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Cyclometallated compounds

VII*. X-Ray crystal structure of the product of cyclometallation of 1-phenylpyrazole with rhodium trichloride

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Abstract

The product of cyclometallation of 1-phenylpyrazole with rhodium trichloride is identified as *rac*-di(μ-chloro)tetrakis[2-(pyrazol-1-yl)phenyl-C^1,$N^{2'}$]dirhodium by an X-ray crystal structure of its 2-methoxyethanol solvate. The complex is the racemic isomer with *trans*-pyrazole and *cis*-phenyl groups.

Introduction

The synthesis and study of cyclometallated compounds which incorporate an internal nitrogen donor have been the focus of much attention during the last two decades [1]. Particular emphasis has been placed on the study of square-planar cyclopalladated compounds because of their importance in organic synthesis [2]. More recently the spectroscopic and physicochemical properties of octahedral cyclometallated complexes of ruthenium(II), rhodium(III) and iridium(III) have been investigated [3–5]. For example, in connection with the considerable current interest in the photophysics of tris(2,2′-bipyridine)ruthenium(II) [6], analogues have been synthesised in which the bipyridine ligands are replaced by cyclometallated 2-phenylpyridine ligands and detailed NMR studies of these complexes have been reported [7,8]. As part of a study of the properties of ruthenium(II) complexes of chelating biheteroaromatic ligands [9], we have reported the synthesis and study of ruthenium(II) complexes of heteroaromatic pyrazoles, such as **1** [10]. 1-Phenylpyrazole (**2**) is a carbocyclic analogue of **1** in which the pyridine ring is replaced by a

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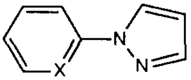
[*] For Part VI see ref. 12e.

phenyl ring and which is also capable of undergoing cyclometallation reactions. Indeed cyclometallated complexes of **2** with Pd^{II}, Pt^{II}, Rh^{III}, Ir^{III} and Ru^{II} have been reported [11].



(1) X = N
(2) X = CH

In continuation of our structural and NMR studies of cyclometallated compounds [11g,12] we are currently studying the NMR spectra of mononuclear octahedral rhodium(III) β-diketonate complexes containing various cyclometallated nitrogen heterocycles. Such compounds are obtained by ligand exchange from the binuclear di-μ-chloro complexes obtained by reaction of the nitrogen heterocycle with rhodium trichloride. Several geometrical isomers are possible for these compounds and it was necessary to unambiguously confirm the structure of one such complex. Thus we herein describe an X-ray crystal structure determination of the chloro-bridged dinuclear complex obtained from a cyclometallation reaction of 1-phenylpyrazole with rhodium(III) chloride.

Results and discussion

Reaction of 1-phenylpyrazole (**2**) with rhodium(III) chloride in 2-methoxyethanol gave a chloro-bridged dimer of formula $[RhL_2Cl]_2$, as previously reported [11c]. Both the ^1H and ^{13}C NMR spectra of this complex indicate that all four cyclometallated phenylpyrazole ligands are symmetrically equivalent, thereby eliminating eight of the twelve possible isomers. From the four remaining isomers with D_2 or C_{2h} symmetry a considerable body of evidence suggests that the rhodium atoms will be substituted with *trans*-nitrogens (pyrazoles) and *cis*-carbons (phenyls). For a number of related octahedral cyclometallated compounds this has been shown to be the case by NMR chemical shift arguments [3,11c,13], NOE experiments [14], infrared spectroscopy [15] and X-ray crystallography [16,17]. However, two recent crystallographic studies have shown that this is not always so. In particular an X-ray structure [18] of a ruthenium(II) complex containing cyclometallated benzo[*h*]-quinoline ligands showed the ruthenium atom to have *trans*-carbon and *cis*-nitrogen substituents, while an X-ray structure [19] of a rhodium(III) complex containing cyclometallated nitrobenzene ligands showed the complex to have an unsymmetrical configuration with both the carbon and oxygen donors mutually *cis*.

Although the NMR spectra for the rhodium complex from 1-phenylpyrazole suggest a configuration with *trans*-nitrogens, NMR does not distinguish between the racemic diastereoisomer **3** (D_2 symmetry) and the *meso* diastereoisomer **4** (C_{2h} symmetry). The previous report [11c] of this complex did not discuss the possibility of this type of isomerism although the same authors [13a] represented the related iridium(III) complex of benzo[*h*]quinoline as the *meso*-isomer. More recently, however, it has been suggested [3] that steric factors should favour formation of the racemic isomer.

