Journal of Organometallic Chemistry, 74 (1974) 115—120

SYNTHESIS OF ORGANORHODIUM(III) COMPLEXES OF 8-METHYLQUINOLINE

MATSUO NONOYAMA

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, 464 (Japan)

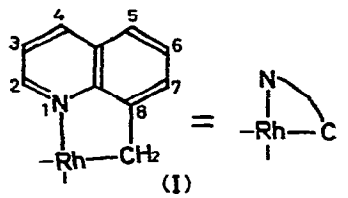
(Received January 23rd, 1974)

Summary

The methyl group of 8-methylquinoline (Hmq) is metallated with rhodium(III) chloride hydrate in boiling 2-methoxyethanol and the complex of composition $RhCl_2(mq)\cdot 1/3\ (Hmq\cdot HCl)$ is obtained, the structure of which is difficult to deduce. This product reacts with ligands (L) to give $RhCl_2(mq)L$ (L = pyridine, dimethyl sulfide, or acetonitrile), $RhCl_2(mq)L_2$ (L = dimethyl sulfoxide, triphenylarsine, or tri-n-butylphosphine), and $RhBr_2(mq)L_2$ (L = pyridine, 4-methylpyridine, or tri-n-butylphosphine). These complexes are characterized by spectroscopic methods.

Introduction

Metallation reactions of organic nitrogen and phosphorus compounds with transition metal ions have been the subject of much research in recent years [1]. Although such reactions with palladium(II) and platinum(II) have been studied widely, similar reactions with the other platinum-group metal ions have been less extensively investigated. Metallation reactions at an aromatic carbon atom with rhodium(III) are known for both organic nitrogen [2,3] and phosphorus [4] compounds but so far such reactions at an aliphatic carbon atom seemed to be limited to organic phosphorus ligand [5]. The results of our study of metallation at the methyl group of 8-methylquinoline (abbreviated as Hmq) with rhodium(III) chloride hydrate now provide an example of a metallation reaction of an aliphatic carbon atom with rhodium(III).



(I)

Results and discussion

The reaction product of Hmq with $RhCl_3 \cdot 3H_2O$ in boiling 2-methoxyethanol was $RhCl_2(mq) \cdot 1/3(Hmq \cdot HCl)$ (Table 1), which is insoluble in common solvents without coordinating ability. Therefore, removal of the adduct component, Hmq·HCl was impossible and no PMR spectrum is available. In the IR spectrum a very strong band observed at 325 cm^{-1} is assignable to ν(Rh—Cl). Other bands are difficult to assign because of the complicated spectral pattern. However, a new broad band at 3060 cm^{-1} may arise from the adduct component, Hmq·HCl and may be assigned to ν(N—H). It was reported that the metallation product of tri-*o*-tolylphosphine ($Ptol_3$) with $RhCl_3 \cdot 3H_2O$ has the composition $RhCl_2(tol_2PC_6H_4CH_2)$ and that it is trimeric [4]. The apparent composition of the reaction product of Hmq with $RhCl_3 \cdot 3H_2O$, $RhCl_2(mq) \cdot 1/3(Hmq \cdot HCl)$ is similar and, therefore, the structure may be related to that of $RhCl_2(tol_2PC_6H_4CH_2)$.

The complex $RhCl_2(mq) \cdot 1/3(Hmq \cdot HCl)$ is appreciably soluble in dimethyl sulfoxide (dmso) and from the solution yellow crystals of $RhCl_2(mq)(dmso)_2$ precipitated slowly in the course of a few days. The PMR spectrum of the freshly prepared dmso-d_6 solution (Fig. 1B) showed a signal at δ 2.87 ppm with the intensity corresponding to 1H and three broad signals at 4.43, 5.10 and 5.41 ppm, the sum of whose intensitites amounts to 2H. The intensity of the complicated signals in a lower field than 7.4 ppm reaches 8H. In the spectrum obtained after a day, the highest field signal showed no change, but the three broad signals between 4.4—5.5 ppm had disappeared and a new broad signal at 4.57 ppm accompanied by a partially overlapping small signal at 4.47 ppm appeared instead (Fig. 1C), the total intensity of which remained 2H. In the spectrum measured after a week, when an appreciable amount of crystals had deposited, the intensity of the signals at 4.57 and 4.47 ppm was reduced compared with that of the signal at 2.87 ppm. These results are interpreted as below.

