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Preliminary communication

THE PREPARATION OF [RuHCl$(PPh_3)_2(C_3H_7NCHCHNC_3H_7)$] AND ITS DISPROPORTIONATION TO GIVE A DIHYDRO AND A DICHLORO COMPLEX

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Summary

[RuHCl$(PPh_3)_3$] reacts with 1,2-bis(isopropylimino)ethane (DAD) to give [RuHCl$(PPh_3)_2$(DAD)]. This complex rearranges in CH_2Cl_2 while in MeOH it disproportionates to give [$Ru_2Cl_3(PPh_3)_2(DAD)_2$]X, [Ru $H_2(PPh_3)_2$(DAD)] and [Ru $H_2(CO)(PPh_3)_3$]. The ionic dinuclear compound reacts with $NaBPh_4$ to give [$Ru_2Cl_3(PPh_3)_2(DAD)_2$]BPh_4 (which can be independently obtained from [Ru $Cl_2(PPh_3)_3$], DAD and $NaBPh_4$.[RuHCl$(PPh_3)_2$(DAD)]) also reacts with water to give the dinuclear [$Ru_2(\mu\text{-OH})_2(\mu\text{-Cl})(H)(PPh_3)_3$(DAD)].

The reactions between diazadienes (α-diimines) and transition metal complexes are of much interest at present. These ligands can stabilize low-valent metal complexes such as [$Fe(DAD)_2$] [1] or [$Ni(DAD)_2$] [2] and confer interesting catalytic properties.

We have been interested in studying the modification of reactivity caused by diazadienes bound to ruthenium, since no diazadieneruthenium compounds have previously been reported. We report here the preparation of [RuHCl$(PPh_3)_2$-$(C_3H_7NCHCHNC_3H_7)$] and its reaction in methanol, which involves disproportionation into a dihydrido and a dichloro compound, as well as its reaction with water.

[RuHCl$(PPh_3)_3$] reacts with two or more molar equivalents of diazadiene (1,2-bis(isopropylimino)ethane) to yield a brown power which can be recrystallised from dichloromethane/ether and analyses for [RuHCl$(PPh_3)_2$(DAD)]. Spectroscopic data (IR ν(Ru—H) 1950 cm^{-1}; ^1H NMR τ 19.5 ppm (J(P—H) 25 Hz) triplet) confirm the presence of a hydrido ligand. In solution in CD_2Cl_2, the compound apparently liberates a phosphine, as a doublet can be seen at τ 29.6 ppm (J(P—H) 26 Hz). The ^{31}P NMR spectrum shows that in solution in $(CD_3)_2CO$ a *trans*-bis-phosphine complex is present (δ 24.8 ppm*). Finally the

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*Chemical shifts are to high frequency of external 85% H_3PO_4.

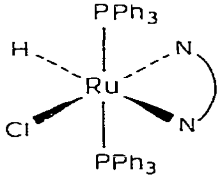


Fig. 1. Structure of $[RuHCl(PPh_3)_2(DAD)]$.

^{1}H NMR spectrum indicates that the two moieties of the diazadiene ligand are nonequivalent, and the integration ratio confirms the analytical data. Since the peaks are broad it is probable that the compound is fluxional and that it rearranges. This compound is thus the *cis*-hydridochloride $[RuHCl(PPh_3)_2(DAD)]$ (see Fig. 1). From these data we are unable to assign the mode of coordination of diazadiene, especially because the compound always decomposes in solution; it reacts in methanol at 50°C to give a red precipitate and a brown solution. The red powder is a mixture of $[RuH_2(PPh_3)_2(DAD)]$ [3] (which was obtained independently from $[RuH_4(PPh_3)_3]$ and DAD) by fractional crystallisation.) The brown solution, after evaporation to dryness and crystallisation from dichloromethane/ether gives brown crystals of an ionic complex. This reacts with $NaBPh_4$ in methanol to give $[Ru_2Cl_3(PPh_3)_2(DAD)_2]BPh_4$. This complex has been obtained independently; the reaction of $[RuCl_2(PPh_3)_3]$ with DAD in toluene or dichloromethane produces $[Ru_2Cl_3(PPh_3)_2(DAD)_2]Cl$, and this with $NaBPh_4$ in methanol gives $[Ru_2Cl_3(PPh_3)_2(DAD)_2]BPh_4$. Conductivity, spectroscopic and analytical data confirm that this compound is a "classical" ionic triply-bridged complex of ruthenium. The only anomaly is that