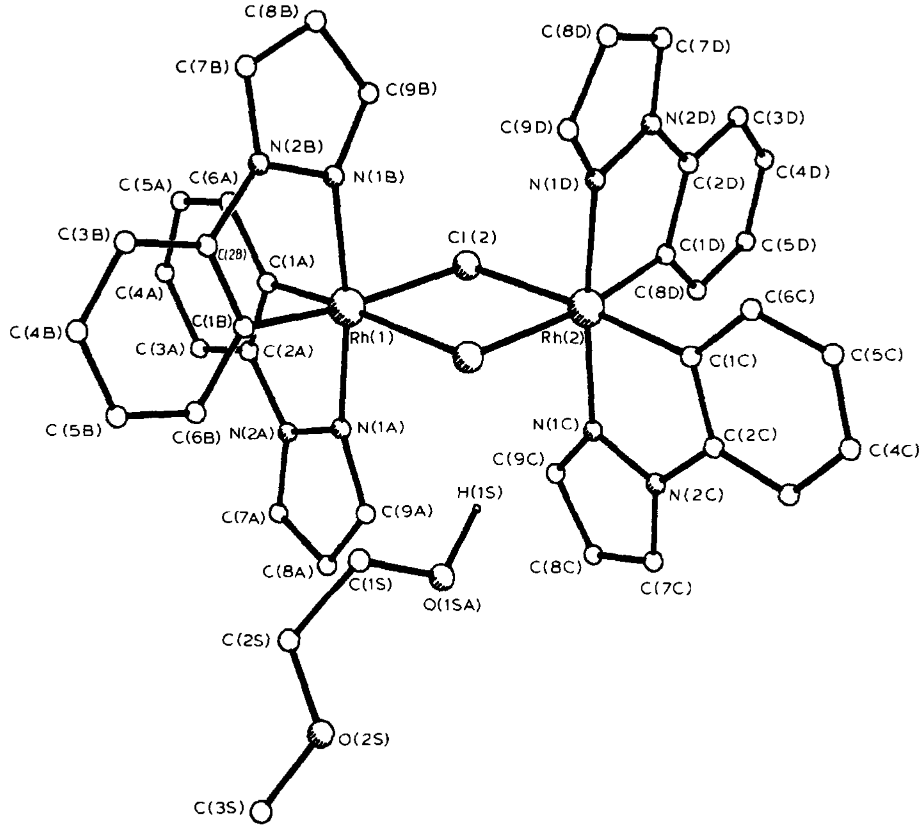
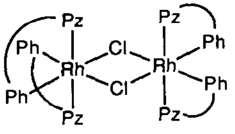
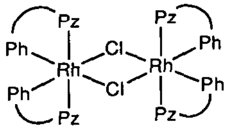


Fig. 1. Perspective view and atom labelling of the X-ray structure of 3.



(3)



(4)

In order to determine the exact structure of the isomer produced in this reaction a single crystal X-ray structure determination was carried out. Figure 1 shows a perspective view of the contents of the asymmetric unit which contains one molecule of the dimer and a molecule of 2-methoxyethanol. Bond lengths and angles are listed in Tables 1 and 2 respectively. The structure of the complex is thus determined to be the racemic stereoisomer with *trans*-pyrazoles at both rhodium centres. The preferential formation of the racemic isomer can undoubtedly be attributed to steric factors since molecular models indicate that the meso isomer would have strong steric interactions between the mirror related pyrazole C3-H's.

