Journal of Organometallic Chemistry, 310 (1986) C8–C10
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

REACTION OF $[Ru(CO)H(NCMe)_2(PPh_3)_2]ClO_4$ WITH 1-HYDROXYMETHYL-3,5-DIMETHYLPYRAZOLE. FORMATION OF AN AMIDINE COMPLEX. THE CRYSTAL STRUCTURE OF $[Ru(CO)H\{NH{=}CMe(Me_2pz)\}(PPh_3)_2]ClO_4$

A. ROMERO, A. VEGAS and A. SANTOS

Instituto de Química Inorgánica "Elhuyar", CSIC, Serrano 113, 28006 Madrid (Spain)

(Received May 5th, 1986)

Summary

The reaction between $[Ru(CO)H(NCMe)_2(PPh_3)_2]ClO_4$ and 1-hydroxymethyl-3,5-dimethylpyrazole has been shown by spectroscopic and X-ray crystallographic methods to give the amidine complex $[Ru(CO)H\{NH{=}CMe(Me_2pz)\}(PPh_3)_2]ClO_4$.

We recently described the reactions of $RuCl_2(PPh_3)_3$, $RuClH(PPh_3)_3$ and $Ru(CO)ClH(PPh_3)_3$ with 1-hydroxymethyl-3,5-dimethylpyrazole, which in all cases gave $Ru(CO)ClH(Me_2Hpz)(PPh_3)_2$ (Hpz = pyrazole) [1]. In an attempt to elucidate the mechanism of these reactions we undertook a study of the reaction between $[Ru(CO)H(NCMe)_2(PPh_3)_2]ClO_4$ (**A**) and the same pyrazole ligand. While this work was in progress information on a related system became available [2] and is discussed below.

The reaction of **A** with 1-hydroxymethyl-3,5-dimethylpyrazole in warm ethanol afforded an air- and moisture-stable white crystalline solid (**B**) in a high yield (75%). The IR spectrum (KBr discs) showed absorptions typical of 3,5-dimethylpyrazole, as well as a band at 3270 cm^{-1} typical of $\nu(NH)$. A medium intensity absorption was also observed at 1645 cm^{-1}, which could be assigned to a $\nu(C{=}N)$ stretching frequency. Other significant IR bands were observed at 1935vs, $\nu(CO)$; 1570m, $\nu(C{=}N$ pyrazole); 1406s, $\nu(C{-}N$ pyrazole); 1108vs, 1060vs, $\nu(Cl{-}O)$ and 618m, 660m cm^{-1} $\delta(Cl{-}O)$.

No $\nu(CN)$ band of a coordinated acetonitrile molecule was found although it is known that MeCN does not always show a $\nu(CN)$ stretch when coordinated, as in $\{Re(NCMe)(PPh_3)_2X_3\}$ (X = Cl, Br) [3]. The ^1H NMR spectrum in $(CD_3)_2SO$ showed three methyl-proton signals in the ratio 1/1/1, two of the pyrazole ligand (δ 1.37, s, 3H and 1.31, s, 3H) and one (δ 1.65, s, 3H) which could be due to an acetonitrile ligand. However the NH signal (δ 10.48, s, 1H) does not correspond to an NH pyrazole proton; this signal appears at δ 11.45 ppm in the ^1H NMR

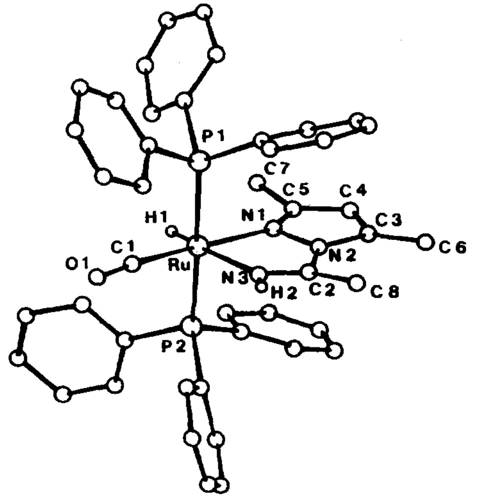

Fig. 1. View of the $[Ru(CO)H\{NH{=}CMe(Me_2pz)\}(PPh_3)_2]^+$ cation.

