Complexes of Ruthenium with 1,3-Bis(dimethylphosphino)propane

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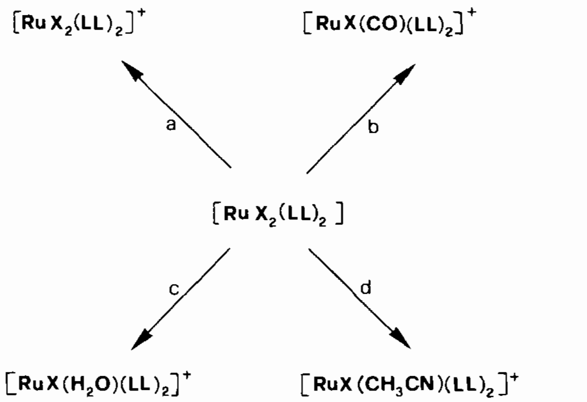
Ruthenium(II) complexes containing bidentate ligands generally give rise to 6-coordinate octahedral structures $[RuX_2(LL)_2]$. However, as we previously found [1, 2] and McAuliffe *et al.* more recently confirmed [3], with a number of ligands, namely the diphosphines $Ph_2P(CH_2)_3PRR'$ ($R, R' = Ph, Me$) [1, 3] and the mixed ligand $Ph_2P(CH_2)_2(2\text{-}Pyr)$ (PPy) [2], stable 5-coordinate $[RuX(LL)_2]^+$ complexes can be easily prepared by dissociation of an anionic ligand X^- from *trans*-$[RuX_2(LL)_2]$. Osmium(II) behaves quite similarly, but in this case only the diphosphine dpp (R=R′=Ph) has been investigated [4]. It is interesting to recall that with related ligands, forming chelate rings either larger or smaller than the 6-membered ones, the conventional octahedral complexes of both ruthenium(II) and osmium(II) are definitely inert towards the dissociation [1].

We now report on the complexes formed by ruthenium(II) with the diphosphine $Me_2P(CH_2)_3PMe_2$ (dmp), which also gives 6-membered chelate rings.

trans-$[RuX_2(dmp)_2]$ complexes are conveniently prepared by reacting $[RuX_2(PPh_3)_3]$ and a slight excess of dmp in benzene; the direct synthesis from $RuCl_3$ and the diphosphine gave in fact low yields, as usual with strongly basic phosphino-ligands [5]. The complexes are diamagnetic and non-electrolytes (1,2-dichloroethane) and the *trans*-stereochemistry is inferred from both the visible spectra, which exhibit the diagnostic absorptions, around 23 000 and 28 000 cm^{-1}, due to the d–d $^1A_{1g} \leftarrow {}^1E_g$ and $\leftarrow {}^1A_{2g}$ transitions (D_{4h} symmetry), and the ^{31}P NMR spectra, where a single signal is observed.

Coordinatively unsaturated $[RuX(dpm)_2]^+$ species have not been isolated as such, although a number of cationic, 6-coordinate complexes of general formulation $[RuX(L)(dmp)_2]^+$ could be obtained, likely to be formed by addition of a sixth ligand L to the 5-coordinate cation, in equilibrium with the *trans*-$[RuX_2(dmp)_2]$ complexes in polar solvents (Scheme 1).

In the presence of water, a white product is isolated, whose elemental analysis suggests a formulation $[RuX(H_2O)(dmp)_2]BPh_4$ (strong absorptions in the 3400–3500 and 1600–1700 cm^{-1} regions). Significantly, by carrying out the same reaction in the presence of excess acetonitrile, the colorless $[RuCl(CH_3CN)(dmp)_2]^+$ adduct is obtained ($\nu(CN) = 2340$ cm^{-1}). Unfortunately, both the aquo and acetonitrile derivatives are rather unstable when dissolved, thus preventing further purifications to be carried out.



Scheme 1. LL = dmp, X = Cl, Br. All the reactions in ethanol (or methanol) and in the presence of: (a) NH_4PF_6 or HBF_4; (b) $NaBPh_4$ or $NaBF_4$; (c) $NaBPh_4$ and H_2O, 20%; (d) $NaBPh_4$ and CH_3CN, 20%.

