methyl analogs of **2** being used as models. ^{103}Rh NMR data for two rhodium(III) complexes are reported.

Introduction

Our interest in coordinated ligands which contain proximate C–H bonds [1–3] has led us to consider a variety of metal complexes derived from **1** and **2**. In both of these the substituents have C–H bonds that can come close to the metal, and for

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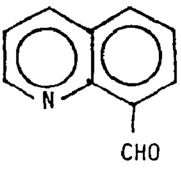
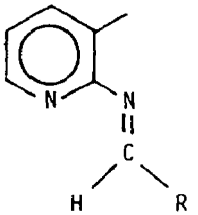


(1)



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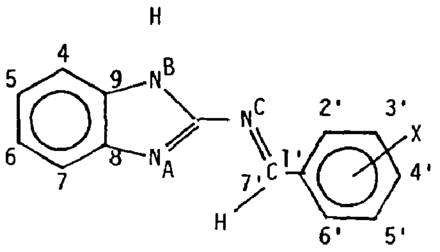
R = aryl moiety

e.g. $3\text{-}NO_2C_6H_4$



(3a : X = $3\text{-}NO_2$;
3b : X = $4\text{-}CH_3$)

these complexes we have established a criterion for recognizing a weak M←H–C interaction using a coupling constant to platinum [1–3]. In an extension of this work we consider here some rhodium chemistry of the benzimidazole ligand **3**, with a view to (i) understanding its coordinating capabilities, and (ii) possibly observing cyclometallation via oxidative addition of the imine C–H bond. We note that **3**, like **2**, contains a substituent imine moiety which might be suitable for weak bonding with the metal, and that ligands **1** [4] and **2** [5] readily take part in cyclometallation.

Results and discussion

X-Ray structure of [Rh(3a)(4-picoline)(1,5-COD)](CF$_3$SO$_3$) (4b)

As we were uncertain as to the ligating site(s) in **3** we prepared several simple 1,5-cyclooctadienerhodium(I) complexes **4**, containing **3a**, and determined the molecular structure for one of these, **4b**, by X-ray diffraction. Table 1 gives the experimental and crystallographic details for the structure, Table 2 the atomic coordinates, and Table 3, a selection of bond distances (Å) and bond angles (°), Fig. 1 presents an ORTEP view for this complex.

The geometry of the complex is distorted square planar at rhodium with the two olefin double bonds, the picoline nitrogen and the imidazole imine nitrogen as the ligating centers. The two Rh–N separations Rh–N(6), 2.095(6) Å and Rh–N(1), 2.100(6) Å, are not significantly different, and are in agreement with the analogous distances found for rhodium complexes of: (a) 2,2′-dibenzimidazolate anions [6]; (b) bridging naphthyridine-2-one [7]; (c) bridging 1,8-naphthyridine [18], and (d) briding 1*H*-pyrrole [2,3–6] pyridine [9]. The distances in **4b** are interesting in that they show that the rather large ligands **3b** are able to attach to the metal without inducing marked distance changes due to steric effects. The four Rh–C(olefin) separations fall in the range 2.112–2.131(9) Å, in excellent agreement with the values found for $[Rh(NH_3)_2(COD)]^+$, 2.110–2.130 Å [10]; and $(Bu_4N)[(COD)Rh(\mu\text{-debi})Rh(COD)]$ (debi = trianion of 4,5-dicarboxy-2-methylimidazole [11]), but much shorter than the Rh–C separations for the olefin *trans* to phosphorus in $RhCl(COD)\{P(p\text{-}FC_6H_4)_3\}$ 2.216(6) and 2.234(7) Å [12]. The COD olefin C–C bond lengths are normal for this type of complex [10–12], as is the C=N(4) length of

Table 1

Crystallographic parameters and experimental data [a] for the X-ray diffraction study of **4b**

Formula	$RhSF_3O_5N_5C_{29}H_{29}$
Mol. weight	719.55
Crystal dim. (mm)	$0.3\times0.2\times0.2$
Cryst. system	Monoclinic
Space group	$P2_1/a$
a (Å)	15.477(5)
b (Å)	11.698(4)
c (Å)	16.891(6)
β (°)	93.83(4)
V (Å^3)	3051.3
Z	4
ρ (calc) (g cm^{-3})	1.569
μ (cm^{-1})	6.79
Radiation	Mo-$K_{\bar{\alpha}}$ (graphite monochromated 0.71069 Å)
Measd. refl.	$\pm h, +k, +l$
θ range (°)	$3.0 \leqslant \theta \leqslant 25.0$
Scan type	ω
Max. scan speed (° min^{-1})	20.2
Scan width (°)	$1.20+0.35 \tan\theta$
Max. counting time (s)	60
Prescan rejection limit	0.6 (1.5σ)
Prescan acceptance limit	0.02 (50σ)
Bkgd. time	$0.5\times$ scan time
Horiz. receiving aperture (mm)	$2.0+\tan\theta$
Vert. receiving aperture (mm)	4.0
No. of independent data	5810
No. of observed data ($F_o \geqslant 2.5\sigma(F_o)$)	2663
R [b]	0.060
R_w [c]	0.065

