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Preliminary communication

GROUP IB METAL EXCHANGE REACTIONS: A NOVEL, HIGH YIELD ROUTE TO HETERONUCLEAR CLUSTER COMPOUNDS CONTAINING $M(PPh_3)$ (M = Cu, Ag or Au) MOIETIES

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Summary

Either one or both (except when M' = Cu) of the $M(PPh_3)$ (M = Cu, Ag or Au) moieties in the heteronuclear metal cluster compounds $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ can be replaced by similar units, containing a different Group Ib metal M', by treating dichloromethane solutions of the clusters with the appropriate amounts of the complexes $[M'X(PPh_3)]$ (M' = Cu or Au, X = Cl; M' = Ag, X = I), in the presence of $TlPF_6$; the new clusters are obtained in ca. 70—80% yield.

During the last five years, interest in gold heteronuclear cluster compounds has grown rapidly, and compounds in which one or more $Au(PR_3)$ (R = aryl or alkyl) moieties are incorporated into structures containing ruthenium, osmium, iron and/or cobalt atoms ligated by carbonyl groups now constitute a well-established area of transition metal cluster chemistry [1]. Although examples of analogous copper and silver clusters are still relatively rare, very recently these species too have attracted much more attention [2]. In contrast to the majority of currently known preparative routes to other types of mixed-metal cluster compound, in which chance still normally plays an important role [3], the study of heteronuclear Group Ib metal clusters has greatly benefitted from the availability of a number of generally applicable rational procedures for their synthesis in high yield. All of these routes increase the cluster nuclearity by incorporating $M(PR_3)$ fragment(s) into a performed cluster, dimer or monomer. The most versatile procedures involve treating a polynuclear carbonylmetal anion with the complexes $[MX(PR_3)]$ (M = Cu, Ag or Au, X = Cl, I or NO_3) [1, 4], $[\{Au(PPh_3)\}_3O]BF_4$ [1, 5] or $[M(NCMe)_4]PF_6$ (M = Cu or Ag), followed by addition of the phosphine ligand in situ [2], condensation reactions between hydridocarbonyl polynuclear metal compounds and $[AuMe(PR_3)]$

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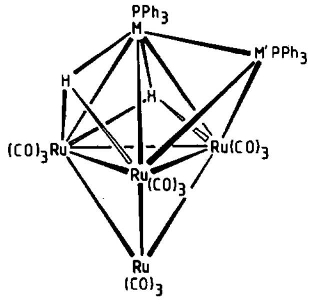
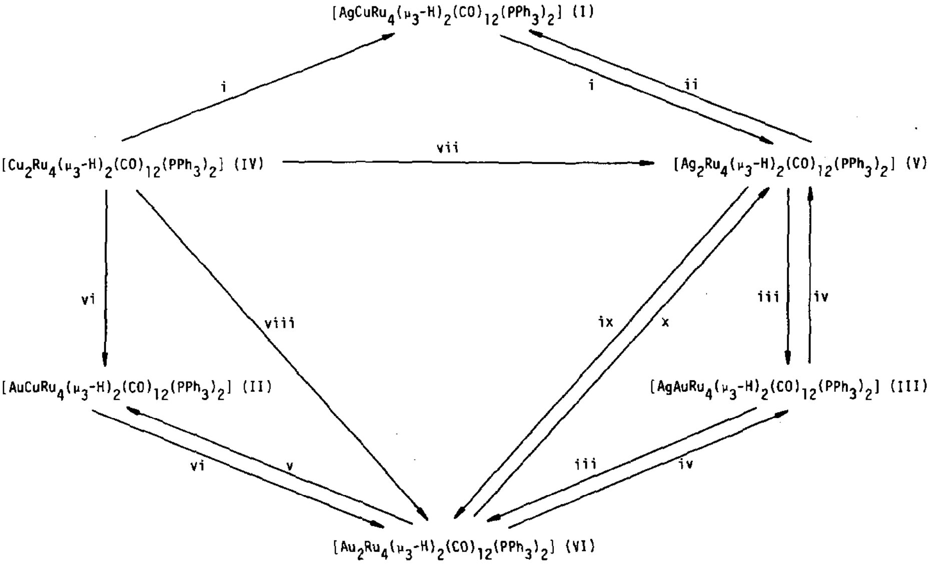
[1, 6] and oxidative addition reactions between neutral carbonylmetal clusters and $[M(C_2R')(PR_3)]$ (M = Cu, Ag or Au; R′ = aryl) [7] or $[AuX(PR_3)]$ (X = halide or SCN) [1, 8]. Herein we demonstrate that metal exchange reactions, in which one or two $M(PPh_3)$ (M = Cu, Ag or Au) moieties in a mixed-metal cluster are replaced by similar fragments containing different coinage metals with no overall change in the cluster nuclearity, can provide a novel alternative method for the synthesis of Group Ib metal heteronuclear clusters in high yield. This new route is complementary to those described above.



