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SYNTHESIS OF SEVERAL BIS(BENZO[*h*]QUINOLIN-10-YL-*N*)RHODIUM(III) COMPLEXES

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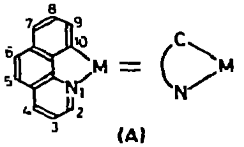
Summary

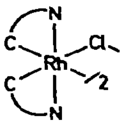
Several new complexes of general forms, [Rh(bhq)$_2$LX](bhq = benzo[*h*]quinolin-10-yl-*N*; X = Cl, Br, L = tri-n-butylphosphine, dimethyl sulfoxide, pyridine, 4-methylpyridine, methylamine), [Rh(bhq)$_2$(L—L)]Cl (L—L = ethylenediamine, *S*-methylcysteamine, 2-picolylamine, 2,2′-bipyridyl, 1,2-bis(diphenylphosphino) ethane), and [Rh(bhq)$_2$L′](L′ = methylmercaptide, acetate ion) were prepared by reactions of [Rh(bhq)$_2$Cl]$_2$ · 1/4CHCl$_3$ with monodentate and bidentate ligands, and were characterized by means of conductivities, and PMR and IR spectra.

Introduction

In a preliminary communication of this study [1], it was reported that the reaction of benzo[*h*]quinoline (abbreviated as Hbhq) with rhodium(III) chloride hydrate in boiling ethanol yielded complex [Rh(bhq)$_2$Cl]$_2$ · 1/4CHCl$_3$ (B, type I), containing the metallacyclic group A, and that this complex reacted with tri-n-butylphosphine (PBu$_3$) and dimethyl sulfide (SMe$_2$) to form the complexes [Rh(bhq)$_2$LCl] (C, L = PBu$_3$, SMe$_2$). A similar reaction of iridium(III) was recently described [2]. We report here that I reacts with a variety of monodentate (L) and bidentate (L—L) ligands to give complexes of types C and D.



(A)



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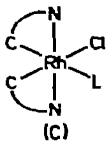

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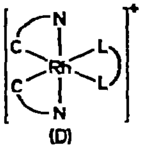

(D)

Results and discussion

Complex I, $[Rh(bhq)_2Cl]_2 \cdot 1/4CHCl_3$, reacted readily with various monodentate ligands (L) to yield complexes of type II, $[Rh(bhq)_2LX]$, where L is PBu_3, SMe_2, pyridine (py), 4-methylpyridine (γ-pic), and dimethyl sulfoxide (dmso), and with bidentate ligands (L—L) to form complexes of type III $[Rh(bhq)_2(L—L)]Cl$, where L—L is ethylenediamine (en), *S*-methylcysteamine (mcy), 2-picolylamine (pa), 2,2′-bipyridyl (bipy) and 1,2-bis(diphenylphosphino)ethane (diphos). Complexes of another type IV, $[Rh(bhq)_2L']$, were obtained for L′ = methylmercaptide (SMe) and acetate (OAc) ion (Table 1). These were characterized by elemental analyses, conductivities, and spectroscopy. The possibility of optical isomers was not taken into account.

Characteristic bands of the metallated bhq moiety (A) in the infrared spectra were reported recently [3] and the features of spectra of the complexes prepared in this study are consistent with those reported. Therefore, in this paper, they are not considered. The presence of normally coordinated ligands (L,L′, L—L) are confirmed by infrared spectra and a few are discussed below.

