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Characterization of Soluble $[RuCl_2P_2]_2$ ($P = PPh_3$), a Species Which has been Postulated to be Present in Solutions of $RuCl_2P_3$; Its Synthesis from Various Ru Compounds *via* a Novel Catalytic Process Involving Pyridylketones

ROB. C. J. VRIENDS, GERARD VAN KOTEN* and KEES VRIEZE

Anorganisch Chemisch Laboratorium, J. H. van't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam, The Netherlands

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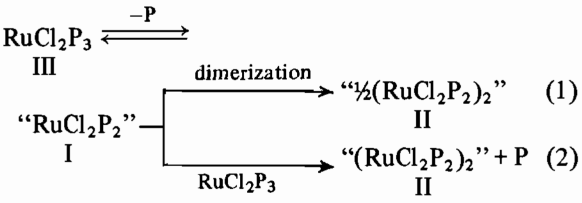
The importance of the 14-electron species "$RuCl_2P_2$" (I) [1] is obvious from its key position in mechanisms proposed for processes catalyzed by $RuCl_2P_3$ [2]. Since I has never been isolated nor observed spectroscopically its existence has been inferred from the observation by ^{31}P-NMR spectroscopy of a species, which has been postulated to be "$(RuCl_2P_2)_2$" (II), in solutions of $RuCl_2P_3$ (III) [3, 4]. Route 1 as well as route 2 can account for the formation of II and each route seems to be supported by ^{31}P-NMR spectroscopic data [3, 4].



It must be emphasized that the only species having a similar stoichiometry is the compound $(RuCl_2P_2)_2$, IV, reported by Wilkinson [5] which, however, is essentially insoluble in all common organic solvents [6].

We now report the synthesis and characterization of soluble $(RuCl_2P_2)_2$ (V) as well as the results of a spectroscopic study of mixtures of P, $(RuCl_2P_2)_2$ and $RuCl_2P_3$ in order to shed more light on the nature of I.

The 1/1 reaction of $RuCl_2P_3$ with 2-pyridylketones or 2-pyridylcarbaldehyde 2-R-C(O)py (VI, R = CH_3; VII, R = Ph; VIII, R = H) in $CHCl_3$ or in benzene afforded purple coloured $(RuCl_2P_2)_2$ (V) in about 75–92% yield (correct C, H, Cl elemental analyses, N absent; dec. at 180 °C; mol. wt. by osmometry in $CHCl_3$, found 1277, calc. 1392). The fact that the pyridylketone was recovered in high yield (*e.g.* 93% in the case of VI) strongly suggested that only catalytic amounts of VI–VIII were required to effect the observed reaction. This was confirmed by the isolation of V in 89% yield from the reaction of $RuCl_2P_3$ with 4 mol.% of VI. Other routes by which V could be isolated almost quantitatively involved: i) the reaction of $RuCl_3 \cdot 3H_2O$ with sixfold excess of PPh_3 in refluxing ethanol using 4 mol.% of VI as a catalyst; ii) the reaction of insoluble IV (black; dec >220 °C; prepared according to ref. 5 by refluxing III in methylethylketone) with a catalytic amount of VI in $CHCl_3$ (92% yield) and iii) the reaction of $RuHClP_3$ [9] with 4 mol.% of VI in $CHCl_3$ which produced V in 83% yield and CH_2Cl_2 quantitatively (according to GLC) [10].

The nature of V was established by IR and ^{31}P-NMR spectroscopy. The IR spectrum of V shows in the 400–200 cm^{-1} region three strong bands at 326, 293 and at 247 cm^{-1} which can be attributed to stretching modes of terminal and bridging Cl atoms (compare these data with bands at 326, 294 and at 271 cm^{-1} for insoluble IV) [11]. ^{31}P-NMR spectra of V in $CDCl_3$ show exclusively one AB pattern (δ_A 43.6 and δ_B 38.8 ppm downfield from 85% H_3PO_4 external, see Fig. 1a) pointing to diastereotopic P-atoms (J_{PP} = 35 Hz). The structure shown in Figure 2 having the P-ligands in *cis*-position and a square pyramidal coordination geometry [12] around each of the Ru-atoms can account for both these spectroscopic data and the dimeric nature of V. Moreover the intensive purple colour of V is a further support for the proposed pentacoordinate geometry around Ru^{II} [3, 13].

The present data for soluble V are in striking disagreement with the data reported for species II (^{31}P-NMR in CH_2Cl_2 at −97 °C, δ_A 58.8 and δ_B 53.0 ppm, J_{PP} 41.5 Hz) [3] which is supposed to have also the structure shown in Figure 2. The following observations make clear that species II must have a different nature [14].

