Journal of Organometallic Chemistry, 284 (1985) C12—C14
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

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

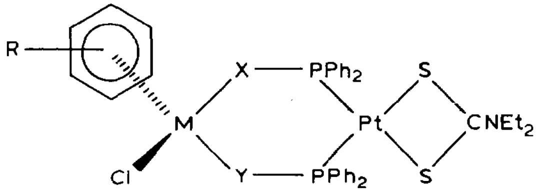
Heterobimetallic complexes such as [η-areneMCl(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (I, M = Ru, Os) and [η-C$_5$Me$_5$RhCl(SPPh$_2$)$_2$Pt(S$_2$CNEt$_2$)] (II) have been synthesised by reaction of NEt$_2$H$_2$[Pt(S$_2$CNEt$_2$)(Ph$_2$PS)$_2$] with either [M(η-arene)Cl$_2$]$_2$ or [Rh(η-C$_5$Me$_5$)Cl$_2$]$_2$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

In the last decade, extensive studies on the synthesis and reactivity of the binuclear complexes [Ru(η-arene)Cl$_2$]$_2$ (arene = C$_6$H$_6$, *p*-MeC$_6$H$_4$CHMe$_2$, C$_6$Me$_6$ etc.) have been published [1]. Such studies include bridge cleavage reactions with a variety of Lewis bases L to give [Ru(η-arene)Cl$_2$L] or [Ru(η-arene)ClL$_2$]$^+$ and with anionic ligands such as $^-$S$_2$PR$_2$, $^-$O$_2$CR [2] (L—L) to afford either [Ru(η-arene)Cl(L—L)] or [Ru(η-arene)(L—L)$_2$]. A wide range of homo-binuclear triple bridged cations of type [Ru$_2$X$_3$(η-arene)$_2$]$^+$ (X = Cl, Br, I, OH, OR, SR), [3] [Ru$_2$HXY(η-arene)$_2$]$^+$ (X = Y = Cl, OCOMe, OCOCF$_3$; X = Cl, Y = OCOMe or OCOCF$_3$) [4] and homo-tetranuclear cations such as [Ru(η-C$_6$H$_6$)(OH)]$_4{}^{4+}$ [5] and [Ru$_4$(η-C$_6$H$_6$)$_4$(μ$_2$-OH)$_4$(μ$_4$-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 (η-arene)Ru$^{\text{II}}$ moiety and related complexes incorporating (η arene)Os$^{\text{II}}$ and (η-C$_5$Me$_5$)Rh$^{\text{III}}$ fragments.

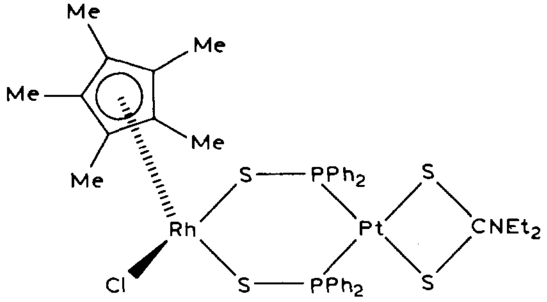
Thus, reaction of [Ru(η-arene)Cl$_2$]$_2$ with NEt$_2$H$_2$[Pt(S$_2$CNEt$_2$)(Ph$_2$PS)$_2$] [7] (1/2 molar ratio) in chloroform at ambient temperature gives,

0022-328X/85/$03.30



(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 [(η-arene)-$RuCl(SPPh_2)_2Pt(S_2CNEt_2)$] (Ia) (arene = C_6H_6, p-$MeC_6H_4CHMe_2$). The same products are formed by treatment of [Ru(η-arene)Cl(OCOMe)] with an equimolar amount of the $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ anion. Similarly, reaction of $NEt_2H_2[Pt(S_2CNEt_2)(Ph_2PS)_2]$ with either $[Os(p\text{-}MeC_6H_4CHMe_2)Cl_2]_2$ or $[Rh(\eta\text{-}C_5Me_5)Cl_2]_2$ (in 2/1 molar ratio) gives high yields of the corresponding yellow $[\eta\text{-}p\text{-}MeC_6H_4CHMe_2)OsCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (Ib) and dark red $[(\eta\text{-}C_5Me_5)RhCl(SPPh_2)_2Pt(S_2CNEt_2)]$ (II) respectively*.



(II)

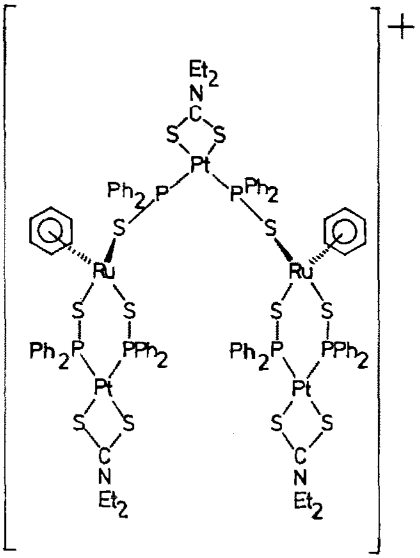
Likewise, preliminary studies indicate that treatment of $[Ru(\eta\text{-arene})Cl_2]_2$ with the anions $[Pt(S_2CNEt_2)(Ph_2PO)_2]^-$ and $[Pt(S_2CNEt_2)(Ph_2PO)Ph_2PS]^-$ [7] (in 1/2 molar ratio) yield the bimetallic complexes Ic and Id respectively.

Reaction of Ia or Ib with neutral ligands (L) under relatively mild conditions, followed by addition of methanolic solutions of $Na[BPh_4]$ precipitates the heterobimetallic cations $[(arene)ML(SPPh_2)_2Pt(S_2CNEt_2)]BPh_4$ (III) (L = PPh_3, $PEtPh_2$, CO, PhC≡CH etc.). These cations can also be prepared in some instances by reaction of the monomers $[M(\eta\ arene)Cl_2L]$ with equimolar amounts of $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ *.

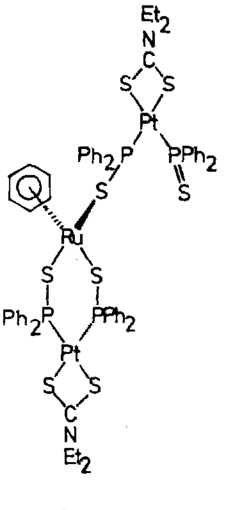
If Ia (arene = C_6H_6) is treated in chloroform with more $[Pt(S_2CNEt_2)$-$(Ph_2PS)_2]^-$ (2/1 molar ratio), the novel pentametallic cation IV is produced, whereas with equimolar ratios of Ia and the platinum anion, spectroscopic

---

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



(IV)



(V)

evidence indicates the in situ formation of the trimetallic compound V containing bidentate and unidentate $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ 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. $[(Et_2NCS_2)Pt(Ph_2PS)_2$-(arene)Ru-μ-$\{SPPh_2Pt(S_2CNEt_2)PPh_2S\}$ Os(arene)$(SPPh_2)_2Pt(S_2CNEt_2]^+$ 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.