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CHELATING *C*-METALLATION OF *N*-PHENYLPYRAZOLE WITH RHODIUM(III) AND IRIDIUM(III)

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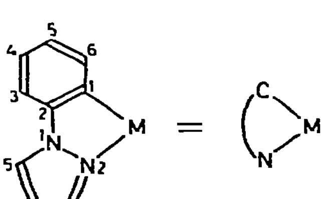
Summary

Chelating *C*-metallation of *N*-phenylpyrazole($C_6H_5C_3N_2H_3$) occurs with Rh^{III} and Ir^{III} to yield $MX(C_6H_4C_3N_2H_3)_2$(M = Rh, X = Cl, Br; M = Ir, X = Cl), where it is coordinated through pyrazolyl 2-N and phenyl 1-C atoms to form a five-membered metallocycle. These complexes react with tri-n-butylphosphine (PBu_3) to give the adduct $MX(C_6H_4C_3N_2H_3)_2(PBu_3)$, which has an octahedral structure with *trans*-N,N, *cis*-C,C, and *cis*-X,PBu_3 donor sets. The ionic ethylenediamine complex $Rh(C_6H_4C_3N_2H_3)_2$(en)Cl is also prepared.

Introduction

Pyrazole and its derivatives are known to form coordination compounds with various Lewis acids [1]. Among its derivatives, *N*-phenylpyrazole is unique in that the phenyl group is metallated by palladium(II) to yield the five-membered metallocycle (I) [2]. Reactions of *N*-phenylpyrazole (abbreviated as N—CH) with other metal ions are, therefore, of interest and preparation of analogous



(I)

rhodium(III) and iridium(III) complexes has been attempted. The successful results are described below as a part of our continuing studies of chelating *C*-metallation [3]. For comparison, the rhodium(III) complex of 3,5-dimethyl-1-phenylpyrazole (N'—CH) was also prepared.

Results and discussion

The analytical data and melting points for the complexes prepared are given in Table 1. The infrared spectrum of free *N*-phenylpyrazole shows characteristic bands at 688 and 752 cm^{-1} due to deformation modes of five adjacent aromatic ring H atoms [5] and upon complexation these bands disappear. For the three complexes, $RhCl(N—C)_2$, $RhBr(N—C)_2$ and $IrCl(N—C)_2$, a new strong band at ca. 741 cm^{-1} accompanying several weak peaks appeared instead. The spectral features are very similar to those of $[PdCl(N—C)]_2$ which contains the metallocycle (I) [2]. The strong band at 230 cm^{-1} of $RhCl(N—C)_2$ which disappears on replacement of Cl with Br, is assignable [5] to ν(Rh—Cl). The corresponding band was found at 247 cm^{-1} for $IrCl(N—C)_2$. The band at 222 cm^{-1} of $RhCl(N'—C)_2$ may be due to ν(Rh—Cl).

The PMR spectra (Table 2) of $RhCl(N—C)_2$, $RhBr(N—C)_2$, and $IrCl(N—C)_2$ in CD_2Cl_2 are very similar to one another which indicates that they have similar structures. Integration of the signals showed that one proton had been lost from the ligand. From the above spectroscopic data, the reaction of *N*-phenylpyrazole with Rh^{III} and Ir^{III} appears to yield compounds containing the metallocycle (I).

The PMR spectrum of $RhCl(N—C)_2$ shows two doublets at δ 8.29 (*J* ca. 3 Hz) and 7.92 (*J* ca. 2 Hz) which are assigned to the pyrazolyl ring 3-H and 5-H, respectively [2], since these two signals are absent in that of $RhCl(N'—C)_2$. In the spectra of mono-chelate complexes such as Pd(N—C)(acac) [2], PdCl(N—C)(PBu_3) [6], and $RhCl_2(N—C)(PBu_3)_2$ [6], there is no signal at a higher field than 6.4 ppm. On the other hand, the spectrum of the bis-chelate complex $RhCl(N—C)_2$ shows a doublet of apparent triplets at 6.04 ppm (*J* 7.5 and ca.