In anhydrous ethanol, the *trans*-$[RuX_2(dmp)_2]$ derivatives do not afford again the desired 5-coordinate species, even in the presence of large excesses of $NaBF_4$ or $NaBPh_4$*. Instead, stable monocarbonyl-derivatives *trans*-$[RuX(CO)(dmp)_2]^+$ are formed, likely through the conventional decarbonylation of a coordinated alcohol (or alcoholate) molecule [6].

$$[RuX(L)_4]^+ \rightleftharpoons [RuX(RCH_2O)(L)_4] \longrightarrow [RuX(CO)(L)_4]^+ \qquad (1)$$

In conclusion, the distinctly different steric requirements of the diphosphine dmp, with respect to other related ligands, *i.e.* containing the two donor atoms separated by four bonds, apparently make the vacant coordination site in the $[RuX(LL)_2]^+$ cations more accessible to a sixth ligand (water or the solvent alcohol itself), to such an extent that the coordinatively unsaturated species could never be isolated. It may be noted that the *trans*-$[RuX_2(LL)_2]$ complexes with the related diphosphine $Me_2P(CH_2)_2PMe_2$ are stable towards the dissociation, even if evidences are

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*When *trans*-$[RuCl_2(dmp)_2]$ is stirred in ethanolic NH_4PF_6, quantitative formation of $[RuX_2(dmp)_2]PF_6$ occurs. The same product could be obtained, in shorter times, in the presence of strong acids, such as HBF_4 or $HClO_4$, thus indicating that H^+ is the actual oxidant.

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reported of formation of ionic species in aqueous solutions, tentatively formulated as aquo-complexes $[RuX(H_2O)(dme)_2]^+$ [5].

Experimental

IR and visible spectra were recorded on a Perkin-Elmer 781 and Lambda 5 respectively and NMR spectra on a Jeol FX 90 Q instrument (positive δ values, ppm, downfields 85% H_3PO_4). The ligand dmp was prepared by literature methods [7]. All preparations were made under nitrogen.

[RuX₂(dmp)₂] (X = Cl, Br)

Dmp (1.8 ml, 11 mmol) was added to a benzene solution of $[RuX_2(PPh_3)_3]$ (5 mmol) and the mixture stirred at room temperature for 2 h. By adding hexane yellow crystals separated (recrystallization from CH_2Cl_2–hexane, yield 60%). *Anal.* Found (calc. for $C_{14}H_{36}Cl_2P_4Ru$): C, 33.6 (33.61); H, 7.7 (7.25); Cl, 14.3 (14.17)%. Found (calc. for $C_{14}H_{36}Br_2P_4Ru$): C, 28.3 (28.54); H, 6.5 (6.16)%. $\lambda_{max}(\epsilon_M)$ in 1,2-$C_2H_4Cl_2$: 23 400 (125) and 28 000 (sh) cm^{-1} (Cl); 22 500 (115) and 28 000 (sh) cm^{-1} (Br). $\delta(^{31}P)$ in CD_2Cl_2: −9.02 (s) (Cl); −11.24 (s) (Br).

[RuI₂(dmp)₂]

$[RuX_2(dmp)_2]$ and LiI (100-fold excess) were refluxed in ethanol for 48 h under nitrogen. The mixture is evaporated to dryness and extracted with benzene. By addition of hexane, a brown powder separates (yield 10%). *Anal.* Found (calc. for $C_{14}H_{36}I_2P_4Ru$): C, 24.4 (24.61); H, 5.3 (5.31)%. λ_{max} in Nujol: 22 500 (115) and 28 000 (sh) cm^{-1}.

[RuCl₂(dmp)₂]PF₆

$[RuCl_2(dmp)_2]$ and NH_4PF_6 (20-fold excess) were stirred overnight at room temperature, in ethanol, yielding green crystals (80%). *Anal.* Found (calc. for $C_{14}H_{36}Cl_2F_6P_5Ru$): C, 26.9 (26.06); H, 6.0 (5.62); Cl, 10.8 (10.99)%. μ_{eff} (20 °C): 2.1 BM.

[RuX(CO)(dmp)₂]BPh₄ (X = Cl, Br)

$[RuX_2(dmp)_2]$ and $NaBPh_4$ (10-fold excess) were refluxed in ethanol under nitrogen for 5 h, yielding a white product (recrystallization from CH_2Cl_2–ethanol, yield 70%). *Anal.* Found (calc. for $C_{39}H_{56}BClOP_4Ru$): C, 57.9 (57.68); H, 6.7 (6.95)%. Found (calc. for $C_{39}H_{56}BBrOP_4Ru$): C, 54.5 (54.68); H, 6.6 (6.59)%. μ(CO) in Nujol: 1995 cm^{-1}. $\delta(^{31}P)$ in CD_2Cl_2: −17.4 (s) (Cl); −19.6 (s) (Br).

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