

Preliminary communication

SYNTHESIS AND REACTIONS OF SOME HETEROBIMETALLIC AND MULTIMETALLIC COMPLEXES CONTAINING η -ARENE-RUTHENIUM(II), -OSMIUM(II) AND η -PENTAMETHYLCYCLOPENTADIENYL-RHODIUM(III) MOIETIES

J.D. FOTHERINGHAM and T.A. STEPHENSON*

Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ (Great Britain)

(Received November 23rd, 1984)

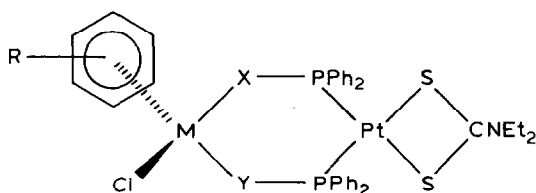
Summary

Heterobimetallic complexes such as $[\eta\text{-areneMCl}(\text{SPPH}_2)_2\text{Pt}(\text{S}_2\text{CNEt}_2)]$ (I, M = Ru, Os) and $[\eta\text{-C}_5\text{Me}_5\text{RhCl}(\text{SPPH}_2)_2\text{Pt}(\text{S}_2\text{CNEt}_2)]$ (II) have been synthesised by reaction of $\text{NEt}_2\text{H}_2[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{Ph}_2\text{PS})_2]$ with either $[\text{M}(\eta\text{-arene})\text{Cl}_2]_2$ or $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$ (2/1) molar ratio). Further reactions of I include facile chloride displacement with a range of neutral ligands L to give $[\eta\text{-areneML}(\text{SPPH}_2)_2\text{Pt}(\text{S}_2\text{CNEt}_2)]^+$ (III) cations and formation of tri- and penta-metallic species on treatment with more $[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{Ph}_2\text{PS})_2]^-$.

In the last decade, extensive studies on the synthesis and reactivity of the binuclear complexes $[\text{Ru}(\eta\text{-arene})\text{Cl}_2]_2$ (arene = C_6H_6 , $p\text{-MeC}_6\text{H}_4\text{CHMe}_2$, C_6Me_6 etc.) have been published [1]. Such studies include bridge cleavage reactions with a variety of Lewis bases L to give $[\text{Ru}(\eta\text{-arene})\text{Cl}_2\text{L}]$ or $[\text{Ru}(\eta\text{-arene})\text{ClL}_2]^+$ and with anionic ligands such as S_2PR_2^- , O_2CR^- [2] (L—L) to afford either $[\text{Ru}(\eta\text{-arene})\text{Cl}(\text{L—L})]$ or $[\text{Ru}(\eta\text{-arene})(\text{L—L})_2]$. A wide range of homo-binuclear triple bridged cations of type $[\text{Ru}_2\text{X}_3(\eta\text{-arene})_2]^+$ (X = Cl, Br, I, OH, OR, SR), [3] $[\text{Ru}_2\text{HXY}(\eta\text{-arene})_2]^+$ (X = Y = Cl, OCOMe, OCOCF₃; X = Cl, Y = OCOMe or OCOCF₃) [4] and homo-tetra-nuclear cations such as $[\text{Ru}(\eta\text{-C}_6\text{H}_6)(\text{OH})_4]^{4+}$ [5] and $[\text{Ru}_4(\eta\text{-C}_6\text{H}_6)_4(\mu_2\text{-OH})_4(\mu_4\text{-O})]^{2+}$ [6] are also available.

In this communication we report the high yield synthesis and some reactions of novel hetero-bimetallic and multimetallic compounds containing the $(\eta\text{-arene})\text{Ru}^{\text{II}}$ moiety and related complexes incorporating $(\eta\text{-arene})\text{Os}^{\text{II}}$ and $(\eta\text{-C}_5\text{Me}_5)\text{Rh}^{\text{III}}$ fragments.