[a] Data collected at r.t. [b] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

1.29(1) Å in the Schiff's base moiety. The Rh–N(4) separation is > 3.3 Å, thereby excluding a bonding interaction between these atoms. The Rh–C(7′) distance is even longer, > 3.6 Å, so that it is clear that this imine function is remote from the metal. The question as to which benzimidazole ring nitrogen is coordinated may be answered by considering the two C(2)–N distances in combination with the position of the Rh atom relative to the plane defined by the heterocyclic ring. The relatively short C(2)–N(1) distance of 1.318(10) Å suggests that the imine ring nitrogen is coordinated, and this is supported by the essentially in-plane position of the Rh atom, in keeping with the expected direction of an Rh–N vector arising from an sp^2 lone-pair on nitrogen. The bong angle N(1)–Rh–N(6) for the monodentate ligands is as expected, as are the ca. 160° N–Rh–C angles involving the COD double bonds. We note that both heterocylic rings are perpendicular to the plane defined by the rhodium and two coordinated nitrogen atoms, thereby reducing steric repulsions between the ligands. The distances and angles in both the picoline and benzene rings are as expected. In summary, ligand **30** coordinates rhodium(I) via the benzimidazole imine nitrogen. Despite the relatively large size of the ligand, the

Table 2

Atomic coordinates for **4b**

Atom	x	y	z
Rh	0.07254(4)	0.15683(5)	0.21715(3)
N(1)	0.14732(40)	0.01332(49)	0.25166(38)
N(3)	0.18890(43)	−0.16663(54)	0.27550(38)
C(2)	0.12562(45)	−0.09525(68)	0.24393(43)
C(4)	0.33780(60)	−0.12396(74)	0.33969(48)
C(5)	0.39160(58)	−0.03471(84)	0.36088(60)
C(6)	0.36471(62)	0.07880(83)	0.34575(56)
C(7)	0.28621(57)	0.10601(75)	0.30777(55)
C(8)	0.23049(53)	0.01622(66)	0.28915(45)
C(9)	0.25656(44)	−0.09723(65)	0.30389(44)
N(4)	0.04505(41)	−0.12568(49)	0.21038(39)
C(1′)	−0.05713(54)	−0.26879(73)	0.16644(51)
C(2′)	−0.12193(53)	−0.18634(73)	0.14276(47)
C(3′)	−0.19899(57)	−0.22889(86)	0.10826(49)
C(4′)	−0.21766(66)	−0.34348(102)	0.09887(59)
C(5′)	−0.15253(72)	−0.42476(89)	0.12251(60)
C(6′)	−0.07306(65)	−0.38575(74)	0.15498(60)
C(7′)	0.02593(59)	−0.23231(76)	0.20277(51)
N(5)	−0.26745(55)	−0.14882(85)	0.08299(57)
O(1)	−0.24115(61)	−0.05294(90)	0.06691(67)
O(2)	−0.33923(51)	−0.17745(96)	0.07408(65)
N(6)	0.03650(41)	0.16787(52)	0.33419(36)
C(10)	−0.03397(52)	0.11467(76)	0.35756(51)
C(11)	−0.05810(58)	0.11842(74)	0.43569(60)
C(12)	0.08757(55)	0.22619(86)	0.38921(51)
C(13)	0.06594(61)	0.22780(99)	0.47003(57)
C(14)	−0.00441(50)	0.17302(77)	0.49388(46)
C(15)	−0.03068(66)	0.17145(101)	0.57899(54)
C(16)	0.15097(77)	0.18196(93)	0.12072(64)
C(17)	0.08015(76)	0.11991(87)	0.09431(50)
C(18)	−0.00178(90)	0.17213(109)	0.04565(67)
C(19)	−0.06778(87)	0.21924(131)	0.09478(69)
C(20)	−0.03276(64)	0.26154(73)	0.17796(55)
C(21)	0.03688(65)	0.33040(71)	0.19453(55)
C(22)	0.09157(90)	0.38191(87)	0.12820(70)
C(23)	0.16552(94)	0.31001(98)	0.11108(81)
S	0.23581(17)	0.53104(20)	0.32908(18)
O(1S)	0.23668(55)	0.41117(55)	0.31650(52)
O(2S)	0.32049(47)	0.58440(67)	0.33538(50)
O(3S)	0.17361(56)	0.59440(62)	0.28118(50)
F(1)	0.24815(55)	0.48640(86)	0.47892(50)
F(2)	0.20323(57)	0.65580(73)	0.44987(61)
F(3)	0.11934(47)	0.51201(78)	0.43376(63)
CF	0.19959(73)	0.54834(106)	0.42801(81)

