Inorganica Chimica Acta, 115 (1986) 169–172

Ruthenium(II) Complexes Derived from 2-(Methylamino)pyridine

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Received October 31, 1985

Abstract

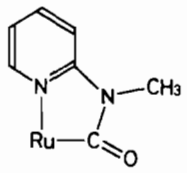
2-(Methylamino)pyridine reacts with $RuCl_2(CO)_3$ to give a carbamoyl complex, $[Ru(C(O)N(CH_3)(C_5H_4N)Cl(CO)_2]$, which yields with pyridine (py) and acetylacetone (Hacac), respectively, $[Ru(C(O)N(CH_3)C_5H_4N)Cl(CO)_2(py)]$ and $[Ru(C(O)N(CH_3)C_5H_4N)(CO)_2(acac)]$. These complexes are characterized spectroscopically. The amino group of the ligand is carbonylated and the resulted carbamoyl ligand is chelating through a pyridine ring-*N* and a carbamoyl-*C* atom. 2-Aminopyridine and 2-aminopyrimidine react similarly with $RuCl_2(CO)_3$ to give the corresponding carbamoyl complexes.

Introduction

Several modes of coordination have been found for 2-aminopyridine and its derivatives in their transition metal complexes [1]. They are coordinated as a monodentate ligand via a pyridine ring-*N* or an amino-*N* atom, as a bidentate one chelating through the two *N* atoms, and as a bridging ligand with the two *N* atoms. When the amino substituent is an aryl group, cyclometallation occurs for palladium(II) [2] and rhodium(III) [3], where the ligand is chelated through the pyridine ring-*N* and *ortho-C* atom of the aryl substituent forming a six-membered metalla heterocycle. Another mode of coordination [4] has been found for the *N*-aryl substituted 2-aminopyridine: the reaction with $RuCl_2(CO)_3$ gives an *N*-aryl-*N*-(2-pyridyl)carbamoylruthenium(II) complex, for instance, $[Ru(C(O)N(C_6H_5)C_5H_4N)Cl(CO)_2]$. The result is in contrast to the report that upon reaction with $RuCl_2(CO)_3$ secondary amines did not readily give characterizable products [5]. The driving force for the reaction of the pyridine derivative seems to result from the formation of a chelate ring. We have extended this investigation and here report the complexes obtained by reactions of 2-aminopyridine, 2-(methylamino)pyridine, and 2-aminopyrimidine with $RuCl_2(CO)_3$.

Results and Discussion

Refluxing a 2-methoxyethanol solution of an equimolar mixture of 2-(methylamino)pyridine (abbreviated as 'map') and $RuCl_2(CO)_3$ for a few hours gave a white precipitate of the complex, $[Ru(C(O)N(CH_3)C_5H_4N)Cl(CO)_2]$ (**A**) (Table I). The infrared spectrum (Nujol mulls) of **A** shows no band of ν(NH), which is at 3265 cm^{-1} for free map. The spectrum of **A** shows a new strong band at 1649 cm^{-1} (with a shoulder at 1653 cm^{-1}) to suggest the presence of an organic carbonyl group [6] (structure **I**). An additional characteristic strong



I

band is observed at 956 cm^{-1}. Two strong ν(CO) bands at 2055 and 1992 cm^{-1} (Table I) indicate a *cis*-arrangement of the two CO groups and in the far infrared spectral region, two strong bands at 272 and 216 cm^{-1} are assignable to ν(RuCl). **A** is soluble only in solvents of donor property, such as dimethylsulfoxide (dmso). The ^1H NMR spectrum of **A** in dmso-d_6 is complicated and difficult to interpret. Upon addition of pyridine(py)-d_5 the spectrum is simplified (as discussed below).

The complex **A** reacted with pyridine to give the adduct, $[Ru(C(O)N(CH_3)C_5H_4N)Cl(CO)_2(py)]$ (**B**). The infrared spectrum of **B** (Nujol mulls) is essentially similar to that of **A** (two characteristic bands at 1639 and 942 cm^{-1}). The skeletal structure **I** is retained in **B**. Only a single band of ν(RuCl) is 257 cm^{-1}, and the low frequency suggests that the Cl ligand is situated *trans* to a donor with strong *trans* influence [7], e.g., a σ-carbon donor. **B** is soluble in common organic solvents. The infrared spectrum of a chloroform solution of **B** shows ν(CO) at 2070 and 2003 cm^{-1} implying a *cis* arrangement of the

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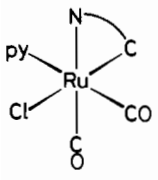
TABLE I. Melting Points, Yields, Analytical Results, and Infrared Spectral Bands of Carbonyl Groups for the Complexes