Thus, reaction of $[\text{Ru}(\eta\text{-arene})\text{Cl}_2]_2$ with $\text{NEt}_2\text{H}_2[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{Ph}_2\text{PS})_2]$ [7] (1/2 molar ratio) in chloroform at ambient temperature gives,



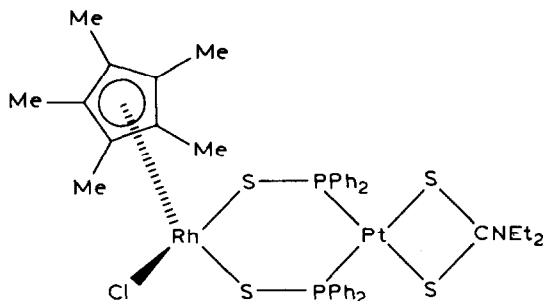
(Ia: M = Ru, X = Y = S;

Ib: M = Os, X = Y = S;

Ic: M = Ru, X = Y = O;

Id: M = Ru, X = O; Y = S)

on addition of methanol, high yields (75%) of the red solids $[(\eta\text{-arene})\text{-RuCl}(\text{SPPH}_2)_2\text{Pt}(\text{S}_2\text{CNET}_2)]$ (Ia) (arene = C_6H_6 , $p\text{-MeC}_6\text{H}_4\text{CHMe}_2$). The same products are formed by treatment of $[\text{Ru}(\eta\text{-arene})\text{Cl}(\text{OCOMe})]$ with an equimolar amount of the $[\text{Pt}(\text{S}_2\text{CNET}_2)(\text{Ph}_2\text{PS})_2]^-$ anion. Similarly, reaction of $\text{NET}_2\text{H}_2[\text{Pt}(\text{S}_2\text{CNET}_2)(\text{Ph}_2\text{PS})_2]$ with either $[\text{Os}(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Cl}_2]_2$ or $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$ (in 2/1 molar ratio) gives high yields of the corresponding yellow $[(\eta\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{OsCl}(\text{SPPH}_2)_2\text{Pt}(\text{S}_2\text{CNET}_2)]$ (Ib) and dark red $[(\eta\text{-C}_5\text{Me}_5)\text{RhCl}(\text{SPPH}_2)_2\text{Pt}(\text{S}_2\text{CNET}_2)]$ (II) respectively*.



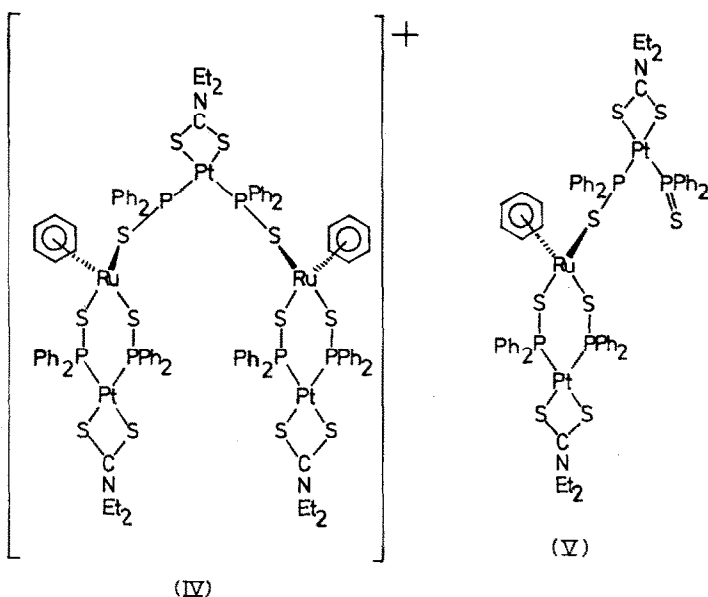
(II)

Likewise, preliminary studies indicate that treatment of $[\text{Ru}(\eta\text{-arene})\text{Cl}_2]_2$ with the anions $[\text{Pt}(\text{S}_2\text{CNET}_2)(\text{Ph}_2\text{PO})_2]^-$ and $[\text{Pt}(\text{S}_2\text{CNET}_2)(\text{Ph}_2\text{PO})\text{Ph}_2\text{PS}]^-$ [7] (in 1/2 molar ratio) yield the bimetallic complexes Ic and Id respectively.

