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Preliminary communication

REACTIONS OF THE CARBIDO CLUSTER ANION $[Re_7C(CO)_{21}]^{3-}$ WITH GROUP IB METALS: X-RAY CRYSTAL STRUCTURE OF THE NOVEL HETEROMETALLIC CARBIDE $[\{Re_7AgC(CO)_{21}\}_2Br]^{5-}$

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Summary

The carbido cluster anion $[Re_7C(CO)_{21}]^{3-}$ reacts with compounds containing metals, M, of Group IB, namely $AuClPPh_3$, $(AgClPPh_3)_4$, $AgBF_4$ and $[Cu(NCMe)_4]PF_6$, to give adducts exhibiting a Re_7M skeleton, of *trans*-bicapped octahedral geometry, as demonstrated by the X-ray investigation of the $[\{Re_7AgC(CO)_{21}\}_2Br]^{5-}$ anion.

We recently described the synthesis and characterization of the first carbido carbonyl clusters of rhenium, namely the anions $[Re_7C(CO)_{21}]^{3-}$ (I) [1], $[Re_8C(CO)_{24}]^{2-}$ [2] and $[Re_6H_2C(CO)_{18}]^{2-}$ [3], and we are now investigating their reactivity. We report below some preliminary results for the trianionic compound I, which shows a good reactivity towards electrophilic species. In particular it reacts readily and reversibly with strong acids, giving the monohydridic derivative $[Re_7HC(CO)_{21}]^{2-}$ [4]. In order to elucidate the stereochemistry of this reaction, we have, in view of the isolobal analogy [5] and the claimed structural similarity between hydrido and $AuPPh_3$ derivatives [6], synthesized the mixed-metal clusters $[Re_7(AuPPh_3)C(CO)_{21}]^{2-}$ (II) and $[Re_7(AgPPh_3)C(CO)_{21}]^{2-}$ (III).

Treatment of an acetonitrile solution of the NEt_4^+ salt of I with the stoichiometric amount of $[AuClPPh_3$ or $(AgClPPh_3)_4]$, at room temperature under nitrogen resulted in the quantitative formation of the mixed-metal derivatives within a few hours (as monitored by IR spectra in the ν(CO) region). The formulation of each species was established on the basis of elemental analyses and ^{1}H NMR spectroscopy. Since attempts to obtain crystals for X-ray investigation were unsuccessful (even when other cations were used), the related species $[Re_7AgC(CO)_{21}]^{2-}$ (IV) and $[Re_7(CuNCMe)C(CO)_{21}]^{2-}$ (V) were prepared by addition of $AgBF_4$ or $[Cu(NCMe)_4]PF_6$ to an acetonitrile solution of I. The reactions in this case were instantaneous, and ^{1}H NMR spectra of the isolated reaction products indicated that a nitrile molecule was coordinated only in the Cu derivative. In contrast compound I failed to react with the $[Re(CO)_3(NCMe)_3]^+$ or $[Re(CO)_3(Me_2CO)_3]^+$ cations, to give the dianion $[Re_8C(CO)_{24}]^{2-}$.

All the species II—V have completely identical IR spectra in the carbonyl region, and are therefore assumed to have closely related structures (ν(CO), in acetonitrile solution: 2040vw, 1989vs, 1958mw, 1925w, 1908mw and 1875vw cm^{-1}).

Crystals suitable for a diffractometric study were obtained only for the NBu_4^+ salt of compound IV (prepared by treatment of its Na^+ salt with NBu_4Br)*.

The X-ray analysis showed the presence of two Re_7Ag moieties (of *trans*-bicapped octahedral geometry, see Fig. 1) joined through a bromine interacting with the two Ag atoms, the overall stoichiometry being therefore $[\{Re_7AgC(CO)_{21}\}_2Br](NBu_4)_5$. This unexpected species, observed as a solid, is formed during the methathesis reaction, and in solution it shows exactly the same ν(CO) bands as the parent anion, possibly because of dissociation.

The structure of one of the two independent $Re_7AgC(CO)_{21}$ moieties is shown in Fig. 2. In spite of the presence of a M_8 core, the distribution of the

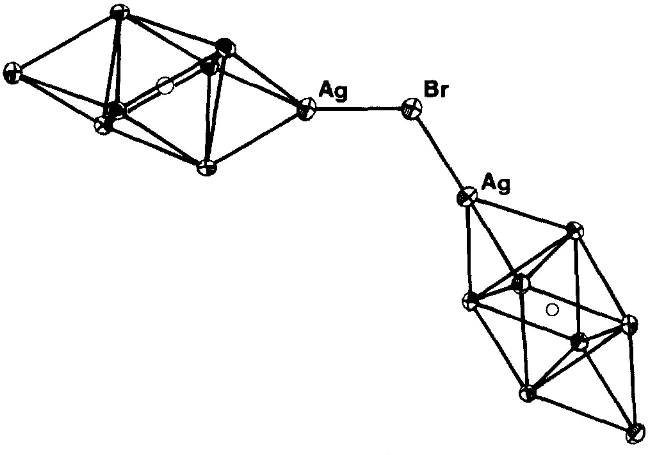

Fig. 1. A view of the metal core of the $[\{Re_7AgC(CO)_{21}\}_2Br]^{5-}$ anion. The two Ag—Br bond distances are 2.521(4) and 2.510(4) Å. The Ag—Br—Ag angle is 121.6(2)°.