Rh–N separation is normal. There is no evidence for weak coordination of a fifth ligand atom and the imine C–H bond is remote from the metal (> 4 Å). There are no unexpected structural *cis*- and/or *trans*-influences.

Table 3

Selected bond lenghts (Å) and torsion angles (°) for compound **4b**

Rh–N(1)	2.100(6)	Rh–N(1)–C(2)	127.6(3)
Rh–N(6)	2.095(6)	Rh–N(1)–C(8)	125.5(3)
Rh–C(16)	2.117(11)	N(1)–Rh–N(6)	88.0(2)
Rh–C(17)	2.131(9)	N(1)–Rh–C(16)	89.5(3)
Rh–C(20)	2.131(9)	N(1)–Rh–C(17)	92.6(3)
Rh–C(21)	2.112(9)	N(6)–Rh–C(20)	90.6(3)
N(1)–C(2)	1.32(1)	N(6)–Rh–C(21)	91.7(3)
N(1)–C(8)	1.40(1)	N(1)–C(2)–N(3)	111.9(5)
N(3)–C(2)	1.37(1)	N(1)–C(2)–N(4)	120.3(5)
N(3)–C(9)	1.39(1)	N(1)–C(8)–C(9)	107.6(6)
N(4)–C(2)	1.376(9)	N(3)–C(2)–N(4)	127.7(4)
N(4)–C(7′)	1.29(1)	N(3)–C(9)–C(8)	107.0(6)
C(8)–C(9)	1.40(1)	N(4)–C(7′)–C(1′)	121.0(6)
C(4)–C(9)	1.39(1)	C(2)–N(1)–C(8)	106.9(5)
C(4)–C(5)	1.37(1)	C(2)–N(3)–C(9)	106.6(6)
C(5)–C(6)	1.41(1)	C(2)–N(4)–C(7′)	118.9(5)
C(6)–C(7)	1.37(1)	(C–S–O) [a]	103.5(1.3)
C(7)–C(8)	1.38(1)	(S–C–F) [a]	111.7(1.2)
C(1′)–C(7′)	1.45(1)	Rh–N(1)–C(2)–N(4) [d]	−0.6
C(16)–C(17)	1.36(2)	Rh–N(1)–C(8)–C(7)	−5.2
C(2)–C(21)	1.36(1)	N(1)–C(2)–N(4)–C(7′)	179.2
(C–C) [a,b]	1.39(2)	C(2)–N(4)–C(7′)–C(1′)	−178.7
(C–C) [c]	1.36(1)	N(4)–C(7′)–C(1′)–C(2′)	−4.0
C–S	1.80(1)	N(1)–Rh–N(6)–C(10)	86.4
(C–F) [a]	1.320(8)	N(1)–Rh–C(16)–C(17)	−85.9
(S–O) [a]	1.43(1)		

[a] Av. bond length; e.s.d's given by $\sigma = \left[\frac{\Sigma_i (x_i - \bar{x})^2}{(n-1)}\right]^{1/2}$. [b] Refers to the aromatic C–C bonds (C(4) to C(9), C(1′) to C(6′)). [c] Refers to the pyridine ring. [d] E.s.d's on torsion angles in the range 0.9–1.4°.