Reaction of Ia or Ib with neutral ligands (L) under relatively mild conditions, followed by addition of methanolic solutions of $\text{Na}[\text{BPh}_4]$ precipitates the heterobimetallic cations $[(\text{arene})\text{ML}(\text{SPPH}_2)_2\text{Pt}(\text{S}_2\text{CNET}_2)]\text{BPh}_4$ (III) (L = PPh_3 , PEtPh_2 , CO, $\text{PhC}\equiv\text{CH}$ etc.). These cations can also be prepared in some instances by reaction of the monomers $[\text{M}(\eta\text{-arene})\text{Cl}_2\text{L}]$ with equimolar amounts of $[\text{Pt}(\text{S}_2\text{CNET}_2)(\text{Ph}_2\text{PS})_2]^-$.*

If Ia (arene = C_6H_6) is treated in chloroform with more $[\text{Pt}(\text{S}_2\text{CNET}_2)(\text{Ph}_2\text{PS})_2]^-$ (2/1 molar ratio), the novel pentametallic cation IV is produced, whereas with equimolar ratios of Ia and the platinum anion, spectroscopic

*All these complexes have been fully characterised by elemental analyses, IR and ^1H , ^{31}P - $\{^1\text{H}\}$ and ^{13}C - $\{^1\text{H}\}$ NMR spectroscopy.



evidence indicates the in situ formation of the trimetallic compound V containing bidentate and unidentate $[\text{Pt}(\text{S}_2\text{CNEt}_2)(\text{Ph}_2\text{PS})_2]^-$ groups.

Further studies on the stoichiometric and catalytic reactions of these compounds, including attempts to synthesise even more exotic multimetallic species starting from compounds of type V, e.g. $[(\text{Et}_2\text{NCS}_2)\text{Pt}(\text{Ph}_2\text{PS})_2 - (\text{arene})\text{Ru}-\mu\{-\text{SPPh}_2\text{Pt}(\text{S}_2\text{CNEt}_2)\text{PPh}_2\text{S}\} \text{Os}(\text{arene})(\text{SPPh}_2)_2\text{Pt}(\text{S}_2\text{CNEt}_2)]^+$ etc. are now in progress.

Acknowledgement. We thank Johnson—Matthey plc for loans of ruthenium trichloride, osmium tetroxide and rhodium trichloride and the SERC (JDF) for financial support.

References

- 1 For detailed references see P.M. Maitlis, *Chem. Soc. Rev.*, 10 (1981) 1; M.A. Bennett, M.I. Bruce and T.W. Matheson in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon, Oxford, Vol. 4, p. 796, 1982; H. Werner, *Angew. Chem. Int. Ed. Engl.*, 22 (1983) 927; E.A. Seddon and K.R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984.
- 2 See D.A. Tocher, R.O. Gould, T.A. Stephenson, M.A. Bennett J.P. Ennett, T.W. Matheson, L. Sawyer and V.K. Shah, *J. Chem. Soc. Dalton Trans.*, (1983) 1571 and ref. therein.
- 3 R.O. Gould, T.A. Stephenson and D.A. Tocher, *J. Organomet. Chem.*, 263 (1984) 375.
- 4 M.A. Bennett and J.P. Ennett, *Organometallics*, 3 (1984) 1365.
- 5 R.O. Gould, C.L. Jones, D.R. Robertson, D.A. Tocher and T.A. Stephenson, *J. Organomet. Chem.*, 226 (1982) 199.
- 6 R.O. Gould, C.L. Jones, T.A. Stephenson and D.A. Tocher, *J. Organomet. Chem.*, 264 (1984) 365.
- 7 D.M. Anderson, E.A.V. Ebsworth, T.A. Stephenson and M.D. Walkinshaw, *J. Chem. Soc., Dalton Trans.*, (1982) 2343.