spectrum of $Ru(CO)HCl(Me_2HPz)(PPh_3)_2$ [1]. Other signals at 6.65–6.54 (m, 20H, C_6H_5), 6.52–6.40 (m, 10H, C_6H_5), 4.89 (s, 1H, HC$<$), −9.42 (t, J(PH) 15 Hz, 1H) (standard Me_4Si) were observed. The analytical data for **B** are consistent with the formula $[Ru(CO)H(NCMe)(Me_2Hpz)(PPh_3)_2]ClO_4$, but the spectral data described above do not correspond to the presence of the nitrile and pyrazole ligands. On the other hand it was clear from the spectra that there was no hydroxy-methyl group on the pyrazole ring. An alternative formulation for the complex, consistent with the spectral data (IR and ^1H NMR), was $[Ru(CO)H\{NH{=}CMe(Me_2Pz)\}(PPh_3)_2]ClO_4$, and this formulation was confirmed by a crystal structure determination.

Crystal data: $C_{44}H_{42}ClN_3O_5P_2Ru$, $M = 891.31$, monoclinic, $P2_1/c$, a 18.264(1), b 12.728(1), c 18.683(1) Å, β 107.69(1)°, U 4137.53 Å^3, $Z = 4$, $D_c = 1.43$ g cm^{-3}, $F(000) = 1832$, Cu-K_α radiation (λ 1.5418 Å), μ(Cu-K_α) 48.9 cm^{-1}, crystal dimensions: 0.10 × 0.16 × 0.02 mm. 5564 reflections measured on a Philips diffractometer up to θ_{max} 57°, 2092 observed reflections with $I > 4\sigma(I)$. The structure was solved by the heavy atom method and refined by full-matrix least-squares calculations and unit weights. Final $R = 0.086$. The oxygens of the perchlorate anion showed extremely high temperature factors and some unresolved disorder and so they were fixed at the positions of the maxima in the Fourier map and refined isotropically *.

The cation is represented in Fig. 1. Ru has a distorted octahedral coordination. The more relevant bond lengths (Å) are Ru–N(1): 2.16(2), Ru–N(3): 2.12(2) Ru–P(1): 2.381(7), Ru–P(2): 2.339(7), Ru–C(1): 1.84(3), Ru–H(1): 1.31, C(1)–O(1): 1.14(3), N(1)–N(2): 1.42(3). The bond lengths in the pyrazole ring present no unusual features. In spite of high standard deviation, the value of 1.30(4) Å for the N(3)–C(2) distance, can be taken as proof of its double bond character and hence of

---

* The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

the insertion of the N–H bond in the acetonitrile ligand. A short contact (2.95 Å) between N(3) and O(3) (ClO_4^- anion) could indicate the existence of a hydrogen bond. This interaction could explain the splitting observed in the IR perchlorate bands.

Similar behaviour was observed recently for the reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with $K[HB(Me_2pz)_3]$ in acetonitrile, which gave $[Ru(\eta\text{-}C_6H_6)\{NH{=}CMe(R_2pz)\}(R_2Hpz)]^{2+}$ [2]. The presence of the amidine group was, however, suggested only on the basis of spectral IR and ^1H NMR data, and its formation was accounted in terms of attack by 3,5-dimethylpyrazole on the coordinated acetonitrile of the postulated intermediate complex $[Ru(\eta\text{-}C_6H_6)Cl_2(NCMe)]$ [2].

We have also shown that the reaction of **A** with 3,5-dimethylpyrazole gives the same 2-(3,5-dimethyl-1-pyrazolyl)ethylidenamine complex **B**. We therefore assume that in a first step of the reaction with 1-hydroxymethyl-3,5-dimethylpyrazole one NCMe molecule is displaced by this ligand. In a second step the hydroxymethyl group breaks down, probably with generation of $CO + H_2$, and an N–H pyrazole bond is formed. Finally an insertion of the N–H pyrazole bond into the C≡N group of the remaining coordinated acetonitrile molecule leads to the formation of the 2-(3,5-dimethyl-1-pyrazolyl)ethylidenamine ligand.

References

1 A. Romero, A. Vegas, A. Santos and A. Cuadro, J. Chem. Soc., Dalton Trans., in press.
2 C.J. Jones, J.A. McCleverty and A.S. Rothin, J. Chem. Soc., Dalton Trans., (1986) 109.
3 G. Rouschias and G. Williamson, J. Chem. Soc. A, (1967) 993.