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES
(N—CH = *N*-phenylpyrazole; N'—CH = 3,5-dimethyl-1-phenylpyrazole)

Complex	M.p. (°C)	Analysis: Found (calcd.) (%)			
		C	H	N	Other
$RhCl(N—C)_2$ [a]	315(dec.)	50.63 (50.91)	3.25 (3.32)	13.20 (13.19)	Cl: 8.37 (8.35)
$RhBr(N—C)_2$	315(dec.)	46.28 (46.48)	3.02 (3.24)	12.10 (12.38)	
$IrCl(N—C)_2$	340(dec.)	41.91 (42.06)	2.77 (2.75)	10.93 (10.90)	Cl: 7.73 (6.90)
$RhCl(N'—C)_2$ [a]	295(dec.)	54.62 (54.96)	4.64 (5.03)	11.63 (11.65)	
$RhCl(N—C)_2(PBu_3)$	186-191	57.15 (57.47)	6.76 (6.59)	8.85 (8.94)	P: 4.13 (4.94)
$RhBr(N—C)_2(PBu_3)$	310(dec.)	53.56 (53.66)	6.10 (6.15)	8.30 (8.34)	
$IrCl(N—C)_2(PBu_3)$	224-226	50.04 (50.30)	5.50 (5.77)	7.86 (7.82)	
$Rh(N—C)_2(en)Cl$	325(dec.)	49.68 (49.55)	4.59 (4.57)	17.49 (17.34)	Cl: 7.67 (7.31)

[a] Dried at 110°C under reduced pressure.

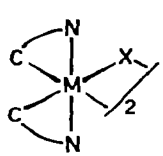
TABLE 2

PMR SPECTRA OF THE COMPLEXES
(δ ppm from TMS)

Complex	Solvent	MHz	Pyrazolyl ring		Phenyl ring	
			3-H	5-H	3-H	6-H
$RhCl(N—C)_2$	CD_2Cl_2	100	8.29d[a]	7.92d	7.25d	6.01dt
$RhBr(N—C)_2$	CD_2Cl_2	60	8.22d	8.05d	7.21dd	5.98dt
$IrCl(N—C)_2$	CD_2Cl_2	100	8.22d	7.87d	7.21d	5.99d
$IrCl(N—C)_2$	DMSO-d_6	60	8.93d	8.48d	7.66dd	6.21dd
			8.79d	8.13d	7.54dd	5.84dd
$RhCl(N'—C)_2$	$CDCl_3$	60	—	—	7.26dd	6.24dt
$RhCl(N—C)_2(PBu_3)$	$CDCl_3$	100	8.44d	8.15d	7.17m	6.19d
			8.19d	7.88d		6.06t
$RhBr(N—C)_2(PBu_3)$	$CDCl_3$	60	8.45d	7.99d	*b*	6.09d
			8.02d	7.70d		5.94t
$IrCl(N—C)_2(PBu_3)$	$CDCl_3$	100	8.38d	7.91d	7.18m	6.29d
			8.13d	8.08d		6.07t
$Rh(N—C)_2(en)Cl$	DMSO-d_6	60	8.92d	8.29d	7.58d	6.06d

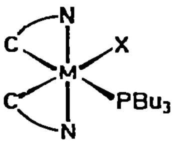
[a] d, doublet; t, triplet; m, multiplet; dd, doublet of doublets; and dt, doublet of triplets. [b] Because of its low solubility, the signal was obscured by that of impurity $CHCl_3$ in $CDCl_3$.

1.5 Hz) and this is assigned to the phenyl ring 6-H. The appearance of the 6-H resonance at such a high field is considered to result from shielding due to the ring current [7] of a pyrazolyl part of the other ligand on the same rhodium atom. A similar argument has been made for the related rhodium(III) and iridium(III) complexes of benzo[*h*]quinoline [3,8]. The structure where the phenyl ring 6-H is above the pyrazolyl ring of the other ligand is thus proposed (II). The molecular weight in CH_2Cl_2 was found to be 855 (calcd. for $[RhCl(N—C)_2]_2$, 849) to show the complex to be dimeric.

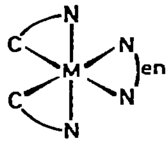


(II)

The complexes $MX(N—C)_2$ reacted with PBu_3 to form $MX(N—C)_2(PBu_3)$. The PMR spectra shows that the two N—C moieties are no longer equivalent (Table 2). The signals due to the pyrazolyl ring 3-H and 5-H of $IrCl(N—C)_2(PBu_3)$ split, respectively, into two and that of the phenyl ring 6-H also into two; one signal observed at 6.29 ppm is a broad doublet (*J* ca. 7 Hz) and the other at 6.07 ppm a broad triplet (*J* ca. 6 Hz). The triplet seems to result from additional coupling [9], *J*(P—H), of the proton with ^{31}P of PBu_3 coordinated at the *trans* position of the metallated C atom *ortho* to the proton. The *trans* position of the other metallated C atom is occupied by Cl and the original doublet does not split further. The spectrum of $IrCl(N—C)_2$ in DMSO-d_6, which may be the spectrum of $IrCl(N—C)_2$(DMSO-d_6), shows two doublets of doublets due to phenyl ring 6-H (*J* 7.5 and 1.7 Hz for both the two). It is, therefore, clear that *J*(P—H) is operative in the spectrum of the PBu_3 complex. $RhX(N—C)_2(PBu_3)$ (X = Cl, Br) show spectra very similar to that of the iridium analogue. Thus the three should have a similar structure (III).