Type II complexes. The two complexes $[Rh(bhq)_2(PBu_3)X]$ (X = Cl, Br) have a nearly identical PMR spectral pattern (Table 2) and that of the chloro complex was shown in the figure of ref. 1. Among the remaining complexes of type II, only $[Rh(bhq)_2(\gamma\text{-pic})Cl]$ is soluble in a suitable solvent for PMR spectroscopy. In contrast to the PBu_3 complexes, which showed signals due to two non-equivalent 9-H protons as a doublet and a triplet [1], this γ-pic complex showed two doublets due to 9-H protons. The assignment that the triplet of the PBu_3 complexes results from coupling between P and 9-H atoms [1] is thus confirmed. One of the two non-equivalent 2-H protons of $[Rh(bhq)_2(\gamma\text{-pic})Cl]$ resonated at a much higher field than the corresponding proton of the PBu_3 complexes (Table 2). This higher field resonance may be caused by shielding due to the ring-current of 4-methylpyridine, since one 2-H is located in the shielding region of 4-methylpyridine, the aromatic ring of which is reasonably assumed to be far from perpendicular to the plane defined by Rh, Cl, and two metallated C atoms because of steric requirements. On the other hand, the other 2-H is directed toward a Cl atom and not shielded in this manner.

A very strong band was found at 222 cm^{-1} for $[Rh(bhq)_2(PBu_3)Cl]$, which was absent in the bromo analog, and is assigned to $\nu(Rh—Cl)$. A similar strong band was also observed for the complexes of type II (X = Cl) in the region 242-219 cm^{-1}. The appreciably low frequency of these bands may be attributed to a high *trans* influence of a C donor [5], at the *trans* position of which is coordinated the Cl ligand (C).

Both the PBu_3 complexes (X = Cl, Br) showed two bands at 434 and 390 cm^{-1} which were absent in the other complexes. These bands may arise from the PBu_3 moiety or from an Rh—P bond. $[Rh(bhq)_2(SMe_2)Cl]$ showed $\delta(CSC)$ at 683 cm^{-1} and a band at 263 cm^{-1} may be attributed to $\nu(Rh—S)$. When the pyridine in $[Rh(bhq)_2(py)Cl]$ was replaced with pyridine-d_5, the two deformation vibrations at 631 and 434 cm^{-1} shifted to 604 and 398 cm^{-1}, respectively, the positions showing the coordination of the pyridine N atom [6], and the band at 210 cm^{-1} shifted below 200 cm^{-1} showing that it may be $\nu(Rh—N)$. $[Rh(bhq)_2(dmso)X]$ (X = Cl, Br) exhibited $\nu(S{=}O)$ at 1092 and

TABLE 1

MELTING POINTS, CONDUCTIVITIES, AND ANALYTICAL DATA FOR THE COMPLEXES PREPARED

Complex	M p.(°C)	Λ_M[a]	Analyses found(calcd.)(%)			
			C	H	N	Other
$[Rh(bhq)_2(py)Cl]$	340 (dec.)		64.60 (64.88)	3.64 (3.69)	7.25 (7.32)	
$[Rh(bhq)_2(\gamma\text{-pic})Cl]$	325 (dec.)		64.82 (65.38)	3.88 (3.94)	7.28 (7.14)	
$[Rh(bhq)_2(NH_2Me)Cl]\cdot EtOH$	340 (dec.)		60.74 (60.90)	4.68 (4.76)	7.56 (7.35)	NH_2Me + EtOH: 12 87(13.49)[b]
$[Rh(bhq)_2(SMe)]\cdot 1/2H_2O$	275 (dec.)		62.89 (62.92)	3.63 (3.91)	5.36 (5.43)	H_2O: 1.42(1.75)
$[Rh(bhq)_2(dmso)Cl]$	295 (dec.)		58.44 (58.70)	3.73 (3.87)	4.92 (4.89)	
$[Rh(bhq)_2(dmso)Br]\cdot H_2O$	295 (dec.)		53.00 (52.93)	3.96 (3.81)	4.04 (4.41)	H_2O: 1.99(2.83)
$[Rh(bhq)_2(PBu_3)Br]$	220-221		61.38 (61.54)	6.09 (5.85)	3.87 (3.78)	
$[Rh(bhq)_2(OAc)]\cdot EtOH$[c]	305 (dec.)		63 63 (63.84)	4.39 (4.46)	4.83 (4.96)	
$[Rh(bhq)_2(en)]Cl\cdot H_2O$	315 (dec.)	97.0	58.80 (58.70)	4.48 (4.57)	9.84 (9.78)	H_2O: 3.12(3.14)
$[Rh(bhq)_2(pa)]Cl\cdot CH_2Cl_2$[d]	295 (dec.)	86.4	57.54 (57.62)	3.66 (3.81)	8.16 (8.15)	CH_2Cl_2: 12.35(12.68)
$[Rh(bhq)_2(bipy)]Cl\cdot H_2O$	325 (dec.)	95.0	64.67 (64.63)	4.07 (3.92)	8.20 (8.37)	H_2O: 2.27(2.69)
$[Rh(bhq)_2(mcy)]Cl\cdot 3H_2O$	265 (dec.)	89.1	54.41 (54.42)	4.46 (4.88)	6.62 (6.57)	H_2O: 9.06(8.44)
$[Rh(bhq)_2(diphos)]Cl\cdot 4H_2O$	316-319	30.3[e]	67 20 (67.19)	4.95 (5.01)	2 87 (2.90)	H_2O: 7.13(7.47)