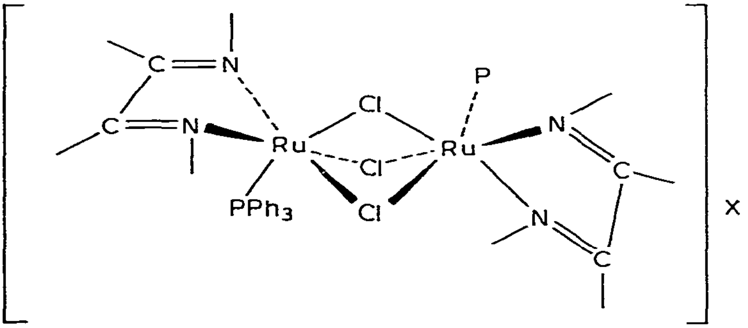


Fig. 2. Structure of $[Ru_2Cl_3(PPh_3)_2(DAD)_2]X$.

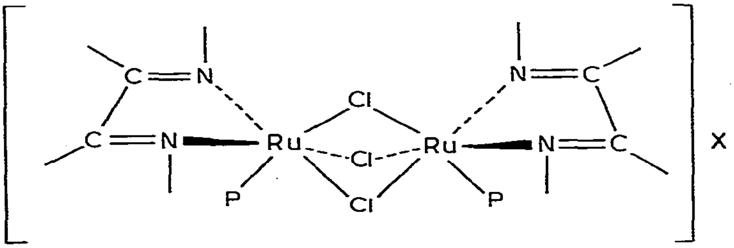
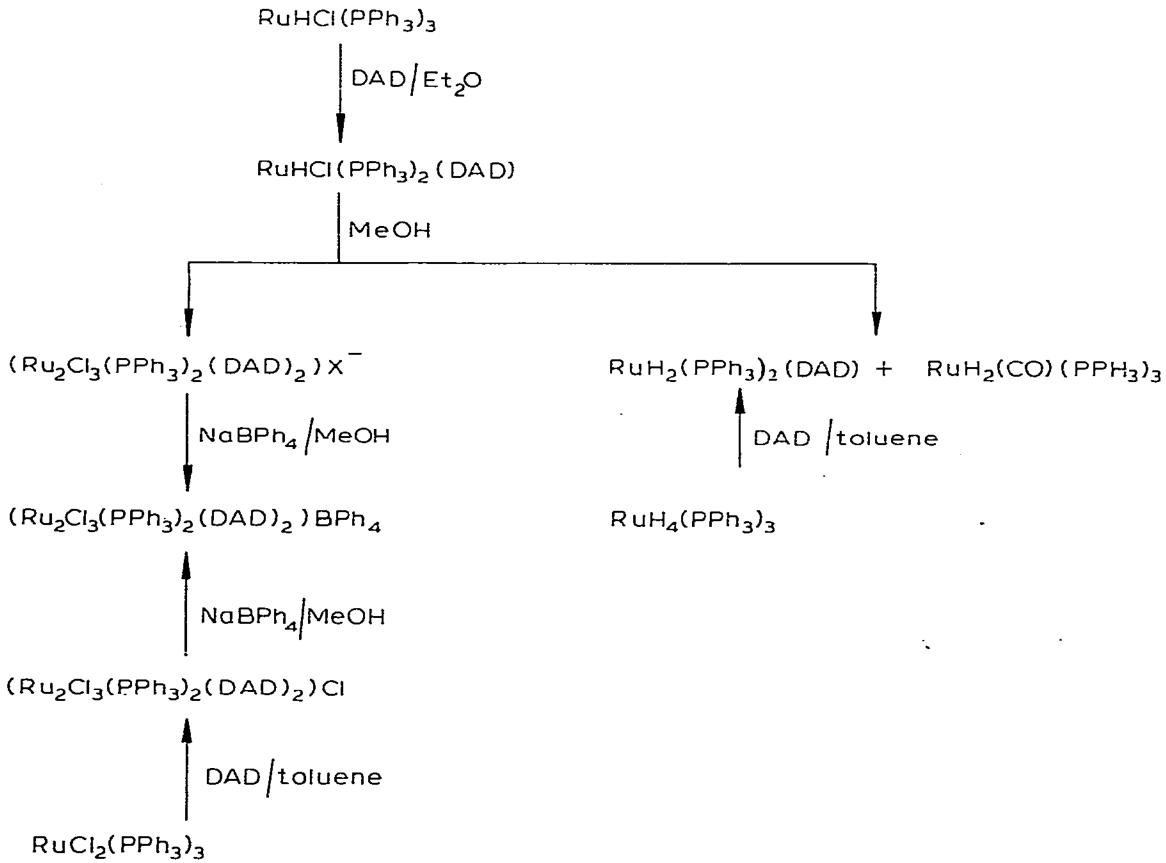