The potential D_2 symmetry of the complex is destroyed in the solid state by the presence of the 2-methoxyethanol molecule which is hydrogen bonded to one of the bridging chlorine atoms (Cl(1) $\cdots$ O(1S) 3.180(4), Cl(1) $\cdots$ H(1S) 2.19(3) Å). This results in a lengthening of the Rh–Cl(1) bonds relative to the Rh–Cl(2) bonds. No

Table 1

Bond lengths [a] (Å) for **3**

Rh(1)–Cl(1)	2.548(2)			
Rh(2)–Cl(1)	2.522(2)			
Rh(1)–Cl(2)	2.507(2)			
Rh(2)–Cl(2)	2.514(2)			
Rh–N(1)	1.995(7)	2.018(6)	2.031(7)	2.021(7)
Rh–C(1)	1.981(9)	1.974(10)	1.991(8)	1.974(10)
N(1)–N(2)	1.379(10)	1.361(10)	1.345(10)	1.349(11)
N(1)–C(9)	1.342(11)	1.326(12)	1.325(11)	1.323(11)
N(2)–C(2)	1.460(12)	1.407(12)	1.411(11)	1.412(12)
N(2)–C(7)	1.344(12)	1.351(11)	1.381(11)	1.349(12)
C(1)–C(2)	1.363(12)	1.394(11)	1.399(11)	1.437(13)
C(1)–C(6)	1.418(13)	1.416(14)	1.401(11)	1.371(12)
C(2)–C(3)	1.389(13)	1.384(13)	1.376(13)	1.372(15)
C(3)–C(4)	1.387(16)	1.397(15)	1.375(13)	1.398(16)
C(4)–C(5)	1.390(15)	1.390(13)	1.383(13)	1.339(15)
C(5)–C(6)	1.371(13)	1.384(13)	1.393(12)	1.418(15)
C(7)–C(8)	1.364(15)	1.347(15)	1.326(15)	1.386(16)
C(8)–C(9)	1.381(12)	1.394(12)	1.416(13)	1.405(15)
O(1S)–C(1S)	1.410(13)			
O(2S)–C(3S)	1.454(15)			
O(2S)–C(2S)	1.402(13)			
C(1S)–C(2S)	1.522(16)			

[a] Four values refer to atoms labelled A–D respectively.

other unusually short intermolecular contacts exist. The geometry at the rhodium atoms and the Rh–N and Rh–C bond lengths are similar to those found in related structures [16–20]. The rhodium–rhodium internuclear distance is 3.741(1) Å, which is comparable with values reported for other di-μ-chlorodirhodium(III) complexes [17]. Each of the eight aromatic rings is planar (r.m.s. deviation 0.006 Å) and within each ligand the phenyl and pyrazole rings are approximately coplanar (mean torsional angle between the meanplanes 5.4°). There is generally good agreement between equivalent bonding geometry within the different parts of the complex. The geometry of the pyrazole rings is normal [21].

Experimental

^1H and ^{13}C NMR spectra were recorded with a Varian XL300 spectrometer for $CDCl_3$ solutions with Me_4Si as internal standard. Definitive assignments of NMR spectra were made by a combination of one- and two-dimensional techniques using methods described in ref. 12b.

Cyclometallation of 1-phenylpyrazole with $RhCl_3$

Reaction of 1-phenylpyrazole with rhodium trichloride in refluxing 2-methoxyethanol was carried out as previously described [11c]. The reaction mixture deposited a light brown powder followed by X-ray quality crystals of the dirhodium complex as a methoxyethanol solvate. Recrystallisation from ethanol/dichloromethane gave *rac*-di(μ-chloro)tetrakis[2-(pyrazol-1-yl)phenyl-$C^1,N^{2'}$]dirhodium as