The signal at 2.87 ppm, the intensity of which remains unchanged while precipitation of $RhCl_2(mq)(dmso)_2$ occurs, is assigned to the methyl group of the adduct component, 1/3(Hmq·HCl), and the intensity 1H is satisfied. The three signals between 4.4—5.5 ppm may be due to methylene groups of mq coordinated to rhodium in three different isomers which are initially formed when dmso attacks the complex $RhCl_2(mq) \cdot 1/3(Hmq \cdot HCl)$. The major portion of the initial products coordinated with dmso then slowly isomerized to the complex which exhibits a signal at 4.57 ppm, and $RhCl_2(mq)(dmso)_2$ crystallized from the solution. The intensity 2H of the methylene signal is consistent with the formulation (I). The intensity 8H of the complicated signals in a lower field than 7.4 ppm is due to the sum of 6H of the coordinated mq ring-protons and 2H of the ring-protons of 1/3(Hmq·HCl).

The signal due to the methyl group of free Hmq is not a real singlet but seems to show long-range coupling (Fig. 1A). The signal due to the coordinated methylene group (I and Fig. 1B—1E) has a larger bandwidth, probably because the two methylene protons are not magnetically equivalent*. Besides the nonequivalency, coupling with the nucleus of ^{103}Rh with $I = 1/2$ and/or the long-

* For the PBu_3 complexes, there should be an AA'XX' pattern neglecting Rh coupling.

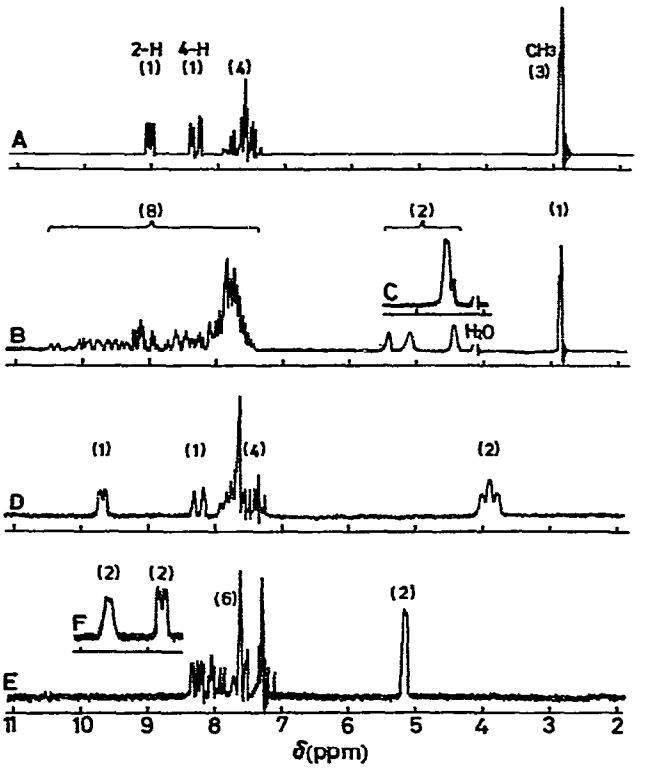


Fig. 1. PMR spectra of A: 8-methylquinoline (Hmq) in dmso-d_6, B: a freshly prepared dmso-d_6 solution of $RhCl_2(mq)\cdot 1/3(Hmq\cdot HCl)$, C: a dmso-$d_6$ solution of $RhCl_2(mq)\cdot 1/3(Hmq\cdot HCl)$ after standing one day, D: $RhCl_2(mq)(PBu_3)_2$ in $CDCl_3$, E: $RhCl_2(mq)$(py-d_5) in $CDCl_3$, and F: $RhCl_2(mq)(py)$ in $CDCl_3$. The signal due to dmso-d_5 of solvent is omitted in spectra A, B and C.