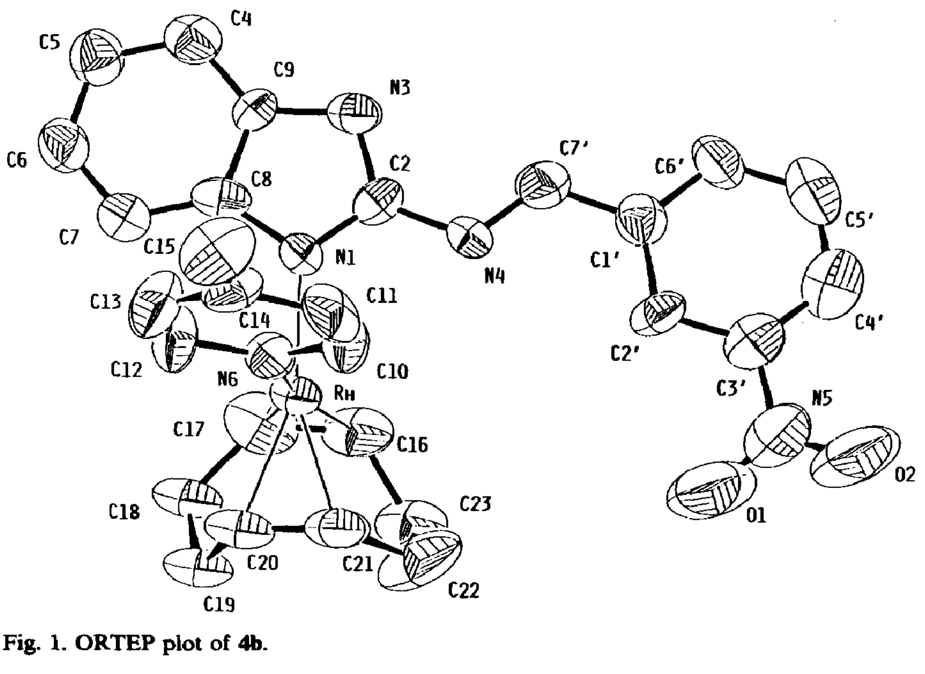
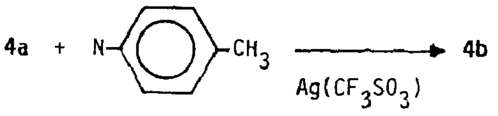


Fig. 1. ORTEP plot of **4b**.

$$[Rh(\mu\text{-}Cl)(COD)]_2 + 2(3a) \longrightarrow 2(4a) \qquad (1)$$



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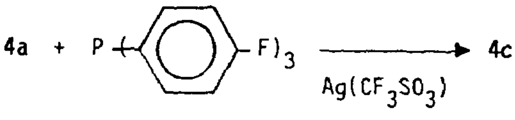

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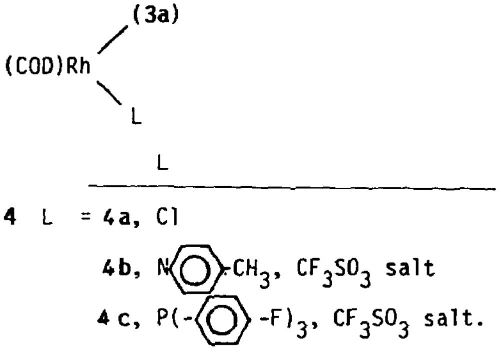


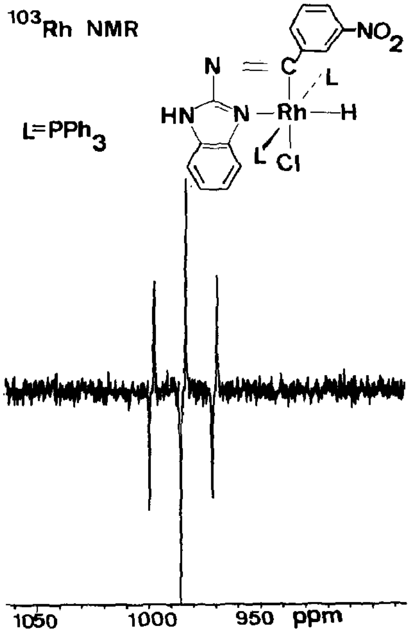


Fig. 2. ^{103}Rh INEPT NMR spectrum of **5a**. The triplet structure stems from coupling to the two equivalent ^{31}P spins while the out-of-phase doublet arises from the Rh–H spin–spin interaction.

Rh and Ir complexes of 3

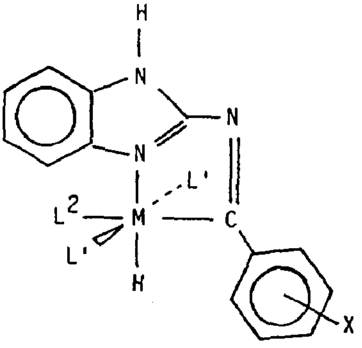
The Rh^I complexes **4** were readily prepared by standard methods, as shown in equations 1–3.