Table 2

Bond angles [a] (°) for **3**

Cl-Rh(1)-Cl	84.1(1)			
Rh-Cl(1)-Rh	95.1(1)			
Cl-Rh(2)-Cl	84.5(1)			
Rh-Cl(2)-Rh	96.3(1)			
Cl(1)-Rh-N(1)	91.9(2)	94.9(3)	92.9(2)	91.6(2)
Cl(2)-Rh-N(1)	92.7(2)	93.2(2)	92.6(2)	93.2(2)
Cl(1)-Rh-C(1)	172.3(2)	97.5(3)	98.5(3)	171.8(2)
Cl(2)-Rh-C(1)	91.9(3)	173.7(3)	172.3(2)	92.3(2)
N(1)-Rh-C(1)	81.7(3)	80.6(3)	80.1(3)	81.1(3)
N(1)-Rh-N(1)	171.4(3)		173.0(3)	
C(1)-Rh-N(1)	92.0(3)		93.9(3)	
N(1)-Rh-C(1)	93.3(3)		94.7(3)	
C(1)-Rh-C(1)	87.2(4)		85.7(4)	
Rh-N(1)-N(2)	113.7(5)	113.0(5)	113.6(5)	114.5(5)
Rh-N(1)-C(9)	141.2(6)	139.1(6)	138.3(6)	138.3(7)
N(2)-N(1)-C(9)	104.5(7)	107.2(6)	108.1(7)	106.7(7)
N(1)-N(2)-C(2)	115.2(7)	117.3(7)	117.7(7)	116.3(7)
N(1)-N(2)-C(7)	111.7(8)	109.1(7)	108.7(7)	111.0(8)
C(2)-N(2)-C(7)	132.8(8)	133.4(8)	133.5(8)	132.6(9)
Rh-C(1)-C(2)	115.6(7)	115.5(7)	115.3(6)	114.2(6)
Rh-C(1)-C(6)	127.7(6)	128.8(6)	128.2(6)	129.2(7)
C(2)-C(1)-C(6)	116.7(8)	115.6(9)	116.4(7)	116.5(9)
N(2)-C(2)-C(1)	113.9(8)	113.2(8)	113.1(7)	113.8(8)
N(2)-C(2)-C(3)	120.4(8)	122.1(8)	123.5(8)	123.5(9)
C(1)-C(2)-C(3)	125.7(9)	124.7(9)	123.3(8)	122.7(9)
C(2)-C(3)-C(4)	116.4(9)	118.1(8)	118.2(8)	118.1(9)
C(3)-C(4)-C(5)	119.8(10)	119.2(9)	121.5(8)	120.9(10)
C(4)-C(5)-C(6)	122.5(9)	121.6(9)	119.2(8)	121.2(10)
C(1)-C(6)-C(5)	119.0(8)	120.6(8)	121.3(8)	120.5(9)
N(2)-C(7)-C(8)	106.1(8)	108.1(8)	108.2(9)	107.0(10)
C(7)-C(8)-C(9)	107.4(8)	106.4(9)	106.5(8)	104.9(8)
N(1)-C(9)-C(8)	110.2(8)	109.1(9)	108.5(8)	110.4(9)
C(2S)-O(2S)-C(3S)	109.6(8)			
O(2S)-C(2S)-C(1S)	108.2(8)			
O(1S)-C(1S)-C(2S)	108.5(8)			

[a] Four values refer to atoms labelled A–D respectively.

a solvent-free powder. ^1H NMR* ($CDCl_3$) δ (ppm) 6.01 (d, H6), 6.54 (t, H4′) 6.60 (d, H5), 6.84 (t, H4), 7.12 (d, H3), 7.88 (d, H3′), 8.16 (d, H5′). ^{13}C NMR ($CDCl_3$) δ (ppm) 106.65 (C4′) 110.90 (C3), 122.45 (C4), 125.07 and 125.19 (C5 and C5′), 133.45 (C6), 140.87 (C3′).

Crystallography

Table 3 lists crystal data and X-ray experimental details for **3**. Intensity data were collected with a Nicolet R3m four-circle diffractometer by using monochromatized Mo-K_α radiation. Cell parameters were determined by least-squares refinement, the setting angles of 18 accurately centred reflections ($2\theta > 25°$) being used. Throughout

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* The assignments for H3′ and H5′ are reversed from those previously reported [11c].

Table 3

Crystal data and X-ray experimental details for **3**

Formula	$C_{36}H_{28}Cl_2N_8Rh_2 \cdot C_3H_8O_2$
Formula weight	925.5
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	22.876(7)
b (Å)	10.787(3)
c (Å)	15.105(5)
β (°)	98.12
V (Å^3)	3690(2)
D_c (g cm^{-3})	1.67
Z	4
$F(000)$	1864
μ (cm^{-1})	10.7
Radiation	Mo-K_α
Wavelength (Å)	0.71069
Temperature (°C)	−120
Crystal dimensions (mm)	0.54×0.33×0.04
Scan mode	ω
2θ range (°)	3–48
Unique reflections	5475
Observed reflections ($I > 3\sigma(I)$)	2543
Number of parameters	478
R	0.042
wR	0.043

data collection the intensities of three standard reflections (900, 151, 006) were monitored at regular intervals and this indicated no significant crystal decomposition. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by conventional Patterson and Fourier methods, and refined on $|F|$ by blocked cascade least-squares procedures. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with isotropic thermal parameters equal to those of their carrier carbons (C–H 0.96 Å) except for the OH-hydrogen which was located from a difference Fourier synthesis. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = [\sigma^2(F_o) + 0.0002F_o^2]^{-1}$. All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL [22].