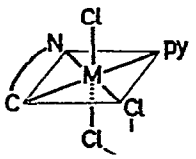
range coupling might be a contribution toward the breadth of these resonances.

The IR spectrum of $RhCl_2(mq)(dmso)_2$ exhibits ν(S=O) at 1119 and 1132 cm^{-1} to show S-coordination of dmso [6]. Two bands at 328 and 232 cm^{-1} are assigned to ν(Rh—Cl), and the bands at 379 and 411 cm^{-1}, which shift to 358 and 392 cm^{-1} when dmso is replaced with dmso-d_6, are assigned to ν(Rh—S) based on the assignment reported [6] for $Pd(dmso)_4(BF_4)_2$. From these spectral data, both the two chlorine atoms and the two dmso molecules are assumed to be located mutually *cis*, respectively.

The complex $RhCl_2(mq)\cdot 1/3(Hmq\cdot HCl)$ is soluble in acetonitrile (an) and from the solution $RhCl_2(mq)$an precipitates after several minutes. The PMR spectrum in dmso-d_6 shows a singlet (intensity 3H) at 2.10 ppm due to CH_3 of acetonitrile, a broad signal (2H) at 5.11 due to CH_2 of mq, a complicated pattern (4H) between 7.4—8.1 due to the ring-protons of mq except 2-H and 4-H, a signal (1H) at 8.46 due to 4-H of mq, and a signal (1H) at 9.45 due to 2-H of mq. The IR spectrum shows ν(C≡N) at 2299 and 2323 cm^{-1}, implying the normal N-coordination of acetonitrile [7]. The two strong bands at 337 and 261 cm^{-1} may be due to ν(Rh—Cl). The structure of this may be dimeric because Rh^{III} prefers six-coordination.

Pyridine (py) reacts with $RhCl_2(mq)\cdot 1/3(Hmq\cdot HCl)$ in $CHCl_3$ to give

$RhCl_2(mq)py$ and, in the presence of lithium bromide, $RhBr_2(mq)(py)_2$. The solubility of the bromide is low and only an unsatisfactory PMR spectrum is obtained. The spectrum is difficult to analyze because of its low quality. The spectrum of the chloride is shown in Fig. 1F, and that of the py-d_5 analogue in Fig. 1E. The two signals at 8.79 and 9.58 ppm, the intensity of each of which is 2H, are clearly attributed to pyridine-ring protons because they disappear on replacement of pyridine with py-d_5. If the spectrum is compared with that of the acetonitrile complex, it is found that the lowest field signal (at 9.45 ppm) due to 2-H of the acetonitrile complex shifts up to 8.4 ppm. The shift of 2-H may be explained in terms of the shielding due to the ring current of pyridine and the structure, where 2-H is nearly above the pyridine ring, seems to be

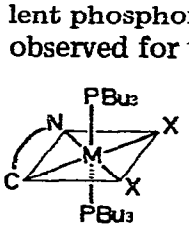


(II)

probable (II) [8]. The IR spectrum shows the bands ν(Rh—Cl) at 335 and 269 cm^{-1}, and ν(Rh—N) at 223 cm^{-1}, the last of which shifts to 219 cm^{-1} upon replacement of pyridine with py-d_5, while the former two of which do not shift. The position of ν(Rh—Cl) are similar to those of the acetonitrile complex, and the structure of the pyridine complex may be a similar one bridged by chlorine atoms and the complex may be formulated as a dimer $[RhCl_2(mq)py]_2$.