Complex[a]		Melting point[b] (°C)	Yield (%)	Analysis (found (calc.))			ν(CO)[c] (cm^{-1})
				C(%)	H(%)	N(%)	
$[\overline{Ru(C(O)N(CH_3)C_5H_4N)}Cl(CO)_2]$	(A)	255(dec.)	39	33.17 (32.99)	2.15 (2.11)	8.77 (8.55)	2055, 1992
$[\overline{Ru(C(O)N(CH_3)C_5H_4N)}Cl(CO)_2(py)]$	(B)	245(dec.)	67	41.28 (41.34)	2.99 (2.97)	10.19 (10.33)	2052, 1977 1971
$[\overline{Ru(C(O)N(CH_3)C_5H_4N)}(CO)_2(acac)]$	(C)	211–212	63	42.79 (42.97)	3.37 (3.61)	7.45 (7.16)	2058, 1976
$[\overline{Ru(C(O)N(H)C_5H_4N)}Cl(CO)_2]$	(D)	245(dec.)	29	30.98 (30.63)	1.79 (1.61)	9.14 (8.93)	2090, 2072 1987, 1993sh
$[\overline{Ru(C(O)N(H)C_4H_3N_2)}Cl(CO)_2]$	(E)	250(dec.)	35	26.72 (26.72)	1.27 (1.28)	13.53 (13.35)	2079, 2016
$[\overline{Ru(C(O)N(H)C_5H_4N)}Cl(CO)_2(py)]$	(F)	240(dec.)	50	39.76 (39.76)	2.47 (2.57)	10.75 (10.70)	2050, 1977
$[\overline{Ru(C(O)N(H)C_4H_3N_2)}Cl(CO)_2(py)]$	(G)	240(dec.)	55	36.32 (36.61)	2.17 (2.30)	14.37 (14.23)	2056, 1990
$[\overline{Ru(C(O)N(CH_3)C_5H_4N)}Cl(CO)_2(map)]$	(H)	245(dec.)	41	41.16 (41.34)	3.46 (3.47)	12.78 (12.86)	2058, 1994

[a]py = pyridine, acac = acetylacetonate ion, map = 2-(methylamino)pyridine. [b]dec. = decomposition. [c]Nujol mulls and sh = shoulder.

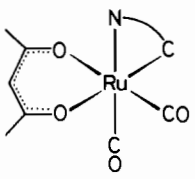
two CO groups. In the ^1H NMR spectrum of the py-d_5 analogue of **B** in dmso-d_6 (the identical spectrum is obtained for **A** in dmso-d_6 with py-d_5, as mentioned above) the broad signal of N–H of free map at 4.87 ppm is no longer observed. Other signals persist but the doublet of N–CH_3 of free map (at 2.88 ppm, $J = 5$ Hz) becomes a singlet at 3.16 ppm. This results from the removal of the N-hydrogen of the $NHCH_3$ group. The signals of the pyridine ring hydrogens shift to lower fields compared with those of the corresponding hydrogens of free map, especially that of the 6-H which appears at 9.14 ppm. Structure **II** is proposed as



II

a probable one. The ^{13}C NMR spectrum (in CD_2Cl_2, in the presence of tris(acetylacetonato)chromium(III) as a relaxation reagent) shows three peaks in the carbonyl region (195.6, 196.6, and 202.4 ppm) confirming that the two CO ligands are in a *cis* arrangement. One of the three peaks is assigned to a metal-bonded carbamoyl carbon atom [8].

The complex **A** reacts with acetylacetone (Hacac) in the presence of a base to give $[\overline{Ru(C(O)N(CH_3)C_5H_4N)}(CO)_2(acac)]$ (**C**). The infrared spectrum (Nujol mulls) of **C** shows strong bands at 1585 and 1515 cm^{-1} to suggest a usual *O,O*-chelating mode of acac [9] and new bands at 413 and 272 cm^{-1} are assigned to ν(RuO). Two characteristic bands at 1635 and 940 cm^{-1} persist. The appearance of two ν(CO) bands at 2063 and 1987 cm^{-1} ($CHCl_3$ solution) suggests a mutual *cis* configuration of the two CO groups. In the ^1H NMR spectrum ($CDCl_3$ solution) the signals of the methyl groups of acac are at 1.77 and 2.10 ppm, showing that the two methyl groups are not equivalent. It should be noted that the chemical shift (7.83 ppm) of the pyridine ring 6-H of **C** is very different from the corresponding value (9.14 ppm) of **B**. The origin is that in **B** the 6-H is directed toward the Cl (structure **II**), while in **C** the 6-H is directed toward the O atom of acac, if structure **III** is assigned to **C**. The assignment is fully consistent

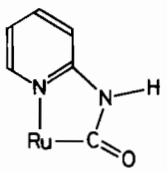


III

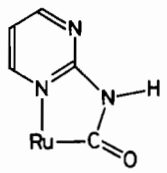
with the ^{13}C NMR spectral results (in $CDCl_3$, in the presence of tris(acetylacetonato)chromium(III) as a relaxation reagent). The methyl groups of acac and the N–CH_3 group give three peaks (27.3, 27.7, and 28.4 ppm). For the carbonyl groups of acac two peaks are observed at 188.1 and 189.7 ppm. Thus the two acetyl moieties of acac are not equivalent. A *cis* geometry of the two CO groups is also borne

out by the ^{13}C NMR spectrum: three peaks (195.2, 195.3, and 201.2 ppm) are observed at a low field region. Two are due to CO groups and the remaining one to a carbamoyl group.

