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Preliminary communication

New anionic, neutral and cationic complexes of ruthenium(II)

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Recently we reported the synthesis and characterization of a ruthenium(II) carbonyl diene anion $M[RuCl_3CO(C_7H_8)]$ ($M = Ph_3BzP^+, Cs^+$)[1] [A]. We now report the reactions of this anion with a range of Lewis bases (L) to generate a series of new anionic, neutral and cationic ruthenium(II) species*. Different types of behaviour are observed depending on both the nature and amount of added L.

For $L = Me_2S, Me_2SO, CH_2{=}CHCN$ (A/L 1/2 mole ratio), displacement of diene occurs giving the new anionic compounds $Ph_3BzP[RuCl_3COL_2]$. Similar compounds are obtained for $L = AsPh_3, SbPh_3, C_5H_5N$ together with neutral species of composition $[RuCl_2CO(C_7H_8)L]$, shown by detailed ^{1}H NMR studies to have structure I. With an excess of $SbPh_3$, the well-known tris-stibine compound $[RuCl_2CO(SbPh_3)_3]$[2] is obtained. Reaction with PPh_3 (1/2 mole ratio) gives the dimeric carbonyl phosphine $[RuCl_2CO(PPh_3)_2]_2$; with an excess of PPh_3 bridge cleavage occurs to give $[RuCl_2CO(PPh_3)_3]$. In contrast, reaction with PMe_2Ph (1/2 or excess) gives only $[RuCl_2(PMe_2Ph)_2C_7H_8]$ shown by ^{1}H NMR and far IR studies to have structure II. Reaction of A with 2,2′-bipyridyl or 1,10-phenanthroline (N-N) (1/1 mole ratio) gives both $Ph_3BzP[RuCl_3CO(N\text{-}N)]$ and $[RuCl_2CO(N\text{-}N)]_2$: with an excess of (N-N), small amounts of the new cationic species $[RuClCO(N\text{-}N)_2]Cl$ are also obtained.

The analogous tertiary phosphine cations $[RuCl(PPh_3)(N\text{-}N)_2]Cl$ can be prepared by treatment of either $[RuCl_2(PPh_3)_3]$[2] or $[RuCl_3(PPh_3)(N\text{-}N)]$[3] with an excess of (N-N) in methanol. Small amounts of the dimeric chloro-bridged cations $[Ru_2Cl_2(PPh_3)_4(N\text{-}N)_2]Cl_2$ are also obtained. Similarly, with *mer*-$[RuCl_3(PMe_2Ph)_3]$[4] and excess (N-N), the orange crystalline cationic compounds $[RuCl(PMe_2Ph)_3(N\text{-}N)]Cl{\cdot}H_2O$ are readily isolated (structure III) together with small amounts of the other geometrical isomer (IV).

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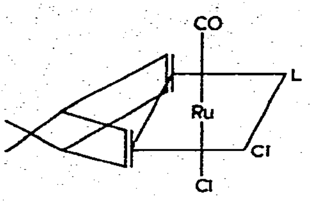
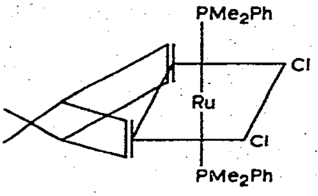
*All these compounds have been fully characterized by elemental analyses, molecular weights, conductivity measurements, ^{1}H NMR, and IR studies.



(I)



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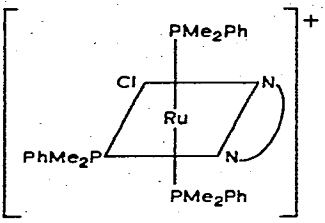

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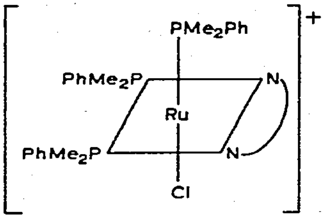

(IV)

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