[a] In water, ca. $10^{-3}M$. [b] Estimated from the weight loss at 110 °C under vacuum and their releases were checked by IR spectra. [c] The presence of EtOH was confirmed by the PMR spectrum. [d] The presence of CH_2Cl_2 was confirmed by the PMR spectrum. [e] In EtOH.

TABLE 2

SELECTED SIGNALS OF PMR SPECTRA(δ, ppm)[a]

Complex	Solvent	2-H	4-H	9-H
$[Rh(bhq)_2Cl]_2 \cdot 1/4CHCl_3$	$CDCl_3$	9.33(d)[b]	8.35(d)	5.99(d)
$[Rh(bhq)_2(PBu_3)Cl]$	$CDCl_3$	10.09(d), 9.11(d)	8.26(d)	6.33(d), 5.94(t)
$[Rh(bhq)_2(PBu_3)Br]$	$CDCl_3$	10.26(d), 9.13(d)	8.33(d)	6.27(d), 6.01(t)
$[Rh(bhq)_2(\gamma\text{-pic})Cl]$	$CDCl_3$	10.14(d), 8.35(d)	8.26(d)	6.31(d), 6.18(d)
$[Rh(bhq)_2(OAc)] \cdot EtOH$	$CDCl_3$	9.21(d)	8.39(d)	6.18(d)
$[Rh(bhq)_2(mcy)]Cl\ 3H_2O$	$CDCl_3$	10 16(d), 9.07(d)	8 39(d)	6.30(d), 6.19(d)
$[Rh(bhq)_2(en)]Cl \cdot H_2O$	$(CD_3)_2SO$	9.43(d)	8.72(d)	6.15(d)
$[Rh(bhq)_2(pa)]Cl \cdot CH_2Cl_2$	$(CD_3)_2SO$	9.66(d), —[c]	8.70(d)	6.25(d), 6.14(d)
$[Rh(bhq)_2(bipy)]Cl \cdot H_2O$	$(CD_3)_2CO$	—[c]	—[c]	6.33(d)

[a] Major part of signals due to bhq moieties appeared between 8.1-6.8 ppm except for $[Rh(bhq)_2(diphos)]$-$Cl \cdot 4H_2O$ which showed extremely complicated signals between 8.1-6.0 ppm. [b] All the multiplicities of signals in this table are assigned by referring to rough shapes with neglecting small splittings (d, doublet, t, triplet). [c] These signals were obscured by ligand (L—L) signals.

1096 cm^{-1}, respectively, and normal S-coordination of dmso is suggested for the two [7]. In the far infrared spectral region, the two bands at 408 and 360 cm^{-1} of the chloro complex lowered to 373 and 337 cm^{-1}, respectively, on replacement of dmso with dmso-d_6, implying that these bands are related to the internal modes of dmso or ν(Rh—S).