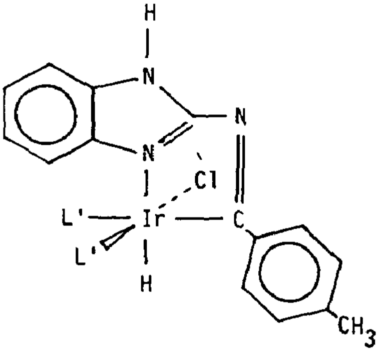
The Rh^{III} complexes derived from **3a**, as well as those of the **4**-CH$_3$ benzylidene analog **3b**, arise as shown in eq. 4.

These and the remaining compounds were characterized by ^{1}H and ^{31}P NMR spectroscopy in combination with elemental analyses and these data are shown in Tables 4–6. The complexes **6** have a *cis* orientation of the ligands L′, whereas those for **5** contain a *trans* geometry for these phosphorus compounds, as shown by ^{31}P{^{1}H} NMR measurements. Complex **5b** arises from **5a** plus $(NH_4)PF_6$ and CH_3CN.

The derivatives **5** and **6** are readily prepared by the method used for the synthesis of Rh^{III} and Ir^{III} analogs of **2** [5]. Moreover, Vrieze and co-workers [13] have

$$[M(\mu\text{-}Cl)(cyclooctene)_2]_2 + 2(\mathbf{3a} \text{ or } \mathbf{3b}) + 4L' \xrightarrow{\text{THF,}} \mathbf{5a}, \mathbf{5c}, \mathbf{5d}, \mathbf{6a}, \mathbf{6b} \qquad (4)$$





	M	X	L'	L^2
5a	Rh	3-NO$_2$	PPh$_3$	Cl
5b	Rh	3-NO$_2$	PPh$_3$	CH$_3$CN(PF$_6$ salt)
5c	Rh	4-CH$_3$	PPh$_3$	Cl
5d	Ir	4-CH$_3$	PPh$_3$	Cl

(**6a** : L′ = P(OPh)$_3$;
6b : L′ = $\frac{1}{2}$diphos)

Table 4

Microanalytical data

Complex	Analysis (Found (calcd.) (%))		
	C	H	N
3a	63.26 (63.15)	3.83 (3.79)	21.22 (21.04)
4a	51.56 (51.53)	4.39 (4.32)	11.18 (10.93)
4b	48.23 (48.41)	4.04 (4.06)	10.08 (9.73)
5a	63.94 (64.63)	4.26 (4.34)	5.98 (6.03)
5b	58.00 (57.84)	4.17 (4.01)	6.47 (6.48)
5c	67.96 (68.20)	4.68 (4.83)	4.74 (4.68)
5d	61.67 (62.02)	4.40 (4.39)	4.40 (4.26)
6a	56.46 (56.53)	3.48 (4.00)	3.70 (3.88)

observed similar imine chemistry, so that this type of oxidative addition to yield a five membered metallocycle seems to have some generality.

By and large, the NMR spectra of **4**–**6** gave fairly routine data, but there is one point worthy of note. We determined the ^{103}Rh chemical shift using INEPT [14]

Table 5

^{1}H NMR data [a] for selected compounds

Compound	H(2′)	H(4′)	H(5′)	H(6′)	H(7′)	Hydride	Comments
3a	8.89	8.39	7.70	8.24	9.61		
4a	8.71	8.31	7.61	8.27	10.19		
4b	9.53	[b]	7.82	[b]	9.55		CH_3, 2.27
4c	9.27	8.65	8.10	8.56	9.34		
5a	8.30	7.92	[b]	7.78		−12.73	^1J(Rh,H) 16.0 Hz ^2J(P,H) 12.0 Hz
5b	8.22	7.96	[b]	7.80		−13.12	^1J(Rh,H) 18.1 Hz ^2J(P,H) 11.8 Hz
	H(2′, 6′)		H(3′, 5′)		H(7′)		
3b	7.89		7.30		9.56		CH_3, 2.44
5c	7.29		6.72			−12.70	^1J(Rh,H) 14.6 Hz ^2J(P,H) 11.0 Hz CH_3, 2.32
5d	7.32		6.71			−16.46	^2J(P,H) 15.1 Hz CH_3, 2.34
6a						−11.20	^2J(P,H) 21.3 Hz ^2J(P,H) 23.1 Hz CH_3, 2.37
6b						−17.35	^2J(P,H) 19.5 Hz CH_3, 2.36

[a] $CDCl_3$ solutions at room temperature, shifts in ppm, coupling constants in Hz. [b] Not assigned.

