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Preliminary communication

The synthesis of heteronuclear cluster compounds containing $M(PR_3)$ ($M = Cu$, Ag, or Au; R = alkyl or aryl) units via Group IB metal exchange reactions

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Abstract

Treatment of dichloromethane solutions of the heteronuclear cluster compounds $[M_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}]$ ($M = Cu$ or Ag) with dichloromethane solutions containing the appropriate quantities of the complex $[Ag(NCMe)_4]PF_6$ or $[AuCl(SC_4H_8)]$ results in the replacement of either one or both of the Group IB metals M by silver or gold atoms. The products from the Group IB metal exchange reactions are obtained in ca. 65–75% yield.

Although a large number of heteronuclear cluster compounds containing one or more $M(PR_3)$ ($M = Cu$, Ag, or Au; R = alkyl or aryl) units bonded to other, different transition metals have now been synthesized [1], species of this type, in which there are different Group IB metals, remain very rare [2,3]. We recently reported [3,4] that Group IB metal exchange reactions can provide a novel route to cluster compounds containing two different coinage metals. However, this type of synthesis is currently restricted to exchanging $M(PR_3)$ groups [3,4], and it cannot be applied to compounds such as the series of hexanuclear clusters $[M_2Ru_4H_2\{\mu\text{-}Ph_2E(CH_2)_nE'Ph_2\}(CO)_{12}]$ ($M = Cu$, Ag, or Au; $E = E' = P$, $n = 1$–6; $E = As$, $E' = As$ or P, $n = 1$ or 2) [5–8], in which the bidentate ligands bridge the two coinage metals. Herein we describe a potentially more generally applicable procedure for Group IB metal exchange reactions.

Treatment of dichloromethane solutions of the previously reported [5] bimetallic species $[M_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}]$ (I, $M = Cu$; II, $M = Ag$) with dichloromethane solutions containing the appropriate amount of the compound $[Ag(NCMe)_4]PF_6$ or $[AuCl(SC_4H_8)]$ results in the replacement of either one or both

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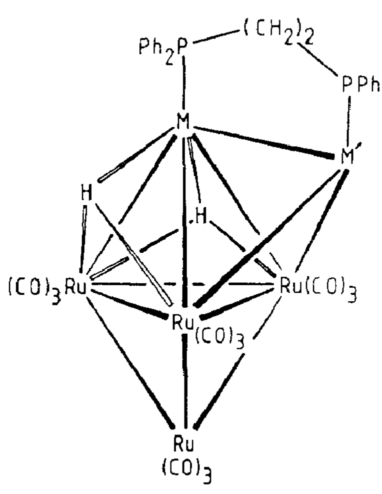
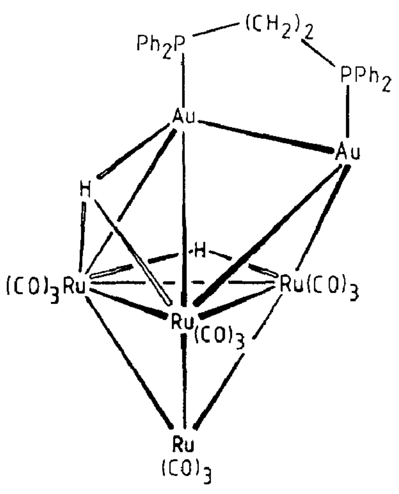
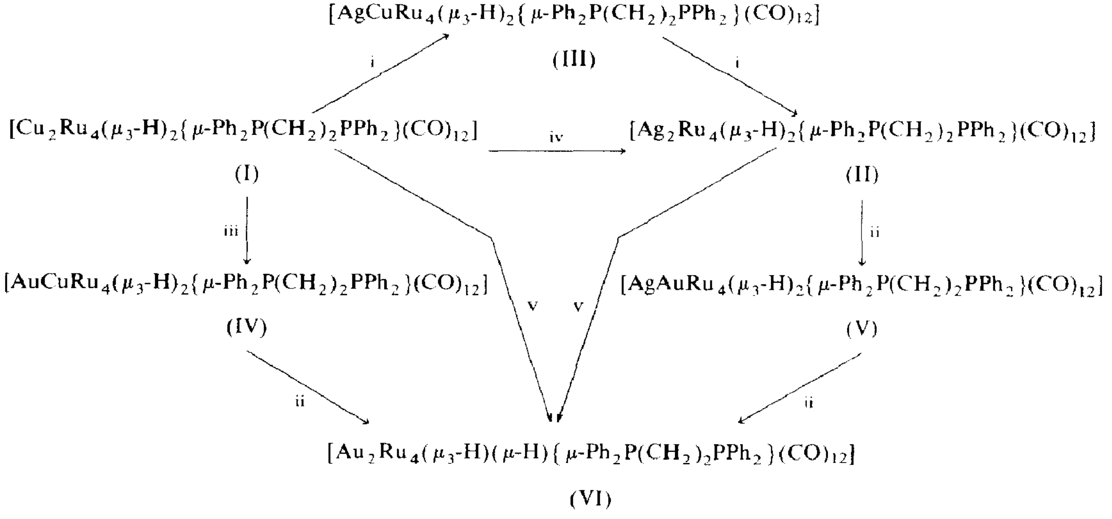


(I, M = M′ = Cu ;
II, M = M′ = Ag ;
III, M = Cu, M′ = Ag ;
VI, M = Cu, M′ = Au ;
V, M = Ag, M′ = Au)