2-Aminopyridine and 2-aminopyrimidine also react with $RuCl_2(CO)_3$ to give, respectively, $[Ru(C(O)N(H)C_5H_4N)Cl(CO)_2]$ (**D**) and $[Ru(C(O)N(H)C_4H_3N_2)Cl(CO)_2]$ (**E**). The infrared spectra of the two are very similar except for the bands due to heterocycles: ν(NH) is at 3150 (**D**) or at 3145 (**E**), two characteristic bands at 1618 and 1095 (**D**) or at 1604 and 1081 (**E**), and ν(RuCl) at 283 and 214 (**D**) or at 283 and 222 (**E**) cm^{-1}. The ^1H NMR spectra of dmso-d_6 solutions are complicated, like those of **A**. The coordination modes of the amines in **D** and **E** are, based on these results together with the following discussion, proposed to be, respectively, structures **IV** and **V**, which are similar to structure **I**.



IV



V

The above complicated ^1H NMR spectra are simplified upon addition of py-d_5 and the same spectra are obtained for the py-d_5 analogues of $[Ru(C(O)N(H)C_5H_4N)Cl(CO)_2(py)]$ (**F**) and $[Ru(C(O)N(H)C_4H_3N_2)Cl(CO)_2(py)]$ (**G**), respectively. In the spectra, the carbamoyl N–H groups give a broad resonance at 10.67 (**F**) or at 11.06 (**G**) ppm. As for **B**, signals of the ring 6-H are observed at low fields (9.06 (**F**) and 9.21 (**G**) ppm). In the infrared spectra ($CHCl_3$ solution) there are two ν(CO) at 2073 and 2008 (**F**) or at 2077 and 2015 (**G**) cm^{-1} and other bands are similar to, those of **D** and **F**, respectively. However, ν(RuCl) is at 257 (**F**) or at 250 (**G**) cm^{-1} (Nujol mulls). The two complexes are assumed to have structure **II** where C–N represents structure **IV** for **F** or **V** for **G**.

Reaction of $RuCl_2(CO)_3$ with an excess of map in CH_2Cl_2 gives $[Ru(C(O)N(CH_3)C_5H_4N)Cl(CO)_2(map)]$ (**H**). The infrared spectral property is similar to that of **B**: ν(CO) at 2070 and 2003 ($CHCl_3$ solution), two characteristic bands at 1589 and 958 (Nujol mulls) and ν(RuCl) at 257 cm^{-1}. The presence of intact map is confirmed by appearance of ν(NH) at 3350 cm^{-1} and of a methyl doublet at 2.84 ppm (J = 5 Hz) in the ^1H NMR spectrum ($CDCl_3$ solution). In the region of pyridine ring proton resonances (6.2–8.1 ppm), the spectrum is complicated but the signal of one pyridine ring 6-H is found separately at 9.23 ppm. A singlet of another methyl group is at 3.18 ppm. These facts support that the carbonylated map has structure **I**; therefore **H** has a similar structure to **II** in which py is replaced with map.

Experimental

Measurements

Measurements were carried out by the methods reported previously [4]. ^{13}C NMR spectra were recorded on a JEOL JNM-FX-100 spectrometer. Chemical shifts (δ ppm) are given relative to internal tetramethylsilane. Melting points, yields, and analytical results for the complexes are summarized in Table I.

Preparations

$[Ru(C(O)N(CH_3)C_5H_4N)Cl(CO)_2]$ (A)

A mixture of 1 mmol of 2-(methylamino)pyridine and 1 mmol of $RuCl_2(CO)_3$ in 15 ml of 2-methoxyethanol was refluxed for a few hours and allowed to stand overnight. A white precipitate was collected, washed with ethanol, and dried in air.

The complexes **D** and **E** were prepared similarly from 2-aminopyridine and 2-aminopyrimidine, respectively.

$[Ru(C(O)N(CH_3)C_5H_4N)Cl(CO)_2(py)]$ (B)

Reaction of **A** with excess pyridine in CH_2Cl_2, addition of equi-volume of n-hexane to the solution, and concentration to a small volume gave **B** as a white powder. The complexes **F** and **G** were prepared similarly from **D** and **E**, respectively.

$[Ru(C(O)N(CH_3)C_5H_4N)(CO)_2(acac)]$ (C)

A mixture of 1 mmol of **A**, 1 mmol of acetylacetone, and 1 mmol of 1,8-diazabicyclo(5.4.0)-7-undecene in a mixture of 15 ml of ethanol and 15 ml of CH_2Cl_2 was stirred on a hot plate for 30 min and concentrated to a small volume. After cooling, a white precipitate was filtered, washed with ethanol, and dried in air.

$[Ru(C(O)N(CH_3)C_5H_4N)Cl(CO)_2(map)]$ (H)

A mixture of 1 mmol of $RuCl_2(CO)_3$ and 4 mmol of map in 40 ml of CH_2Cl_2 was stirred overnight. The resultant solution was filtered and to the filtrate was added 10 ml of ethanol. The mixture was concentrated to a small volume and allowed to stand overnight. White crystals were filtered, washed with ethanol, and dried in air.

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