Table 6

^{31}P NMR data [a] for the complexes

Complex	^{31}P	^{1}J(Rh,P) (Hz)
4c	28.53	155
5a	31.35	111
5b [b]	34.96	108
5c	32.13	114
5d	4.98	
6a	94.28; J(P,P) 34 Hz 91.55	
6b	18.41; J(P,P) 14 Hz 13.93	

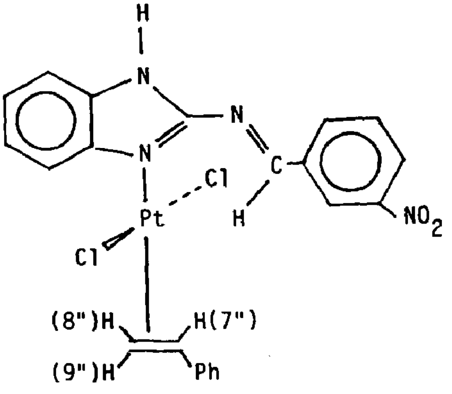
methods for **5a** and its P(4-FC$_6$H$_4$)$_3$ analog, δ 984.3 and 996.7 ppm (rel. to 3.16 MHz), respectively, see Fig. 2; the signals fall ca. 160 ppm to lower field than those for comparable complexes arising from ligand **2** [15]. There are relatively few ^{103}Rh NMR data for hydride complexes [16].

Pt chemistry of ***3a***

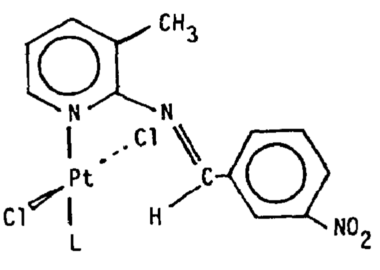
Having shown that **3a** can coordinate via the ring imine nitrogen and that the substituent imine C–H is susceptible to oxidative addition to both Rh and Ir complexes, we return to simple platinum derivatives of type **7** in order to consider possible Pt←H–C bonding.

We first make two interesting negative points: (a) we observe no J(Pt,H) value to the imine proton in **7** (though for **8b** this value is 8 Hz), and (b) the benzimidazole **3a** does not cleave the Cl bridge in the complexes [Pt(μ-Cl)ClL]$_2$ (L = AsEt$_3$, PMe$_2$Ph whereas the pyridine-imine **2** does react to afford the expected *trans*-PtCl$_2$L(**2**) complex.

The second observation contributes to our general knowledge of **3a** and suggests that this ligand is of only relatively modest strength (although both **2** and **3** afford **8** and **7**, respectively, from K[PtCl$_3$(PhCH=CH$_2$)]).



(**7**)



(**8a** : L = PEt$_3$:
8b : L = PhCH=CH$_2$)

The first point is more interesting in connection with our study of weak $M \leftarrow H{-}C$ interactions [1–3] and prompts the question of why there is no coupling in **7**. We suggest that the answer is partly revealed by the molecular structure of **4b**. In contrast to *trans*-$PtCl_2(AsEt_3)$(**2**) (R = mesityl), whose molecular structure reveals a relatively short $Pt \leftarrow H{-}C{=}N$ distance of ca. 2.4 Å [2], in **4b** the distance is much longer. It would seem that the imine substituent of the benzimidazole prefers to remain distant from the metal. A closer look at **2** and **3** (and even **1**) suggests that the imine function of **2** cannot escape the coordination sphere as readily (should it wish to do so) owing to the presence of the 3-CH_3 pyridine substituent; i.e., rapid rotation around C(2)–N(imine) is restricted. In **1**, the bicyclic structure prevents the escape of the CHO-function; however, for **3**, rotation about the exocyclic C(2)–N(imine) bond can relieve steric strain. We sought molecules to test this structure/steric effects hypothesis, and found the complexes **9a**–**9c** to be useful models in this context. In **9a**, J(Pt,H) 10.0 Hz, the presence of the 3-CH_3 substituent prevents the imine C–H from completely escaping from the coordination sphere. Moving the methyl to the 5-position, **9b**, allows the imine function more freedom and the result is a fall in J(Pt,H) to 4.4 Hz. For the more sterically hindered 6-CH_3 complex, **9c**, we observe no coupling constant to the imine proton, and take this to mean that the imine moiety spends even more time remote from the metal. A summary of the pertinent ^1H data is shown in Table 7. We note two further spectroscopic points for **9**: (a) the imine proton chemical shift is responsive to the position of the CH_3 group (our previous studies [1] suggested a high frequency shift to be associated with a weak $C{-}H \rightarrow M$ interaction), and (b) there is a $^4J(Pt,CH_3)$ value of 9.5 Hz to the pyridine methyl in **9c**. There are precedents for such couplings [17].