(III)



(IV)

The broad strong band at 206 cm^{-1} of $RhCl(N—C)_2(PBu_3)$ disappears upon replacement of Cl with Br and may be assigned to ν(Rh—Cl). The corresponding band was found at 242 cm^{-1} for $IrCl(N—C)_2(PBu_3)$. The structure III is also borne out.

Ethylenediamine (en) reacted with $RhCl(N—C)_2$ to yield the ionic complex $Rh(N—C)_2(en)Cl$ with Λ_M = 90.6 ohm^{-1} cm^2 mol^{-1} (in a 10^{-3} *M* aqueous solution at 25°C). In the infrared spectrum no band assignable to ν(Rh—Cl) appeared. The PMR spectrum (Table 2) shows that the two N—C moieties are equivalent. Thus structure IV seems to be most probable [10].

Experimental

Instrumentation

PMR spectra were measured with a JEOL C-60H spectrometer at 60 MHz or with a JEOL JNM-MH-100 at 100 MHz using TMS as an internal reference. Infrared spectra were recorded on JASCO DS-402G and Hitachi EPI-L infrared spectrophotometers by the mull method.

Preparation

$RhCl(N—C)_2$. A mixture of 4 mmol (1.05 g) of rhodium(III) chloride hydrate and 12 mmol (1.73 g) of *N*-phenylpyrazole in 50 ml of 2-methoxyethanol was refluxed for 16 h. The resulting light brown powder was recrystallized from dichloromethane—ethanol to give dull white fine crystals. The product was dried at 110°C under vacuum to give 0.61 g (36%).

The three complexes, $RhBr(N—C)_2$, $IrCl(N—C)_2$, and $RhCl(N'—C)_2$ were prepared in a similar way: the bromide was prepared in the presence of excess lithium bromide, the iridium complex from sodium hexachloroiridate(III), and the last one by using 3,5-dimethyl-1-phenylpyrazole.

$RhCl(N—C)_2(PBu_3)$. To a dichloromethane solution (20 ml) of 1 mmol (0.42 g) of $RhCl(N—C)_2$ was added 1 mmol (0.20 g) of PBu_3. To the mixture was added 30 ml of methanol and the solution was concentrated to a small volume to crystallize the white product. The yield was 0.47 g (75%).

Metathesis of $RhCl(N—C)_2(PBu_3)$ with lithium bromide in acetone—dichloromethane yielded $RhBr(N—C)_2(PBu_3)$. In a similar way as above, $IrCl(N—C)_2(PBu_3)$ was also prepared.

$Rh(N—C)_2(en)Cl$. One mmol (0.06 g) of ethylenediamine was added to a suspension of 1 mmol (0.42 g) of $RhCl(N—C)_2$ in methanol and the mixture was heated until it had become clear. On concentration of the solution the product was obtained in 80% yield (0.39 g).

References

1 S. Trofimenko, Chem, Rev., 72 (1972) 497.
2 S. Trofimenko, Inorg. Chem., 12 (1973) 1215.
3 M. Nonoyama, Bull. Chem. Soc. Japan, 47 (1974) 767; M. Nonoyama and K. Yamasaki, Inorg. Nucl. Chem. Lett., 7 (1971) 943; M. Nonoyama, J. Organometal. Chem., 74 (1974) 115.
4 L.J. Bellamy, The Infrared Spectra of Complex Molecules, 2nd ed., Methuen, New York, 1966, p. 75.
5 H. Onoue and I. Moritani, J. Organometal. Chem., 44 (1972) 189.
6 M. Nonoyama, unpublished results.
7 L.M. Jackman and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd ed., Pergamon, Oxford 1969, p. 94.
8 M.I. Bruce, B.L. Goodall and F.G.A. Stone, J. Organometal. Chem., 60 (1973) 343.
9 M. Nonoyama amd K. Yamasaki, Nippon Kagaku Zasshi, 91 (1970) 1058; Chem. Abstr., 74 (1971) 68397; M. Nonoyama, K. Suzuki and K. Yamasaki, Proc. Japan Acad., 45 (1969) 605.
10 R.J. Hoare and O.S. Mills, J. Chem. Soc. Dalton (1972) 2138, 2141.