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

We have previously reported [9] that the novel hexanuclear clusters $[MM'Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (I, M = Cu, M′ = Ag; II, M = Cu, M′ = Au; III, M = Ag, M′ = Au) can be synthesized in ca. 40% yield by treating the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with 1 equivalent of each of the two respective Group Ib metal complexes $[MX(PPh_3)]$ and $[M'X(PPh_3)]$ ($M \neq M'$; M, M′ = Cu or Au, X = Cl; M, M′ = Ag, X = I), followed by the addition of $TlPF_6$. Alternatively, the thermodynamic site-preferences for the different types of coinage metal can be utilized to prepare the trimetallic clusters I—III from metathesis reactions between the two appropriate bimetallic species $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}(PPh_3)_2]$ (IV, M = Cu; V, M = Ag; VI, M = Au) [9]. This latter observation suggested that Group Ib metal exchange might provide a useful general synthetic route to heteronuclear clusters containing different coinage metals, if a more convenient reagent than a mixed-metal cluster compound could be found to perform these reactions.

We have now discovered that treatment of dichloromethane solutions of the bimetallic clusters IV—VI with the appropriate amounts of the complexes $[M'X(PPh_3)]$ (M′ = Cu or Au, X = Cl; M′ = Ag, X = I), in the presence of $TlPF_6$, results in replacement of either one or both of the original $M(PPh_3)$ moieties present in the cluster by similar units containing the different Group Ib metal M′, as shown in Scheme 1. The crude products are readily purified by column chromatography, on Florisil at −20°C for I and IV or on alumina, at ambient temperature for II, III and VI and at −20°C for V. The yields for all these reactions lie in the range ca. 70—80%, and the IR and $^{31}P\text{-}\{^1H\}$ NMR spectra of samples of the clusters I—VI prepared in this manner are identical with those previously reported [9]. From Scheme 1, it can be seen that the reactions in which the lighter of a pair of Group Ib metals to be exchanged is initially present in the cluster and also the reaction between [CuCl(PPh$_3$)] and the gold-ruthenium species VI require only relatively small excesses (between 1.2 and 2×) of the mononuclear complexes, whereas very much larger excesses (between 3.5 and 5×) of these compounds are needed to replace silver or gold atoms already present in the hexanuclear clusters with lighter coinage metals. It is not possible to replace the silver atom in I or the gold atom in II by copper, even if very large excesses of [CuCl(PPh$_3$)] are employed. In addition, similar coinage metal exchange reactions can be used to replace both Group Ib metals in the bimetallic clusters IV—VI, although the copper-ruthenium cluster IV cannot be made from V or VI in this manner, however much excess [CuCl(PPh$_3$)] is present.



SCHEME 1.

All reactions performed on an initial solution of the appropriate mixed-metal cluster (1 equiv.) in dichloromethane and stirred for 2 h.

(i) [AgI(PPh$_3$)] (2 equiv.) and TlPF$_6$ (3 equiv.).
(ii) [CuCl(PPh$_3$)] (5 equiv.) and TlPF$_6$ (7 equiv.).
(iii) [AuCl(PPh$_3$)] (1.5 equiv.) and TlPF$_6$ (2 equiv.).
(iv) [AgI(PPh$_3$)] (3.5 equiv.) and TlPF$_6$ (5 equiv.).
(v) [CuCl(PPh$_3$)] (1.5 equiv.) and TlPF$_6$ (2 equiv.).
(vi) [AuCl(PPh$_3$)] (1.2 equiv.) and TlPF$_6$ (2 equiv.).
(vii) [AgI(PPh$_3$)] (4 equiv.) and TlPF$_6$ (6 equiv.).
(viii) [AuCl(PPh$_3$)] (2.4 equiv.) and TlPF$_6$ (4 equiv.).
(ix) [AuCl(PPh$_3$)] (3 equiv.) and TlPF$_6$ (4 equiv.).
(x) [AgI(PPh$_3$)] (7 equiv.) and TlPF$_6$ (10 equiv.).

Of the Group Ib metal exchange reactions shown in Scheme 1, those which afford the trimetallic clusters I—III, without using uneconomically large excesses of the mononuclear complexes, have the most potential for utilization as more generally applicable synthetic procedures. At present, cluster compounds containing two different coinage metals are extremely rare [9], but in principle these metal exchange reactions could allow the preparation, with predictable stoichiometry and controlled regiochemistry, of a wide range of desired clusters of this type. In addition, some of the other metal exchange reactions described herein may sometimes prove to be useful on occasions when not all the Group Ib metal congeners in a series are accessible via the more conventional routes.

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