In summary, our results for this benzimidazole ligand, taken together with those for **9**, help to define geographic criteria for a weak $Pt \leftarrow H{-}C$ interaction, whereas our Rh and Ir chemistry extends the cyclometallation and oxidative addition chemistry of imine functions. It is useful to recognize that a weak $M \leftarrow H{-}C$ interaction is not a necessary ground state condition for cyclometallation.

Experimental

^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker WM-250 MHz spectrometer. The ^{103}Rh INEPT spectrum was recorded on an AM-250 Bruker

<u>trans</u>-$PtCl_2(AsPr^i_3)L$

(**9a** : 3-CH_3;
b : 5-CH_3;
c : 6-CH_3)

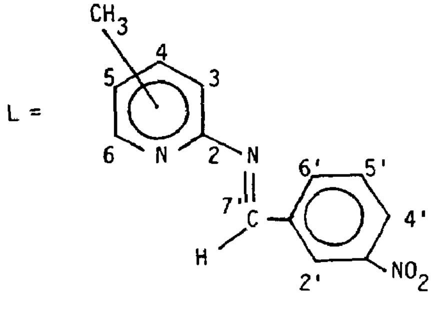


Table 7

^1H NMR data [a] for complexes **9**

Complex	δH(7′)	$\Delta\delta$ [b]	δCH_3	$\Delta\delta$ [b]
9a	9.48 (10.0)	+0.30	2.30	−0.19
9b	9.06 (4.4)	−0.21	2.39	+0.01
9c	8.74	−0.41	3.26 (9.5)	+0.74

[a] $CDCl_3$ solutions at room temperature. Coupling constants to ^{195}Pt in parentheses. [b] $\Delta\delta$ = (δ complex) − (δ ligand).

spectrometer in Fällanden, Switzerland. Microanalyses were performed by the microanalytical laboratory of the ETH Zürich.

Preparation of **3a** A suspension of 2-aminobenzimidazole (6.4 g, 48 mmol) and 3-nitrobenzaldehyde (7.3 g, 48 mmol) in 100 ml toluene was heated under reflux for 20 h with continuous distillation of the water produced. The solid was filtered off and dried in vacuum to afford 12.5 g (98%) of the product.

Preparation of **4a**. $[Rh(\mu\text{-}Cl)(1,5\text{-}COD)]_2$ (500 mg, 1.01 mmol) was treated with **3a** (540 mg, 2.03 mmol) in 20 ml CH_2Cl_2 and the solution stirred for 2 h. The product that separated was filtered off and dried in vacuum to give 1.02 g (98%) of **4a**.

Preparation of **4b**. Complex **4a** (120 mg, 0.230 mmol) in 20 ml acetone was treated with $Ag(CF_3SO_3)$ (60.2 mg, 0.230 mmol). Stirring for 10 min was followed by filtration and injection of 100 μl of 4-picoline (= 4-methylpyridine). Stirring for 1 h was followed by removal of the solvent in vacuum. The resulting material was recrystallized from CH_2Cl_2/hexane to afford 145 mg (87%) of orange crystals, one of which was suitable for X-ray analysis.

Preparation of **4c**. This complex was prepared as described above for **4b**. From **4a** (80 mg, 0.16 mmol), $Ag(CF_3SO_3)$ (41 mg, 0.16 mmol) and $P(4\text{-}FC_6H_4)_3$ (51 mg, 0.16 mmol), 123 mg (81%) of product were obtained.

Preparation of **5a**. $[Rh(\mu\text{-}Cl)(cyclooctene)_2]_2$ (130 mg, 0.18 mmol) in 30 ml THF was treated first with solid **3a** (97 mg, 0.36 mmol) and then with solid PPh_3 (191 mg, 0.73 mmol). The resulting suspension was refluxed for 1 h after which hexane was added to induce precipitation of the product. This was recrystallized from CH_2Cl_2/hexane, 280 mg (84%).

Preparation of **5b**. Complex **5a** (200 mg, 0.22 mmol) was treated with a solution of NH_4PF_6 (160 mg, 0.98 mmol) in 2 ml CH_3CN, and 20 ml methanol then added. Stirring for 2 h was followed by removal of the solvent in vacuum. The residue was dissolved in a minimum of CH_2Cl, the solution filtered, and the product precipitated with hexane. After filtration and drying 195 mg (82%) of product was obtained.

Ligand **3b** was prepared in 98% yield as given for **3a**.