(VI)

of the Group IB metals initially present in the cluster by the coinage metal contained in the mononuclear complex, as shown in Scheme 1. The yields are in the range ca. 65–75%. The syntheses of the trimetallic clusters $[MM'Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}]$ (III, M = Cu, M′ = Ag; IV, M = Cu, M′ = Au; V, M =



Scheme 1. In all of the reactions, a dichloromethane solution containing the appropriate amount of the mononuclear complex $[Ag(NCMe)_4]PF_6$ or $[AuCl(SC_4H_8)]$ was added dropwise over a period of 1 h to a stirred dichloromethane solution of the bimetallic cluster (1 equiv.) at ambient temperature. (i) $[Ag(NCMe)_4]PF_6$ (1.5 equiv.), (ii) $[AuCl(SC_4H_8)]$ (1 equiv.), (iii) $[AuCl(SC_4H_8)]$ (0.9 equiv.), (iv) $[Ag(NCMe)_4]PF_6$ (3 equiv.), (v) $[AuCl(SC_4H_8)]$ (2 equiv.).

Ag, M' = Au) [9*] also produce very small amounts of the silver-containing bimetallic cluster II or $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}]$ (VI), in which both of the Group IB metals initially present in the starting material have been replaced. However, the products in each crude reaction mixture are readily separated and purified by column chromatography, on Florisil (100–200 mesh) at −20 °C for III and on alumina (Brockman activity II) at ambient temperature for IV and V.

The identity of the bimetallic clusters II and VI, which were synthesized via the Group IB metal exchange reactions (Scheme 1), was confirmed by comparison of their spectroscopic data with those of known samples [5,6,10]. However, the coinage metal exchange reactions described herein are potentially much more useful as a generally applicable synthetic route to very rare clusters containing two different Group IB metals. The IR and NMR spectroscopic data for the unusual trimetallic species III–V [11*] are fully consistent with the proposed formulations, and are very similar to those previously reported [3] for the closely related PPh_3-ligated species $[MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (M = Cu, M' = Ag or Au; M = Ag, M' = Au). Thus, it seems very likely that III–V adopt similar capped trigonal bipyramidal metal framework structures, in which the Group IB metal site with the higher coordination number is occupied by the lighter of the pair of coinage metals, to those previously established [3] for the analogous PPh_3-containing species. In addition, the NMR spectra of III–V show that the metal skeletons of these trimetallic species, like those of the analogous PPh_3-ligated clusters [3], are stereochemically rigid at ambient temperature in solution. Interestingly, this stereochemical rigidity is in marked contrast to the dynamic behaviour, involving coinage metal site-exchange, which the metal cores of the closely related bimetallic clusters I, II, and VI show at ambient temperature in solution [5,6,8,10].

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References and notes

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* Reference number with asterisk indicates a note in the list of references.

9 The synthesis of the cluster $[AgCuRu_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}]$ via an alternative route, which involved treating the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with a mixture of one equivalent of $[Cu(NCMe)_4]PF_6$ and one equivalent of $[Ag(NCMe)_4]PF_6$, followed by the addition of one equivalent of $Ph_2P(CH_2)_2PPh_2$, has been very briefly mentioned in a preliminary communication: S.S.D. Brown, I.D. Salter, and B.M. Smith, J. Chem. Soc., Chem. Commun., (1985) 1439.

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11 Selected spectroscopic data. For compound III, $\nu_{max}(CO)$ at 2070s, 2033vs, 2020vs, 2004s, 1976m(br), and 1935w(br) cm^{-1} (CH_2Cl_2). NMR: ^1H (CD_2Cl_2), δ -17.91 (d, 2 H, μ_3-H, J(PH) 12 Hz), 2.30–2.62 (m, 4 H, $P(CH_2)_2P$), and 7.50–7.64 (m, 20 H, Ph); $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2/CH_2Cl_2) (rel. to 85% H_3PO_4 (ext.)) at $-80\,^\circ C$, δ 11.2 ($2\times$d of d, 1 P, PAg, $J(^{109}AgP)$ 465, $J(^{107}AgP)$ 403, J(PP) 2 Hz) and 2.9 ppm (s br, 1 P, PCu). For compound IV, $\nu_{max}(CO)$ at 2071s, 2035vs, 2022vs, 2009s, 1979m(br), and 1948w(br) cm^{-1} (CH_2Cl_2). NMR: ^1H (CD_2Cl_2), δ -18.12 (d, 2 H, μ_3-H, J(PH) 13 Hz), 2.34–2.65 (m, 4 H, $P(CH_2)_2P$), and 7.69–7.62m, 20 H, Ph); $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2/CH_2Cl_2) at $-80\,^\circ C$, δ 69.6 (s, 1 P, PAu) and 4.5 ppm (s br, 1 P, PCu). For compound V, $\nu_{max}(CO)$ at 2069s, 2034vs, 2020s, 2008_5(sh), 1970m(br), and 1935w(br) cm^{-1} (CH_2Cl_2). NMR: ^1H (CD_2Cl_2), δ -17.66 ($2\times$d of d of d, 2 H, μ_3-H, $J(^{109}AgH)$ 39, $J(^{107}AgH)$ 34, J(PH) 11 and 1 Hz), 2.46–2.71 (m, 4 H, $P(CH_2)_2P$), and 7.51–7.72 (m, 20 H, Ph); $^{31}P\text{-}\{^1H\}$ (CD_2Cl_2/CH_2Cl_2), δ 69.6 (d, 1 P, PAu, $J(AgP)_{av.}$ 12 Hz) and 14.2 ppm ($2\times$d of d, 1 P, PAg, $J(^{109}AgP)$ 601, $J(^{107}AgP)$ 521, J(PP) 1 Hz).