Similarly to pyridine, 4-methylpyridine(γ-pic) reacts with $RhCl_2(mq)\cdot 1/3(Hmq\cdot HCl)$ in the presence of lithium bromide to yield $RhBr_2(mq)(\gamma\text{-pic})_2$. The γ-pic complex is more soluble than the pyridine analogue and the PMR spectrum in $CDCl_3$ shows that the two γ-pic molecules are not equivalent, because the 4-methyl groups resonate at 2.39 and 2.53 ppm (each intensity 3H). The broad signal of the metallated CH_2 group at 5.34 ppm has an intensity 2H and its bandwidth is about three times that of the 4-methyl signals. The reason has been mentioned above. Signals in a lower field than 6.5 ppm are difficult to assign since signals due to ring-protons of mq and two non-equivalent γ-pic appear to overlap. The PMR spectrum shows only that the γ-pic complex does not have the structure in which two γ-pic molecules are attached *trans* to each other since in the structure two γ-pic molecules are equivalent.

The two tri-n-butylphosphine (PBu_3) complexes, $RhX_2(mq)(PBu_3)_2$ (X = Cl, Br) have nearly identical PMR spectra and that of the chloride is shown in Fig. 1D. The triplet (J = ca. 7 Hz) observed at 3.89 ppm (2H) is assigned to CH_2 of mq and the splitting arises from the coupling of the protons with two equivalent phosphorus atoms (I = 1/2) [9]. The two strong bands at 318 and 218 cm^{-1} observed for the chloride, which disappear in the spectrum of the bromide, are



(III)

assigned to ν(Rh—Cl). The higher frequency band is attributed to the Rh—Cl bond *trans* to an N donor and the lower one to that *trans* to a C donor atom [4], or ν_{as}(Rh—Cl) and ν_s(Rh—Cl). Structure III is therefore proposed.

The reaction products of $RhCl_2(mq)\cdot 1/3(Hmq\cdot HCl)$ with dimethyl sulfide (SMe_2) and triphenylarsine ($AsPh_3$) are practically insoluble in common solvents. In their IR spectra, strong bands observed at 270 and 325 cm^{-1} for $RhCl_2(mq)(SMe_2)$ may be assigned to ν(Rh—Cl), while assignment of the corresponding bands is impossible for $RhCl_2(mq)(AsPh_3)_2$, which exhibits bands due to $AsPh_3$. Structures for the two complexes are difficult to propose from these data alone.

Experimental

Instrumentation

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

Syntheses

Reaction of Hmq with $RhCl_3\cdot 3H_2O$. To a solution of 1.0 g (3.8 mmol) of $RhCl_3\cdot 3H_2O$ dissolved in 100 ml of 2-methoxyethanol was added 1.1 g (7.7 mmol) of Hmq at room temperature. The mixture was stirred for a day and then refluxed gently for 4 h. The brown suspension became nearly clear and the hot solution was filtered. The filtrate was refluxed for another 4 h to yield a yellowish orange powder. The product was washed with ethanol and dried in air. The yield was 1.0 g (70%). This product is difficult to purify because of its insolubility in common solvents. It was analyzed as $RhCl_2(mq)\cdot 1/3(Hmq\cdot HCl)$ (Table 1).

Solution of $RhCl_2(mq)\cdot 1/3(Hmq\cdot HCl)$ in dimethyl sulfoxide and acetonitrile. The complex $RhCl_2(mq)\cdot 1/3(Hmq\cdot HCl)$ was soluble in dimethyl sulfoxide and acetonitrile, and the crystals which are deposited from the solution are not the starting material, but solvent adducts, $RhCl_2(mq)(dmso)_2$ and $RhCl_2(mq)$an, respectively. The two complexes were not purified because no solvent suitable for recrystallization was found. The analytical results for these are given in Table 1.