Complex **5c** was prepared in 82% yield as described above for **5a**, as were **5d**, **6a** and **6b**: from $[Ir(\mu\text{-}Cl)(cyclooctene)_2]$ (**10**, 130 mg, 0.15 mmol), **3b** (68 mg, 0.29 mmol) and PPh_3 (152 mg, 0.58 mmol) was obtained 237 mg (83%) of **5d** as yellow crystals. From **10** (90 mg, 0.10 mmol), **3b** (47 mg, 0.20 mmol), and $P(OPh)_3$ (124 mg, 0.40 mmol) was obtained 170 mg (80%) of **6a** as white crystals. From 10 (110 mg, 0.12 mmol), **3b** (58 mg, 0.25 mmol) and $Ph_2PCH_2CH_2PPh_2$ (100 mg, 0.25 mmol) was obtained 180 mg, (84%) of **6b** as white crystals.

The complexes **9** were prepared from 2 equiv. of the appropriate benzylidene methylpyridine and $[Pt(\mu\text{-}Cl)Cl(AsPr^i{}_3)]_2$ [2].

The complexes **7** and **8** were prepared from $K[PtCl_3(PhCH{=}CH_2)]$ and the appropriate ligand. for **7**: ^1H NMR δ (H3) 10.11, δ(H4) 7.12, δ(H5) 7.11, δ(H6) 7.23, δ(H7) 7.23, δ(H2′) 8.59, δ(H4′) 8.40, δ(H5′) 7.61, δ(H6′) 8.10, δ(H7′) 9.99, δ(H7″) 6.85, J(Pt,H) 59 Hz, δ(H8″) 4.99, J(Pt,H) 58 Hz, δ(H9″) 5.48, J(Pt,H) 53 Hz. Found: C, 40.74; H, 2.61; N, 8.64; calcd: C, 41.52; H, 2.85; N, 8.80%. For **8**: ^1H NMR δ(H4) 7.69, δ(H5) 7.22, δ(H6) 8.34, $\delta(CH_3)$ 2.24, δ(H2′) 8.87, δ(H4′) 8.31, δ(H5′) 7.63, δ(H6′) 8.25, δ(H7′) 9.06, J(Pt,H) 8 Hz, δ(H7″) 6.44, J(Pt,H) 62 Hz, δ(H8″) 4.61, J(Pt,H) 62 Hz, δ(H9″) 5.17, J(Pt,H) 58 Hz. Found: C, 41.09; H, 3.12; N, 6.82; calcd: C, 41.26; H, 3.13; N, 6.87%. The styrene protons were assigned based on their geminal and vicinal proton coupling constants.

X-ray structure determination.

Crystals suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2/hexane and are air stable.

A crystal of approximately prismatic shape was mounted on a glass fiber at a random orientation and used for the data collection. A Nonius CAD4 diffractometer was used for the cell constants and space group determination and for the data collection. Cell constant values were obtained by least squares fit of 25 high angle reflections using the CAD4 centering routines. Refined cell parameters, experimental conditions and other crystallographic data are given in Table 1. Data were collected at variable scan speed to obtain a constant statistical precision of the measured intensities. Three standard reflections ($\bar{3}$ 2 7; 2 2 $\bar{6}$; 1 $\bar{3}$ 7) were monitored every hour to check the stability of the crystal and of the experimental conditions; no significant variation or decay was detected. The crystal orientation was checked by measuring three standards (3 2 $\bar{7}$, 2 $\bar{2}$ $\bar{6}$, $\bar{3}$ 3 6) every 200 reflections. Data were corrected for Lorentz and polarization factors; an empirical adsorption correction was applied using azimuthal (ψ) scans of 2 reflections at high χ angles and increasing θ values: 4 $\bar{5}$ 0, $\bar{3}$ 4 0; transmission factors were in the range 0.97–0.99; calculations were performed using the data reduction programs of the CAD4-SDP package [18]. Reduced data were considered as observed if $F_o \geqslant 2.5\sigma(F_o)$ while an $F_o = 0.0$ was given to those reflections having negative net intensities. The structure was solved by a combined use of Patterson and Fourier methods and refined by block-diagonal least squares using anisotropic temperature factors for all atoms. The correction for anomalous dispersion was taken into account [19]; scattering factors were taken from ref. 19. A Cruickshank weighting scheme [20] was used for the refinement; the function minimized being $[\Sigma w(F_o - 1/kF_c)]^2$. Final atomic coordinates are listed in Table 2. An extended list of bond lengths and angles, a list of thermal parameters and a table of F_o/F_c may be obtained from the authors.

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