The ^{31}P-NMR spectrum of pure $(RuCl_2P_2)_2$ (V) is temperature independent (up to 60 °C) which indicates that intramolecular interchange of ligands is slow on the NMR time-scale or does not occur at all. While evidence for interaction of V with added triphenylphosphine might be deduced from a slight decrease in intensity of the AB pattern at 58 °C, bridge cleavage in V by PPh_3 to produce $RuCl_2P_3$ definitely does not occur [15].

In the ^{31}P-NMR spectrum of our samples of $RuCl_2P_3$ at −97 °C the AB pattern, which would point to the presence of species II in solution (*cf.* refs. 3 and 4) is clearly lacking (see Fig. 1b). That this is not caused by the presence of Ph_3PO or of excess of PPh_3 [16] in these solutions is implied by the ^{31}P-NMR spectra of solutions of a 1/1/1 mixture of P,

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*To whom correspondence should be addressed.

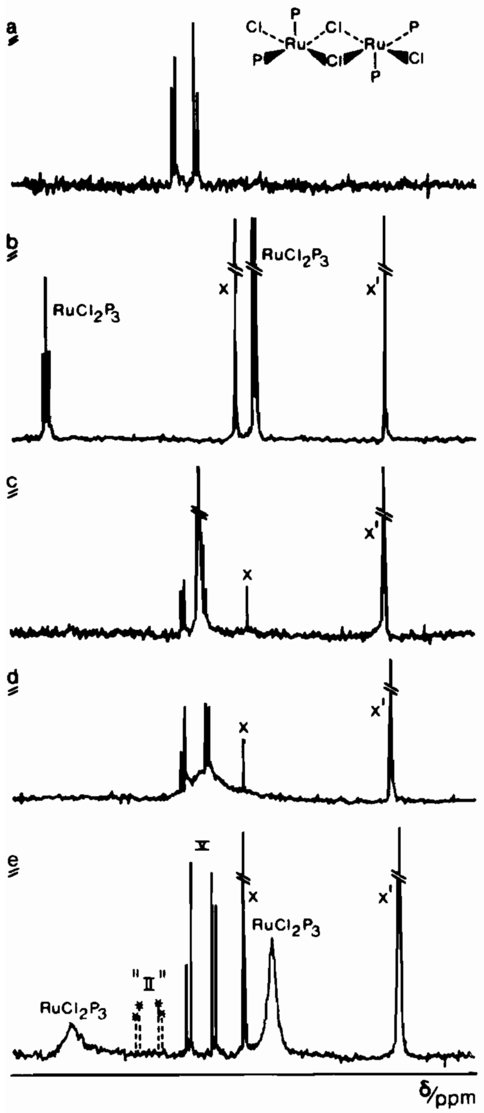

Figure 1. ^{31}P-NMR spectra of V in $CDCl_3$ at RT (a); of $RuCl_2P_3$ in CH_2Cl_2 at −97 °C (b); of $RuCl_2P_3/(RuCl_2P_2)_2/PPh_3$ in $CDCl_3$ at RT (c), 0 °C (d) and at −55 °C (e). In the latter spectrum the position of the AB pattern of II reported in refs. 3 and 4 has been indicated with asterisks. ($X = Ph_3PO$; $X' = PPh_3$).

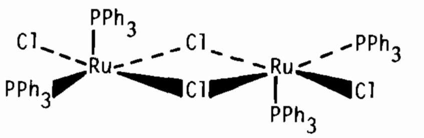

Figure 2. Proposed structure for $RuCl_2(PPh_3)_2$ dimer (V).

$RuCl_2P_3$ and $(RuCl_2P_2)_2$ (0.05 *M* in each of the components) in $CDCl_3$ at different temperatures (see Fig. 1c–e).

These spectra reveal that i) the AB pattern of V is located at a chemical shift position different from that reported for II; ii) the AB pattern is not coalesced at room temperature (*cf.* Fig. 1b in ref. 3) and iii) no ligand site-exchange between the various components of the mixture occurs on the NMR time-scale below room temperature.

These results indicate that the real nature of species II must be a point of further discussion. In this respect it is noteworthy that reduction of $RuCl_3$-P_2 with H_2 (1.5 atm, 1 hr) in DMA [17] affords a red–brown coloured solution of which the ^{31}P-NMR spectrum shows only one broadened resonance at 55.7 ppm. This is near the position reported for the coalesced AB pattern of II [3, 4]. However, no change in the shape of the resonance was observed on cooling to temperatures down to −10 °C whereas addition of 4 mol.% of VI to this solution afforded the $RuCl_2P_2$ dimer (V) which was isolated in 84% yield. This suggests that the resonance at 55.7 ppm might be attributed to $RuCl_2P_2$ (DMA), the solvent stabilized 14-electron species "$RuCl_2P_2$", which subsequently dimerizes upon addition of the pyridylketone VI.