Type III complexes. All type III complexes, $[Rh(bhq)_2(L—L)]Cl$, were 1/1 electrolytes in solutions (Table 1) [8] and showed no band assignable to ν(Rh—Cl). These complexes are, therefore, formulated as D and the Cl atom is not coordinated. The PMR spectra of the ethylenediamine and 2,2′-bipyridyl complexes showed no splitting of the resonances due to 2-H and 9-H, while these signals split into two for the 2-picolylamine and *S*-methylcysteamine complexes, because they are unsymmetrically bidentate ligands. The signals due to the SMe group were observed as a singlet at 1.04 ppm and no evidence was obtained for the presence of isomers arising from an asymmetrically coordinating sulfur atom.

In the case of the 2-picolylamine complex only one 2-H resonance appeared as an isolated signal, and the other 2-H signal may be at a much higher field and may overlap with the major part of signals above 8.0 ppm. This may be due to the fact that the pyridyl moiety can shield one 2-H as 4-methylpyridine. It is interesting that no signals are observed at lower field than 8.1 ppm for the 1,2-bis(diphenylphosphino)ethane complex and for the 2,2′-bipyridyl complex no signals lower than 8.9 ppm. These facts may also result from the shielding effect of an aromatic ring-current, since molecular models reveal that both the 2-H protons can be located in the shielding region of aromatic rings.

Type IV complexes. The infrared spectrum of $[Rh(bhq)_2(SMe)] \cdot 1/2H_2O$ showed characteristic bands of an SMe group at 2960 and 2905 cm^{-1}. However, other bands are difficult to assign because of the complicated spectral pattern. This complex is insoluble in common solvents for PMR measurements.

The methyl resonance due to the OAc group of $[Rh(bhq)_2(OAc)] \cdot EtOH$ was observed as a singlet at 1.85 ppm, and the 2-H and 9-H signals of the bhq moieties did not split (Table 2) to indicate that they are, respectively, equivalent. The infrared spectrum exhibited two strong bands at 1564 and 1404 cm^{-1}, the positions of which are close to those expected for a bidentate acetate ion [9]. The bands observed at 667 and 226 cm^{-1} are tentatively assigned to π(C=O) and ν(Rh—O), respectively. The structure is, therefore, assumed to be of type D, but not charged, where L—L is a bidentate acetate ion. The proposed structure is consistent with that of bis(2-(phenylazo)phenyl-*N*)acetatorhodium(III) determined by X-ray spectroscopy [10].

Experimental

It was found that complex I was more conveniently prepared by using 2-methoxyethanol as solvent instead of ethanol [1], and stirring for a day at room temperature and then refluxing for another day. The crude product $[Rh(bhq)_2Cl]_2$ (V), which was obtained in a yield of 93%, was used as a starting material in all preparations unless otherwise noted. Analysis: found, C, 62.36; H, 3.33; N, 5.69. $Rh_2C_{52}H_{32}N_4Cl_2$calcd.: C, 63.25; H, 3.26; N, 5.67%.

When complex V was recrystallized from chloroform and n-hexane, complex I, reported previously [1], was obtained.

[Rh(bhq)$_2$(py)Cl]

To a suspension of 1 mmol of V in 30 ml chloroform was added 1.0 ml pyridine and the mixture was heated on a hot plate. When the mixture became clear, it was immediately filtered and the filtrate was allowed to stand at room temperature. The fine yellow crystals obtained were washed with chloroform and dried in air. The yield was 85%.

In a similar manner, [Rh(bhq)$_2$(γ-pic)Cl] was prepared by using 4-methylpyridine, but addition of ethanol to the filtrate was necessary to precipitate the more soluble complex. The product was washed with ethanol.

[Rh(bhq)$_2$(NH$_2$Me)Cl] · EtOH

To a dichloromethane solution (30 ml) of 1 mmol of V was added 1.5 ml of a 30% ethanolic solution of methylamine. To the mixture, concentrated to ca. 20 ml, was added 20 ml ethanol and the mixture allowed to stand at room temperature. A yellow powder precipitated, which was washed with ethanol and dried in air. The yield was 60%.