Reactions of $RhCl_2(mq)\cdot 1/3(Hmq\cdot HCl)$ with several ligands. To a chloroform suspension (30 ml) of 1 mmol of $RhCl_2(mq)\cdot 1/3(Hmq\cdot HCl)$ was added 2 mmol of tri-n-butylphosphine or an excess of pyridine and the mixture was heated on a hot plate until most of the suspended material had dissolved. To the filtered solution was added 30 ml of ethanol and the mixture was concentrated to a small volume to give yellow crystals, $RhCl_2(mq)(PBu_3)_2$ and $RhCl_2(mq)$py, respectively.

The bromo analogues of the two were prepared in the presence of lithium bromide in a mixture of chloroform and acetone as a solvent. Triphenylarsine, dimethyl sulfide, and 4-methylpyridine complexes were prepared in a similar way. These complexes were recrystallized from chloroform or a mixture of chloroform and ethanol. The analytical data and melting points are given in Table 1.

TABLE 1

ANALYTICAL RESULTS AND MELTING POINTS FOR THE COMPLEXES

Complex[a]	M.p. (°C)	Analyses, found (calcd.) (%)			
		C	H	N	Other
$RhCl_2(mq)\cdot 1/3(Hmq\cdot HCl)$	280(dec.)	42.43 (42.61)	3.03 (3.04)	4.89 (4.97)	Cl 21.63 (22.01)
$RhCl_2(mq)(PBu_3)_2$	245—247	56.33 (56.67)	8.67 (8.67)	1.92 (1.94)	P 8.32 (8.60)
$RhBr_2(mq)(PBu_3)_2$	230—232	51.00 (50.45)	7.76 (7.72)	1.68 (1.73)	
$RhCl_2(mq)(AsPh_3)_2$	270(dec.)	59.39 (59.51)	4.14 (4.13)	1.56 (1.51)	
$RhCl_2(mq)(SMe_2)$	250(dec)	37.95 (38.12)	3.77 (3.73)	3.59 (3.70)	
$RhCl_2(mq)py$	260(dec.)	45.22 (45.60)	3.35 (3.32)	7.82 (7.09)	
$RhBr_2(mq)(py)_2$	238(dec.)	42.95 (42.66)	3.33 (3.22)	7.37 (7.46)	
$RhBr_2(mq)(\gamma\text{-pic})_2$	215(dec.)	45.03 (44.70)	3.64 (3.75)	7.23 (7.23)	
$RhCl_2(mq)an$	280(dec.)	40.50 (40.37)	3.08 (3.11)	8.34 (7.85)	Cl 19.47 (19.86)
$RhCl_2(mq)(dmso)_2$	280(dec.)	35.56 (35.61)	4.26 (4.27)	2.92 (2.97)	S 13.92 (13.58)

[a] Hmq = 8-methylquinoline, mq = 8-quinolylmethyl, py = pyridine, γ-pic = 4-methylpyridine, an = acetonitrile, and dmso = dimethylsulfoxide.

References

1 G.W. Parshall, Accounts Chem. Res., (1970) 139.
2 M. Nonoyama and K. Yamasaki, Inorg. Nucl. Chem. Lett., 7 (1971) 943.
3 M.I. Bruce, M.Z. Iqbal and F.G.A. Stone, J. Organometal. Chem., 40 (1972) 393, and references therein.
4 J.M. Duff and B.L. Show, J. Chem. Soc. Dalton, (1972) 2219.
5 R. Mason and A.D.C. Towl, J. Chem. Soc. (A), (1970) 1611.
6 B.B. Wayland and R.F. Schramm, Inorg. Chem., 8 (1969) 971.
7 D.A. Baldwin, R.M. Pfeiffer, D.W. Reichgott and N.J. Rose, J. Amer. Chem. Soc., 95 (1973) 5152.
8 M. Nonoyama and K. Yamasaki, Nippon Kagaku Zasshi, 91 (1970) 1058; Chem. Abstr., 74 (1971) 68397.
9 G.E. Hartwell, R.V. Lawrence and M.J. Smas, Chem. Comm., (1970) 912.