The nature of the catalytic pathway resulting in the formation of V in these ruthenium(II)–phosphine/pyridylketone reactions remains unclear. The first step, dissociation of PPh_3 from $RuCl_2P_3$, can be effected by acetone [5], ethylmethylketone [5], as well as by acetophenone [5] but all these reactions yielded insoluble IV. In contrast, interaction of pyridine or 4-acetylpyridine with $RuCl_2P_3$ results in the formation of complexes of the type $RuCl_2P_2(L)_2$ (L = py [5] or 4-MeC(O)py, monomer, dec. at 205 °C). It is obvious then that the specific geometry of the N=C–C=O skeleton present in VI–VIII must be of decisive importance in stabilizing the 14-electron intermediate $RuCl_2P_2$ and in determining the logistics of the bridge-making process which leads to the exclusive formation of the soluble $RuCl_2P_2$ dimer V.

Further investigations into the nature of the catalytic process as well as of the reactivity of V are in progress.

Acknowledgements

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References

1 Throughout this communication P represents PPh_3. Other complexes in which P is $(p\text{-tolyl})_3P$, diphos, *etc.* are in hand.
2 B. R. James, *Inorg. Chim. Acta Rev.*, 73 (1970).
3 K. G. Caulton, *J. Am. Chem. Soc.*, *96*, 3005 (1974). P. R. Hoffman and K. G. Caulton, *ibid.*, *97*, 4221 (1975).
4 P. W. Armit, A. S. F. Boyd and T. A. Stephenson, *J. Chem. Soc. Dalton Trans.*, 1663 (1975).

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6 Poddar *et al.* [7] reported the synthesis of $RuCl_2(AsPPh_3)_2$ dimer which is only partly soluble.

7 R. K. Poddar and U. Agarwala, *J. Inorg. Nucl. Chem., 35,* 567 (1973).

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9 P. S. Hallman, B. R. McGarvey and G. Wilkinson, *J. Chem. Soc. A,* 3143 (1968).

10 A possible route for this reaction involves the formation of $Cl_2CHPPh_3^+Cl^-$ which subsequently is attacked by "$RuClHP_2$" thus producing CH_2Cl_2 and "$RuCl_2P_2$". The latter species dimerizes to V by reaction with methylpyridylketone VI. When benzene was used instead of $CHCl_3$ as a solvent no reaction occurred.

11 On the basis of these data Gilbert and Wilkinson [5] proposed a dimeric structure for IV containing bridging Cl atoms with the two PPh_3 ligands bonded in a *trans* manner to pentacoordinate Ru-atoms. The dimeric nature, however, could not be established by molecular weight determinations as a result of the insolubility of IV.

12 Alternatively, the Ru-atoms in V can have a trigonal bipyramidal structure. However, on the basis of the arguments put forward by Caulton [3] and by Stephenson [4] the structure in Fig. 2 is preferred. An X-ray analysis of the structure of V is underway.

13 B. N. Chaudret, D. J. Cole-Hamilton, R. S. Nohr and G. Wilkinson, *J. Chem. Soc. Dalton Trans.,* 1546 (1977).

14 V which is very soluble in CH_2Cl_2 and $CHCl_3$ does not dissolve in benzene or toluene which contrasts with the observation of species II in benzene/toluene solutions of $RuCl_2O_3$ (*cf.* ref. 4, p. 1664).

15 V does not react with the H_2 or with HCl. Reaction of V with CO yields a dimer $[RuCl_2(CO)P_2]_2$ in which Ru is six-coordinate [ν(CO) 1964 (vs), 1939 (vs), 1925 (sh) cm^{-1}] while the bands in the 400–200 cm^{-1} region [326 (m), 278 (m) 253 (m) cm^{-1}] indicate that the bridging and terminal halogen atoms are still present like in V. Reaction of V with excess NEt_3 yields $Ru(NEt_3)_4Cl_2$ [mol. wt. in $CHCl_3$, 479 (calc. 576); dec. at 140 °C. Correct C, H and N analyses].

16 Armit and Stephenson have shown that the concentration of species II increases when solutions of $RuCl_2P_3$ are exposed to the air [4].

17 B. R. James, A. D. Rattray and D. K. W. Wang, *Chem. Comm.*, 792 (1976).