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

Table 4

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for **3**

Atom	x	y	z	U_{eq} [a]
Rh(1)	2109(1)	5827(1)	−101(1)	17(1)
Rh(2)	3449(1)	4957(1)	1493(1)	16(1)
Cl(1)	2426(1)	5772(2)	1585(1)	22(1)
Cl(2)	3120(1)	4973(2)	−167(1)	22(1)
N(1A)	1750(3)	4142(6)	−94(5)	24(2)
N(2A)	1523(4)	3714(6)	−933(5)	27(2)
C(1A)	1881(5)	5626(8)	−1408(6)	30(3)
C(2A)	1609(5)	4536(8)	−1672(6)	29(3)
C(3A)	1411(5)	4192(9)	−2550(7)	35(3)
C(4A)	1495(6)	5048(10)	−3206(8)	52(4)
C(5A)	1775(6)	6166(8)	−2966(7)	34(4)
C(6A)	1961(5)	6483(7)	−2093(6)	26(3)
C(7A)	1221(5)	2653(7)	−890(7)	33(4)
C(8A)	1263(5)	2363(7)	−4(7)	25(3)
C(9A)	1585(4)	3291(7)	469(6)	23(3)
N(1B)	2367(3)	7595(6)	−248(5)	21(2)
N(2B)	1909(3)	8412(6)	−352(5)	23(2)
C(1B)	1345(4)	6676(7)	−90(6)	27(3)
C(2B)	1346(4)	7946(7)	−262(6)	24(3)
C(3B)	854(4)	8703(8)	−319(6)	29(3)
C(4B)	316(5)	8165(9)	−194(7)	36(3)
C(5B)	298(4)	6908(8)	4(7)	29(3)
C(6B)	791(4)	6160(7)	19(6)	25(3)
C(7B)	2105(4)	9528(7)	−589(6)	26(3)
C(8B)	2692(5)	9441(8)	−603(7)	37(4)
C(9B)	2846(4)	8215(7)	−392(6)	24(3)
N(1C)	3198(3)	3166(6)	1612(5)	20(2)
N(2C)	3305(4)	2730(6)	2453(5)	25(2)
C(1C)	3712(4)	4697(7)	2793(5)	21(3)
C(2C)	3594(4)	3522(7)	3118(6)	23(3)
C(3C)	3759(5)	3166(8)	3992(7)	33(3)
C(4C)	4055(4)	4008(8)	4575(6)	28(3)
C(5C)	4195(4)	5179(8)	4295(6)	32(3)
C(6C)	4020(4)	5520(7)	3408(6)	25(3)
C(7C)	3121(5)	1511(8)	2454(8)	34(4)
C(8C)	2918(5)	1191(7)	1620(7)	34(4)
C(9C)	2961(4)	2260(7)	1088(6)	26(3)
N(1D)	3781(4)	6694(6)	1496(5)	27(2)
N(2D)	4362(3)	6750(6)	1429(5)	24(2)
C(1D)	4267(4)	4548(7)	1340(5)	22(3)
C(2D)	4645(4)	5609(9)	1314(6)	29(3)
C(3D)	5222(4)	5514(10)	1170(7)	35(3)
C(4D)	5444(5)	4335(11)	1026(7)	43(4)
C(5D)	5108(5)	3322(9)	1057(7)	38(4)
C(6D)	4512(4)	3415(8)	1208(6)	28(3)
C(7D)	4563(5)	7925(9)	1523(7)	37(3)
C(8D)	4087(5)	8665(8)	1650(7)	39(4)
C(9D)	3611(5)	7839(8)	1644(6)	28(3)
O(1S)	1488(3)	655(6)	−2427(5)	44(3)
O(2S)	298(3)	1012(7)	−2166(5)	39(2)
C(1S)	1045(5)	−246(9)	−2641(7)	41(4)
C(2S)	459(5)	413(9)	−2919(7)	39(4)
C(3S)	−228(6)	1755(11)	−2427(10)	59(5)

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

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