***Crystal data.* $C_{124}H_{180}Ag_2BrN_5O_{42}Re_{14}$, $M = 5315.3$, monoclinic crystals, space group $P2_1/n$ (No. 14), a 22.302(6), b 22.701(5), c 30.997(7) Å, β 95.07(2)°, $Z = 4$. The structure was solved by direct methods and subsequent difference Fourier synthesis on the basis of 5132 independent counter data with $I \geqslant \sigma(I)$. The final values for R and R_w are 0.050 and 0.045, respectively. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain).

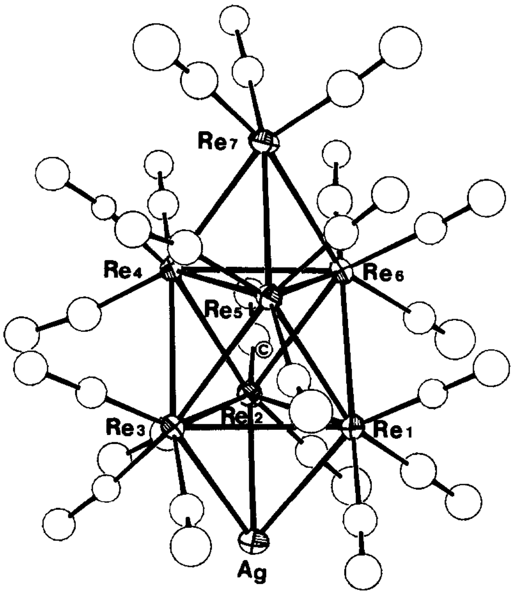

Fig. 2. A view of one of the two $[Re_7AgC(CO)_{21}]$ units. The metal—metal bond lengths (Å) in moiety A (with those for the moiety B in parentheses) are: Ag—Re(1) 2.927 (2.912), Ag—Re(2) 2.832 (2.880), Ag—Re(3) 2.892 (2.850), Re(1)—Re(2) 3.102 (3.109), Re(1)—Re(3) 3.054 (3.086), Re(2)—Re(3) 3.094 (3.081), Re(1)—Re(5) 2.971 (2.987), Re(1)—Re(6) 2.994 (2.988), Re(2)—Re(4) 2.983 (2.986), Re(2)—Re(6) 2.988 (2.978), Re(3)—Re(4) 3.008 (2.992), Re(3)—Re(5) 3.003 (2.994), Re(4)—Re(5) 2.959 (2.952), Re(4)—Re(6) 2.967 (2.966), Re(5)—Re(6) 2.970 (2.963), Re(4)—Re(7) 2.937 (2.946), Re(5)—Re(7) 2.965 (2.970), Re(6)—Re(7) 2.959 (2.946), maximum e.s.d.s 0.003 Å. Re—C(carbide) 2.13 Å (mean).

Re—Re bond distances and the overall carbonyl stereochemistry are more closely related to those of the $[Re_7C(CO)_{21}]^{3-}$ anion rather then to those of $[Re_8C(CO)_{24}]^{2-}$. In fact the idealized symmetry of the $Re_7AgC(CO)_{21}$ moiety is C_3 rather then C_{3v}, because of a twisting of the carbonyl ligands, as in complex I. Moreover the Re—Re interactions in the Ag capped triangle have a mean value of 3.088 Å, as in the uncapped triangle of the $[Re_7C(CO)_{21}]^{3-}$ anion (3.080 Å), while the corresponding value for the (rhenium)-capped triangle is 2.963 Å in the title compound and 2.955 Å in I.

The Re—Ag distances (mean value 2.882 Å) are similar to that in the $[Ag\{ReH_7(PPhPr^i_2)_2\}_2]^+$ cation [7] (2.873 Å), which has been considered to be indicative of a "substantial" metal—metal interaction. However the main ν(CO) band in the IR spectrum of all the Re_7M species reported here has a lower frequency (about 10 cm^{-1}) than the corresponding band in the hydridic derivative, revealing a marked polar nature of the bond to the Group IB metals: others have pointed out that the electron density on transition metals bound with gold atoms is intermediate between that of the free anion and that of its hydride [6].

The Ag—Br bond distances (mean value 2.515 Å) are short compared with those found in ionic compounds such as AgBr (2.887 Å) [8] or Ag_2BrNO_3, where the shortest Ag—Br interaction is of 2.665 Å [9]. This suggests the presence of a covalent bond, which is in keeping with the bent geometry of the Ag—Br—Ag linkage [121.6(2)°].

Preliminary NMR studies on the monohydridic derivative $[Re_7HC(CO)_{21}]^{2-}$ have shown a dynamic behaviour of the H ligand [4]. In this case, however, a ^{31}P NMR spectrum of the $AuPPh_3$ derivative at −90°C, in acetone solution showed only one signal (78.0 ppm relative to external H_3PO_4), indicating the absence in solution of interchanging isomers such as were recently reported for the related species $Ru_6(AuPR_3)_2C(CO)_{16}$ [10].

Finally we observe that compound IV was the only product of the reaction with $AgBF_4$, irrespective of the amount of added Ag^+. This result is different from that obtained with the prismatic $[Rh_6C(CO)_{15}]^{2-}$ anion, which gave a series of adducts of general formula $\{[Rh_6C(CO)_{15}]^{2-}\}_n\{Ag^+\}_m$ on treatment with various amounts of Ag^+ [11].

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