[Rh(bhq)$_2$(SMe)] · 1/2H$_2$O

To a suspension of 1 mmol of pure complex I in 50 ml ethanol was added 1.5 mmol of a 20% aqueous solution of sodium methylmercaptide, and the mixture stirred for a day at room temperature. The resulting orange-brown powder was washed with ethanol, water, and ethanol, and dried in air. The yield was nearly quantitative.

[Rh(bhq)$_2$(dmso)Cl]

In 5 ml dimethyl sulfoxide 0.5 mmol of V was dissolved and to the solution was added 15 ml ethanol, yellow crystals precipitated, which were washed with ethanol and dried in air. The yield was 85%.

$[Rh(bhq)_2(dmso)Br]\cdot H_2O$

To a dimethyl sulfoxide solution (5 ml) of 1.0 g lithium bromide was added 0.5 mmol of V and the mixture heated for 3 h. To the filtered solution was added 15 ml of ethanol to precipitate yellow crystals in 75% yield.

$[Rh(bhq)_2(PBu_3)Br]$

This complex was obtained by a metathesis reaction of $[Rh(bhq)_2(PBu_3)\text{-}Cl]$ [1] with lithium bromide in an acetone—chloroform mixture.

$[Rh(bhq)_2(OAc)]\cdot EtOH$

The mixture of 1 mmol of V and 1.5 mmol of silver acetate in 50 ml chloroform was refluxed for 2 h. and then filtered. The filtrate was concentrated to ca. 15 ml and 20 ml ethanol was added to precipitate yellow crystals in 65% yield.

$[Rh(bhq)_2(en)]Cl\cdot H_2O$

To a suspension of 1 mmol of V in 50 ml ethanol was added 1 mmol of ethylenediamine and the mixture heated until all the suspending material had been dissolved. The solution was filtered and concentrated to a small volume to precipitate yellow fine crystals. The yield was 65%.

In a similar manner, $[Rh(bhq)_2(L\text{—}L)]Cl$, where L—L is bipyridyl, *S*-methylcysteamine, and 1,2-bis(diphenylphosphino)ethane, were prepared in reasonable yields.

$[Rh(bhq)_2(pa)]Cl\cdot CH_2Cl_2$

To a dichloromethane solution (30 ml) of 1 mmol of V was added 1 mmol of 2-picolylamine and the mixture heated on a hot plate for a few minutes. Fine, light yellow crystals resulted, which were washed with dichloromethane and dried in air. The yield was 85%.

Measurements

The methods of measurements were the same as those reported previously [11], but conductivities were measured with a TOA CM-6A conductivity apparatus for ca. 10^{-3} *M* solutions at 25.0 °C.

References

1 M. Nonoyama and K. Yamasaki, Inorg. Nucl. Chem. Lett., 7 (1971) 943.
2 M. Nonoyama, Bull. Chem. Soc. Japan, 47 (1974) 767.
3 M.I. Bruce, B.L. Goodall and F.G.A. Stone, J. Organometal. Chem., 60 (1963) 343.
4 M. Nonoyama and K. Yamasaki, Nippon Kagaku Zasshi, 91 (1970) 1058; Chem. Abstr., 74 (1971) 68397.
5 T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.
6 M. Pfeffer, P. Braunstein and J. Dehand, Spectrochim. Acta, 30A (1974) 331, 341.
7 B.B. Wayland and R.F. Schramm, Inorg. Chem., 8 (1969) 971.
8 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.
9 S.D. Robinson and M.F. Uttley, J. Chem. Soc. Dalton, (1973) 1912.
10 R.J. Hoare and O.S. Mills, J. Chem. Soc. Dalton, (1972) 2138, 2141.
11 M. Nonoyama, J. Organometal. Chem., 74 (1974) 115.