Fig. 3. Possible structure of $[Ru_2Cl_3(PPh_3)_2(DAD)_2]$, rearranged in chlorinated solvents.

although the phosphines are equivalent, there is an inequivalence in the diazadiene ligands. We suggest that it is due to different groups *syn* to each end of the diazadiene ligands (N or P) as shown in Fig. 2. It is noteworthy that in $CDCl_3$ it is converted into a compound containing symmetrically bonded diazadienes (Fig. 3).



We have thus observed a disproportionation of a hydridochloro complex into a dihydrido and a dichloro complex. To our knowledge this is the first example of such a reaction (see Scheme 1). The mechanism of this reaction is not clear. The first step could be the reversible formation of $[RuCl_2(PPh_3)(DAD)]$, which readily dimerises into the dinuclear cation, and "$[RuH_2(PPh_3)_3]$" as well as a molecule of diazadiene. Separate studies have shown that (1) $[RuH_2(PPh_3)_4]$ and $[RuH_2(PPh_3)_2(DAD)]$ are in equilibrium in toluene: $RuH_2(PPh_3)_4 + DAD \rightleftarrows RuH_2(PPh_3)_2(DAD) + 2\ PPh_3$ and (2) low valent ruthenium complexes react with alcohols in basic media to give carbonyl complexes [5], and $[RuH_2(PPh_3)_4]$ reacts with acetone to give $[RuH_2CO(PPh_3)_3]$ [6]. The same reaction probably takes place between $[RuH_2(PPh_3)_4]$ and MeOH [7].

The driving forces for this reaction may be the great stability of the dinuclear trichloro bridged cation and the formation of $RuH_2(CO)(PPh_3)_3$ which is inert. In any case it seems that the presence of diazadiene in the complex labilizes the one electron ligands Cl^- and H^-.

The cationic part of the brown complex obtained in methanol is evidently $[Ru_2Cl_3(PPh_3)_2(DAD)_2]$ [1] but the nature of the ionic part (we write it X^-) is not clear. We have been unable to assign a structure to this anion by spectroscopic or analytical methods although its IR spectrum shows strong bands in the region 3200—3400 cm^{-1} which could be due to ν(O—H) or ν(N—H). The same reaction occurs in acetone to give similar ionic complexes, but we were unable in this case to isolate neutral dihydrido species.

In order to see whether water would interfere with this reaction we added $[RuHCl(PPh_3)_2(DAD)]$ to a toluene/water mixture. After 15 h stirring at 50°C and appropriate work up brown crystals of a complex analysing for $[Ru_2Cl(OH)_2(H)(PPh_3)_3(DAD)]$ were obtained. The ligand ratios are confirmed by integration of the ^1H NMR spectrum. Infrared spectra in Nujol and in dichloromethane as well as ^1H NMR spectra show the presence of hydride and hydroxo ligands (ν(Ru—H) 1995 cm^{-1}; ν(Ru—O—H) 3565, 3578 cm^{-1}; τ(Ru—H) 29.1 dd ppm (J(P(1)H) 28.6 Hz, J(P(2)H) 34.9 Hz); τ(RuOH(1)) 11.3 d ppm (J(PH) 2.2 Hz); $RuOH_2$ 12.0 t ppm (J(PH) 2.9 Hz)). The ^{31}P NMR spectrum shows a singlet (δ 34.9 ppm) and two broad doublets (δ 77.2 and 71.1 ppm). The chemical shifts of the hydroxo groups as well as the coupling with the phosphines show that the complex is dinuclear, bridged by a chlorine and two hydroxo groups [7]; one ruthenium accomodates a hydride and two phosphines, the other a phosphine and a diazadiene (Fig. 4). It is noteworthy that although this reaction seems completely different from that in methanol, a triply bridged compound is again formed and a hydride is eliminated from one ruthenium complex and a chloride from the other.

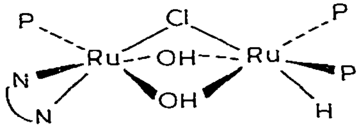


Fig. 4. Structure of $[Ru_2(\mu\text{-}OH)_2(\mu\text{-}Cl)(H)(PPh_3)_3(DAD)]$.

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